FIRST

ECERS

MEETING AND EXHIBITION

1st EUROPEAN CERAMIC SOCIETY CONFERENCE
including Science of Ceramics 15

Abstracts ECerS '89

June 18-23, 1989

The European Ceramic Society
c/o Prof. R. Metselaar
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INTRODUCTION

This booklet contains the abstracts of (most of) the more than 450 presentations of the 1st European Ceramic Society Conference, ECerS '89, which will be held from 18-23 June 1989 in the Maastricht Exhibition and Congress Centre (MECC), the Netherlands

First, the abstracts of the key-note lectures are given in the order of presentation.
Second, the other abstracts are given, classified according to the topics: Basic Science, Engineering Ceramics, Electronic Ceramics, Traditional Ceramics, Bioceramics, High T_c Superconductors and Standardization.
The presentations are divided over four parallel oral sessions and one poster session, to be given in the morning and in the afternoon. A the beginning of each session there is a heading which indicates the title, date and time, chairman and room number.

The official conference programme is published as a special issue of "Klei Glas Keramiek", the journal of the Dutch Ceramic Society.

ECerS '89 Meeting Abstracts:

	Monday 19 June		Tuesday 20 June		Wednesday 21 June		Thursday 22 June		Friday 23 June
	Morning	**Afternoon**	**Morning**	**Afternoon**	**Morning**	**Afternoon**	**Morning**	**Afternoon**	**Morning**
Basic Science 1	Characte-rization (Audit. 1)	Synthesis (Audit. 1)	Synthesis (Audit. 1)	Forming (Audit. 1)	Densifica-tion (Audit. 2)		Forming (Audit. 2)	Forming (Audit. 1)	Densifica-tion (Audit. 1)
Basic Science 2	Composites (Audit. 2)	Mechanical Properties (Audit. 2)	Phases & Reactions (Audit. 2)	Phases & Reactions (Audit. 2)				Densifica tion (Audit. 2)	
Engineering Ceramics	Fracture (Room 0.2)	Methods in Fracture (Room 0.2)	Analysis of Stresses (Room 0.2)	Corrosion & Coatings (Room 0.2)	Corrosion & Coatings (Room 0.2)		Deformation & Reinforcement (Room 0.2)	Toughening & Struct. Prop. (Room 0.2)	Creep (Room 0.2)
Electronic Ceramics					Magnetic Materials (Room 0.1)		Non-linear Resistors (Room 0.1)	Conducting Ceramics (Room 0.1)	Dielectric & Piezoelect. Mat. (Room 0.1)
Traditional Ceramics	New Trends (Room 0.1)	White Wares (Room 0.1)	Heavy Clay Products (Room 0.1)	Refractories (Room 0.1)					
Bioceramics							Bioceramics (Room 0.3)		
High T_c Superconductors					Processing (Room 0.6/0.7)				Characte-rization (Room 0.6/0.7)
Standardization								Standardi-zation (Room 0.3)	

Basic Science: Monday 19, 10.20

BORON CARBIDE - A COMPREHENSIVE REVIEW,

Thévenot F.
Ecole Nationale Supérieure des Mines de Saint-Etienne
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Boron carbide, which has a high melting point, outstanding hardness, good mechanical properties, low specific weight, great resistance to chemical agents and high neutron absorption cross section ($^{10}B_xC$, x>4) is currently used in high-technology industries : fast-breeder, light weight armors, and high-temperature thermoelectric conversion.
The contents of this review are
1. - Preparations
1.1 - Industrial preparative routes, powders, sintering (additives, pressureless, hot pressing, HIP)
1.2 - Laboratory methods of synthesis : CVD, PVD, plasma, crystal growth..
2. - Phase diagram : a peritexy near pure boron, and a wide phase homogeneity range (B_4C-$B_{10.5}C$).
3. - Rhombohedral crystal structure - A comprehensive model of the whole solid solution may be proposed.
4. - Physical properties : density, mechanical (strength, hardness, toughness..), thermo-electrical properties..
5. - Main industrial applications.

Engineering Ceramics: Monday 19, 14.00

ENGINEERING CERAMICS,

Prof.-Dr. F. Thümmler, Institut für Keramik im Maschinenbau, Institut für Werkstoffkunde II, Universität Karlsruhe, Bundesrepublik Deutschland

The field of engineering ceramics (structural ceramics) is much more limited in volume than functional ceramics. Engineering ceramics are often subject of high thermal and or high mechanical loadings including severe multiaxial stressing. For many actual or perspective applications it is difficult to meet the requirements with respect to reliability and cost. Nevertheless, a lot of successful developmental work occured during the past. A variety of engineering and wear parts for many applications is commercially manufactured, including bioceramics for hip, teeth and other implants. The introduction of ceramic parts for Diesel and spark ignited road engines, where extremely high reliability is required, occures step by step. In Japan and USA the waterless "adiabatic" ceramic intensive Diesel engine seems to be a technically and economically feasible goal for the 90th. The ceramic gas turbine will be a long range approach, however. Considerable progress in engineering ceramics is expected in future, when several requirements are fulfilled, namely: Improvement of processing by using precisely controlled raw materials and processing steps; better understandig of long term degradation phenomena; development and use of composits with high fracture toughness and, last not least, to promote the interdisciplinary work of material experts and engineers in order to utilize the existing technical and economical possibilities.

Traditional Ceramics: Tuesday 20, 14.00

ASPECTS OF TRADITIONAL CERAMICS,

J.E. Enrique
SOCIEDAD ESPAÑOLA DE CERAMICA Y VIDRIO
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In the last years there has been a strong technological development in the traditional ceramic products such as tiles, sanitary ware, bricks and roof tiles.

The ceramic manufacturing processes evolution towards higher performance, more flexible production and lesser quality variation systems is tremendous.Because of that, we cand find old fashioned process stages or even old fashioned whole processes whithin the implantation period which is sometimes smaller than five years.

Clear examples of those features in tile manufacturing are the development and evolution of single firing not only in wall tiles but also in floor tiles which includes several piece sizes. These pieces had decorations which had to be obtained with double slow firing processes.

Refering to sanitaryware the progress has ocurred not only in the under pressure slip casting methods but also in the implantation of highly flexible manufacturing units which allow a great product variety.

According to that, we can mention the development of bricks and roof tile products towards higher technical quality and more varied products.

In this work it is shown these evolution development in the last years and the possible trend not only in the technical field but also the market tendency in the future.

Electronic Ceramics: Wednesday 21, 09.00

ELECTRONIC CERAMICS: CURRENT ISSUES AND FUTURE PROSPECTS, L. Eric Cross. Director, Materials Research Laboratory, Pennsylvania State University, University Park, PA 16802, USA.

The talk will discuss current and emerging new needs for electronic ceramic materials and composites with property combinations tailored for specific electronic and photonic fields of application. New needs in dielectrics for capacitors and electronic packages will be discussed emphasizing the problems and opportunities as applications move toward thinner films and lower processing temperatures. Thin ferroelectric films on silicon have sparked renewed interest in possible application for non-volatile memory but some problems with fatigue and retention must be resolved. Developments in piezoelectrics and electrostrictors for sensors and actuators suggest new possibilities for "agile" systems and for sensor:responder combinations which may engender a new generation of "smart" solids. In photonics the needs generated by fiber optic communications and optical computing are clamant, but the response is necessarily slower in view of the quality and homogeneity of crystals required. The status in electro-optic, non-linear optic, and photo-refractive crystals will be briefly reviewed and new thin film approaches explored. New "wild cards" in the electronic materials pack are the high T_c supeconductors and the recent emergence of techniques to generate diamond and diamond-like films by plasma assisted vapor deposition. Possible impacts of these developments will be discussed.

Bioceramics: Thursday 22, 09.00

Bio-Ceramics, G. Heimke,
Dept. of Bioengineering, Clemson University, Clemson, SC,

From the large number of ceramic materials, a few oxide and calciumphosphate ceramics as well as Ca-phosphate containing glasses and glass-ceramics only have either already stood the test of clinical applications or have a property combination worth to be considered for medical applications. From the point of view of the reactions they stimulate in the adjacent tissue, these materials can be grouped into bioinert or bioactive ceramics. -Whilst the range of application of the bioinert ceramics can be regarded as well established already, most of the uses of the bioactive, Ca-phosphate based materials must be regarded as experimental still. Their fascinating ability to stimulate the formation of a mechanically strong bond to living bony tissue inherently implies some kind of surface reactivity which increases their fatigue sensitivity. As their initial strength is relatively low already, their applications have been confined to essentially load free situations. At present, considerable efforts are aiming at using the bonding ability of these bioactive materials for the fixation of load bearing implants by coating them onto high strength substrates or combining them with other materials like organic or ceramic cements.

Standardization: Thursday 22, 14.00

REVIEW OF THE NATIONAL AND INTERNATIONAL STANDARDIZATION OF ADVANCED CERAMICS,
G.C. Padgett, British Ceramic Research Limited, Queens Road, Penkhull, Stoke-on-Trent ST4 7LQ United Kingdom

The review is confined to the standardization of advanced ceramics as practised in Europe, the United States of America and Japan. The general concept of standardization will be described from an historical point of view. The standardization of advanced ceramics is examined under the headings of terminology, sampling, test methods, product standards, specifications and codes of practice. The most important of these initially is methods of test, which will facilitate the evaluation of ceramic products on an international basis. It will concentrate mainly on Europe as the role to be played by standards in the European Community will become more important when the completion of the single internal market is achieved at the end of 1992. The paper concludes by discussing the attitudes taken by the main National Standards Organizations from USA, Japan and Europe particularly with regard to their international outlook.

High Tc Superconductors: Friday 23, 09.00

THE CRYSTAL STRUCTURE OF HIGH-Tc Bi-BASED SUPERCONDUCTORS
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*Ube Industries Ltd. Ube, Yamaguchi 755, Japan

It is important to analyze the crystal structure of materials, from the viewpoint not only of the interpretation on the origin of the physical and chemical properties but also of finding the guideline for exploring further new materials. We have examined and noticed that the crystal structure of the high-Tc Bi-based superconductors shows two outstanding characteristics, 1) very large lattice bending and 2) structural modulation, as compared to the previous high-Tc $YBa_2Cu_3O_x$. Because of these the conventional x-ray or neutron diffraction method are not so useful for the Bi-based superconducting materials and, therefore, we have tried to analyze the crystal structure mainly by means of high-resolution transmission electron microscopy (HRTEM).

24, 30 and 37 Å phases, whose critical temperature Tc are 20, 80 and 105 K respectively, were obtained by different heating processes. Powder x-ray diffraction and electrical resistivity were measured. Small blocks of the crystals were crushed in an agate mortar and fine fragments created were examined in the electron microscopes.

The crystal lattice planes are prominently bended and, moreover, dark island-like areas are formed. The lattice bending reaches about 20 % at maximum. From the standpoint of the image formation we have considered that the dark areas are due to the concentration of Bi atoms and we have named these as Bi-concentrated bands. This has been proved true with aid of computer simulation on image intensity.

Another structural interest of these superconductors is the intergrowth of layers with different thickness. Any specimens intended for getting the 37 Å phase have always showed the intergrowth for the system Bi-Sr-Ca-Cu-O.

The 30Å phase has been examined by the low-temperature electron microscopy, where the specimen is kept under 10K. The results show that the crystal structure with the modulation along the b axis is not substantially changed on the transition to the superconducting state.

BA 1 11.30

CHARACTERIZATION OF GRAIN BOUNDARIES IN TWO HEXAGONAL CERAMICS, S. Lay, E. Laurent-Pinson, G. Nouet and J. Vicens, LERMAT-URA CNRS 1317, 14032 Caen Cedex, FRANCE

Parallel studies have been performed in two hexagonal ceramics, tungsten carbide and silicon carbide. Both materials have been prepared by a sintering process. They exhibit different mechanical behaviour at high temperature and first investigations have confirmed the disparity of micromechanisms during creep.
Due to their high participation for the mechanical response at high temperature studies have been undertaken on grain boundaries in the two materials.
Several techniques have been used : TEM, HREM and STEM.
A preliminar understanding of the manufacturing process shows the difference induced on the microstructure of each material.
Many grain boundaries have been orientated by TEM analysis. In WC-Co composites, many WC grain boundaries can be described by a 3 dimensional coincidence orientation with a low index.
For SiC 4H and 6H polytypes grain boundaries, only few have a 3 dimensional coincidence orientation and in these cases, higher indices Σ and larger deviations from coincidence have been found. However, in SiC, a good bidimensional matching can occur in the asymetric tilt boundaries $(0001)_1(hkil)_2$ even when $(hkil)_2$ is a high indices plane.
HREM studies have allowed to study more precisely the defects structure of the grain boundaries.
Chemical analysis reveal the presence of the additive phase in the two materials. In the case of WC-Co a correlation between cobalt segregation and grain boundary orientation has been found among twenty grain boundaries analyzed.

BA 2 11.50

THE USE OF CAPACITANCE MEASUREMENTS TO ASSESS THE QUALITY OF GREEN CERAMICS

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Injection moulding of ceramics is an established process, involving the mixing of ceramic powders with binders and plasticisers, injection, removal of organics and sintering. Properties of ceramics made by injection moulding can be adversely influenced by ceramic particle agglomerates whose size, shape and distribution can cause defects and degradation of properties. It will be shown how multiple capacitance measurements can be combined to assess the quality of a green compact as a form of NDT since the distribution of the measurements relates to the size and distribution of binders or ceramic agglomerates. The behaviour of a alumina/wax system will also be compared to a computer simulation.

BA 3 12.10

THIN FILM ALUMINA-FERRITE SUBSTRATE INTERACTIONS AND MICROSTRUCTURAL CHARACTERISTICS, L.M.Gignac and S.H.Risbud, Dept. of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721

Alumina thin films sputtered on Ni-Zn ferrite substrates showed reluctant etchability in hot phosphoric acid. The films were categorized according to their degree of etchability in H_3PO_4 and were examined using various microanalytical characterization techniques. TEM analysis directly showed the existence of crystalline γ-Al_2O_3 in the film at the film-substrate interface. The γ-Al_2O_3 phase grew with a preferred orientation coincident with the growth. The occurrence of this film phase was related to the oxygen partial pressure, the substrate material, and the substrate temperature and was believed to be related to the etching behavior.

BA 4 15.00

CHEMICAL SYNTHESIS OF CERAMIC POWDERS,
R.F.Hill*, L.C. Montgomery, L.Parrish and W.-M.Shen, Union Carbide Corporation, Cleveland, Ohio, USA.

A review of powder synthesis developments at Union Carbide is presented.

Titanium diboride and boron carbide powders made by a continuous carbothermic process are characterized by high purity and small particle size consisting of few and large crystallite domains. These powders have been introduced commercially. Fine extremely pure silicon nitride powders have been made by thermal decomposition of silane. Dense, homogeneous bodies have been fabricated from this powder. High-purity alumina (boehmite)and chemically homogeneous cordierite have been prepared by hydrolysis of metal alkoxide solutions. Boehmite and calcined aluminas are available in commercial quantities.

BA 5 15.20

SYNTHESIS AND PROPERTIES OF NANOSCALE CERAMICS AND COMPSITES

A.J. Burggraaf, K. Keizer, A.J.A. Winnubst
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A review will be given on recent very interesting developments in the synthesis of i) dense ceramics with a grain diameters in the range of 15-50 nm and ii) of porous ceramics and membranes with pore diameters in the ranges of 1-3 nm and 3-100 nm respectively. Composites with modified internal surfaces and nanophase substructures will be discussed. The materials show i) superplastic behaviour and improved microdefect structure or ii) interesting transport properties (perm selectivity) or chemical properties (catalytically active membranes). Illustrative results will be shown.

Refs. 1 A.J. Burggraaf, K. Keizer, B. v. Hassel
Nanostructure materials, membranes and layers.
Solid State Ionics 1989 in press.
2 J. Karch, R. Birringer, H. Gleiter
Ceramics ductile at low temperature.
Nature 330 (1987) 556.

BA 6 15.40

INFLUENCE OF CHEMICAL COMPOSITION OF GASEOUS SPECIES ON POLYTYPE COMPOSITION OF SiC WHISKERS

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al.Mickiewicza 30, A3.

The present use of SiC-whiskers and platelets for reinforcing of ceramic matrices renewed the interest in control of morphology and polytype composition of these forms of SiC which are usually grown by a vapour-solid process. In the present paper SiC whiskers were grown using gaseous species of a composition in which the Si:C ratio varied between 1:1 to 1,3:1 and the morphology and polytype composition of which was examined by bright and dark field TEM as well as by localised electron diffraction. A clear-cut dependence of the polytype composition (2H, 6H, 15R) and morphology on the Si:C ratio in the gaseous species has been found. The results have been rationally explained in terms of the number of lattice correspondence points in gaseous Si_nC_n clusters of different planes of the various SiC polytypes.

BA 7 16.00

PREPARATION OF FINE PARTICLES OF $SrTiO_3$ BY ALKOXIDE METHOD AND THEIR SINTERABILITY,

J. Hojo* and H. Kimura,
Dep. Appl. Chem., Fac. Eng., Kyushu Univ. Fukuoka-shi, 812 Japan

Fine particles of $SrTiO_3$ having the size of 0.01μm were prepared by the hydrolysis of mixed alkoxide of $Sr(i\text{-}OPr)_2$ and $Ti(i\text{-}OPr)_4$. Although the product was amorphous at 30°C, crystalline $SrTiO_3$ particles were produced at 80°C by using a large excess of H_2O. When the powder was dried by heating, large agglomerates having the size of maximally 0.5μm were included. This powder needed a sintering temperature of 1300°C to give the sintered body with the relative density above 95%. The freeze-drying and the treatment with NH_3 aq. solution were effective to disperse $SrTiO_3$ particles. The dispersed powder was densified to above 95% at 1200°C, indicating that the dispersiveness is important to enhance the sinterability. The addition of V_2O_5 to $SrTiO_3$ particles also lowered the sintering temperature, in which the relative density reached about 90% at 1100°C. The sintering may be accelerated by a liquid phase mechanism with molten V_2O_5.

BA 8 16.20

LASER SYNTHESIZED SUBMICRON SILICON AND SILICON NITRIDE POWDERS FROM CHLORINATED SILANES, R.A. Bauer, J.G.M. Becht, J. Schoonman, Inorganic Chem.; E. Kruis, B. Scarlett, Powder Techn., T.U.Delft, the Netherlands.

In the state-of-the-art laser driven gasphase synthesis of submicron Si based ceramic powders silane is used as the reactant. In this study the Laser-Chemical Vapour Precipitation (L-CVP) of Si and Si_3N_4 powders has been studied using the chlorinated silanes SiH_2Cl_2, $SiHCl_3$ and $SiCl_4$ along with NH_3 as reactants in order to introduce cheaper and less hazardous reactants into the L-CVP process. Ammonia was mixed with the irradiated silanes at different heights above the laser beam, thus preventing low temperature reactions and agglomeration of the particles. The use of a sensitizer, SF_6, has been explored to improve energy transfer from the CO_2-laser radiation to the reactants. Particle diameters are typically 20-40 nm for Si_3N_4 and 50 nm for Si. The produced silicon nitride was collected and seperated from NH_4Cl in an electrostatic Precipitator.

BA 9 16.40

PYROLYTIC PREPARATION OF CERAMIC POWDERS
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Methods for pyrolytic fabrication of alumina or zirconia based ceramic powders are described. Basis are aquous solutions of nitrates, chlorides or other water soluble compounds. Using a two phase nozzle, the solutions are sprayed into a stream of hot carrier gas. After evaporation of the water, pyrolysis is obtained by heating the dried particles with light. The particles obtained are spherical with sizes between o.1 and 3 µm. Depending on spray parameters specific surfaces between 10 and 50 m^2/g can be obtained. Using a proper selection of process parameters hollow spheres can be largely avoided. Especially in the systems ZrO2(Y2O3)-Al2O3 and for MgAl2O4 it is possible to obtain powders with interesting sintering properties within an amorphous region. In a second process the energy is introduced by a hydrogen flame where hydrogen is propellant gas for the nozzle and heating gas at once. Powder particles obtained by this process are alsomainly spherical. Hollow spheres are nearly not found. In contrast to the process described firstly, these powders are dry and crystallized. The specific surfaces are in the same range. The content of nitrate or chloride in the final powder is,depending on the process, very small or negligible.

BASIC SCIENCE I : SYNTHESIS

Tuesday 20th June; 09.00 - 11.00 **Chairman : P. Reijnen (FRG)** **Room : Auditorium I**

BA 10 09.00

STUDIES OF NEW POLYSILAZANE PRECURSORS TO Si-C-N-O CERAMICS, C.Colombier
ATOCHEM, Rhône-Alpes Research Centre, BP 20, 69310, Pierre-Bénite, France.

Today, most polysilazanes are obtained by reacting ammonia with chlorosilanes followed by catalytic treatments in order to increase their molecular weight and ceramic yields. This paper described a new route of synthesis of organosilicon precursors.
These precursors are obtained by a simple process and lead by pyrolysis to ceramics with high yields. The article described the influence of the starting chlorosilanes on ceramic yields as well as the composition and high temperature behaviour of the obtained ceramics. Possible applications of such preceramic polymers for coatings or composites are also discussed.

BA 11 09.20

WET CHEMICAL PREPARATION AND CHARACTERISTICS OF TETRAGONAL $ZrO_2(-Y_2O_3)-CeO_2$ CERAMICS

G.S.A.M. Theunissen*, A.J.A. Winnubst, R.S.A. de Lange, A.J. Burggraaf.
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$ZrO_2(-Y_2O_3)-CeO_2$ powders are prepared by means of a gel-precipitation method. This preparation implies the hydrolysis of a metal chloride solution in ammonia. After calcination a powder is obtained with a primary crystallite size of about 10 nm. In this study the sintering behaviour of different compositions are compared. This is done by studying the microstructure development during the sintering process. From sintering experiments it became clear that the Zirconia-Ceria compacts densify more rapidly when a small amount of Yttria is added. When yttria is added it is also observed that the resulting grain size is smaller.
Besides this, the M_s temperature is examined as a function of the grain size in the Zirconia-Ceria system.

BA 12 09.40

CHARACTERISATION OF A NEW TERNARY TETRAGONAL ZIRCONIA

B. BASTIDE*, P. CANALE and P. ODIER

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* CRICERAM, 38560 JARRIE and presently at PECHINEY, 38340 VOREPPE, FRANCE.

A class of zirconia toughened ceramic is elaborated from a new commercial powder stabilized with ceria. The fine grained microstructure (0.5 um) of this TZP (Tetragonal Zirconia Phase) is presented and characterized. This very homogeneous material has an improved thermal and chemical stability even at very high temperature. The effect of ceramic grain size and stabilizer concentration on the phase composition and the mechanical properties after ageing is discussed with respect to the very low martensitic transformation temperature.

BA 13 10.00

PROPERTIES OF SOL-GEL CERAMICS AND VITRO CERAMICS WITH THE CORDIERITE COMPOSITION,

J.C.Broudic, J.Guille and S.Vilminot*
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Sol-gel synthesis have been used in the case of cordierite powders. According to some elaboration parameters such dilution temperature, nature of the solvent, two kinds of samples are obtained. After firing at 1100°C, the first one yields the formation of α-cordierite, while the second one yields the formation of a vitroceramic in which the presence of spinelle $MgAl_2O_4$ and μ-cordierite is revealed by X-ray diffraction.
Both kinds of samples have been characterized by X-ray diffraction, Infra-red spectroscopy and sintering ability. In view of the use of such ceramics in electronic packaging, we have investigated their ceramic properties such dielectric constant, expansion coefficient and microhardness. M.E.B. observations of the samples after thermal etching will also be presented.

BA 14 10.20

MODELLING CHEMICAL COMPOSITION AND MICROSTRUCTURE OF Mg-Al HYDROXIDES COPRECIPITATED FOR Mg-Al SPINEL FORMATION

D.Beruto*, R.Botter, M.Giannetti, M.Giordani; G.Gusmano+, E.Proverbio+, E.Traversa+,
Centro Interdipart. di Ing. dei Materiali, Univ. di Genova, Italy;
+ Dip. di Sc. e Tecnol. Chim., II Univ. di Roma "Tor Vergata", Italy.

In a recent paper we have proved that Mg-Al spinel formation from solid state reaction is strongly dependent upon the mixing degree. Coprecipitation of Mg-Al hydroxides is a promising process to get such mixing at molecular scale. Mg-Al hydroxides form a rather extended family where the ratio n_{Mg}/n_{Al} is varying. The optimum chemical composition to produce $MgAl_2O_4$ spinel would be the one corresponding to a ratio $n_{Mg}/n_{Al} = 1/2$. In this paper we investigate the coprecipitation reaction in order to get ultrafine particles of Mg-Al mixed hydroxides from nitrates and chlorides solutions. Chemical composition and microstructure of the coprecipitates have been investigated as a function of precipitation parameters and critical comparison have been made with mixed hydroxides obtained under the influence of non uniform electric field.

BA 15 10.40

THE INFLUENCE OF POWDER CONDITIONING ON THE SINTERABILITY OF SILICON NITRIDE,

R. Gilissen, Studiecentrum voor Kernenergie (SCK/CEN), Mat. Dev. Dept., Boeretang 200, B-2400 Mol, Belgium.

When fabricating sintered Si_3N_4 from fine sinterable powders it is common practice to admix the sintering additives by intense milling. In addition to intimate mixing this powder conditioning step affects particle size distribution, specific surface area and oxygen content of the powder. The purpose of this study is to evaluate the specific influence of each aforementioned powder characteristic on the sinterability of the powder. The relative importance of the milling step is obtained from the comparison of a standard commercial powder with a commercial deagglomerated powder recently launched on the market.

BA 16 15.00

AN OVERVIEW OF FORMING IN CERAMICS,

Piet Reijnen
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Ecole Nationale Supérieure de Céramique Industrielle, ENSCI, F 87060 Limoges

Usually materials are produced in a desired shape.Different shaped parts are joined together to make an utility (a car, a plane). Sintered materials are formed before firing. A mixture of powder and forming aids (water,organic liquids, binders) are brought into shape, for which a large number of techniques are available. This is the main subject of the paper, with emphasis on recent developments.
Ceramics can also be brought into shape by plasma spraying, CVD and PVD e.g in the production of ceramic coatings.

The physical properties of ceramics depend in a sensitive way on the micro structure which has been developed during heat treatment. The forming process must therefore provide appropriate green micro-structures. Powder synthesis, forming and sintering, although distinct technological steps, are closely related. This aspect will be given special attention in the paper.

BA 17 15.40

COLLOIDAL PROCESSING THROUGH SURFACE MODIFICATION

M. Persson*, E. Bostedt and R. Carlsson, Swedish Institute for Silicate Research, Box 5403, 402 29 Göteborg, Sweden

Colloidal processing is necessary to produce high performance ceramics. To be able to obtain a stable, highly concentrated suspension it is important to have knowledge of the surface characteristics of the ceramic powder. Since the surface of different ceramic powders varies with type of powder, producer and sometimes even batch it is often necessary to develop a processing agent for each separate powder. When producing multicomponent ceramics, where more than one powder has to be dispersed, there will be difficulties in obtaining high stability and homogeneity of the system.
In this paper a surface modification technique, using Al-alkoxide, will be presented. With this technique the surfaces of different powders (Si, Si_3N_4, SiC, ZrO_2 etc) have been transformed to an "alumina like surface". This new and uniform surface will simplify the mixing and forming. The surface modification could be optimized by using controlled hydrolysis and polymerization of the alkoxide. Different techniques such as electrophoretic mobility, specific surface area analysis and X-ray fluorescence were used to analyze the surface modified powders.

BA 18 16.00

PROPERTIES OF AQUEOUS α-Al_2O_3 SUSPENSIONS IN THE PRESENCE OF ADSORBING POLYMER AND POLYELECTROLYTE

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Wet processing techniques as colloidal filtration, i.e. slip casting or pressure filtration become increasingly important as advanced processing tools for the forming of technical dense or porous ceramics.
At the same time the need for a thorough knowledge of the colloid science and rheology of ceramic suspensions and the effect of polymeric additives as deflocculants and binders thereupon is increasing. In this presentation we will discuss some colloidal properties of aqueous α-Al_2O_3 ($d_{s_0} \approx 0.6$ µm) suspensions in the presence of anionic polyelectrolyte or both polyelectrolyte and the uncharged polymer polyvinylalcohol (PVA). The effect of the polymer(s) content(s) was studied by adsorption measurements, electrophoresis, static light scattering, sediment volume measurements and rheometry.
It is found that both PVA and the polyelectrolyte adsorb on the alumina surface. PVA stimulates the forming of agglomerates at intermediate polyelectrolyte adsorptions but this is not the case at high polyelectrolyte content.

BA 19 16.20

RHEOLOGICAL PARAMETERS OF MULLITE AQUEOUS SUSPENSIONS

R. Moreno*; L. Tabernero; J. Requena; P. Miranzo; M.I. Osendi.
Instituto de Cerámica y Vidrio, CSIC, Arganda del Rey, Madrid, España.

In this work the rheological parameters of mullite aqueous suspensions have been studied. Electrophoretic measurements have been carried out in order to determine the corresponding zeta potential values and the isoelectric point of this material. Viscosity measurements have been studied in order to obtain thense and well dispersed suspensions. The effect of organic defloculants on the rheology have been also considered. From these parameters the best conditions for the obtention of dense mullite bodies by a colloidal filtration method can be selected.

BA 20 16.40

INCORPORATION OF SINTERING AIDS IN SILICON NITRIDE BY MEANS OF SURFACTANTS, R. de Jong* and R. A. Mc Cauley, Center for Ceramic Research, Rutgers University, NJ 08855-0909

Stable dispersions of various well-characterized silicon nitride powders have been obtained in an aqueous medium. Colloidal processing allowed for control over particle size distribution under electrostatic/steric stabilization. Regarding the latter, a well-defined organic complex containing a metal group has been investigated. Under the proper conditions, the charged complex molecules interact with polar groups at the powder surface. Rather than using the complex primarily as a dispersant, the selection of the system was based upon the metal-containing group. Heating the green body in a controlled atmosphere will remove the organic part but will leave the metal in the desired oxidation state at the surface. This allows coating of the powders with metal compounds, to be used as densification aids, in a controlled manner. Unlike a mixing process, a uniform, reproducible microstructure can be obtained.

BASIC SCIENCE I : DENSIFICATION

Wednesday 21th June; 10.00 - 12.00 — **Chairman : D.T. Beruto (Italy)** — **Room : Auditorium II**

BA 21 10.00

HIPing GLASS-ENCAPSULATED SILICON NITRIDE TO FULL DENSITY,

N. D. Butler*, M. A. Hepworth, T&N Technology Ltd, Cawston House, Cawston, Rugby, Warwickshire, CV22 7SA, England; I. Iturriza, F. Castro, Centro de Estudios e Investigaciones Tecnicas de Guipuzcoa (CEIT), Barrio de Ibaeta, s/n, 20009 San Sebastian, Spain.

Cold isostatically pressed silicon nitride green compacts have been successfully glass encapsulated and HIPped to full density. The densification behaviour of several powder mixtures, using yttria as a sintering aid, has been investigated and compared to that of silicon nitride with no additions. The resulting microstructures have been characterised by SEM and TEM. The influence of composition, on both the relative amounts of α and β-Si_3N_4 and the characteristics of the intergranular phases formed after HIPing, was investigated by XRD. The room temperature hardness of several specimens was also determined and represented as a function of the characteristic parameters of different HIPing cycles.

BA 22 10.20

EFFECT OF O_2-HIP FOR OXIDE CERAMICS,

Y. Manabe*, T. Fujikawa, K. Uehara and M, Ueda
Kobe Steel, Ltd., Kobe, 651, JAPAN

Sintered alumina and PSZ samples were HIPed under several atmospheres and the differences in colour and mechanical properties before and after HIP were investigated, focussing on the influence of the HIPing atmosphere, such as the heating element materials used and the pressure medium gases.
The properties after an aging test in air (1000°C, 1200 hrs) were compared with the values before aging.
Large differences in color and slight differences in density and bending strength were obsereved and microstructural diffrerences were examined using X-ray diffraction, ESCA and TEM.
The results obtained in this study suggest HIPing of oxide ceramics under an oxidizing atmosphere will lead to great changes in the manufacturing processes of oxide ceramic industries.

BA 23 10.40

HOT ISOSTATIC PRESSING OF PURE BORON CARBIDE,
J. Adlerborn, L. Björk, H. T. Larker,
ABB Cerama AB, S-915 00 Robertsfors, Sweden

The influence of maximum particle size and degassing temperature on density, content of free carbon, hardness, microstructure and strength on hot isostatically pressed (HIPed) pure boron carbide has been investigated. To reach optimal properties both separation of over-sized particles and agglomerates from the starting powder and a high degassing temperature of the preformed powder bodies are necessary. With these precautions a boron carbide material with homogeneous microstructure and high density, hardness and strength can be obtained.

BA 24 11.00

GAS PRESSURE SINTERING OF SILICON NITRIDE
D. Lange, H. Thaler and K. Schwetz
Elektroschmelzwerk Kempten GmbH, West-Germany

The exploration of sintering mechanisms in silicon nitride has stimulated the development of dedicated gas pressure sintering furnaces. These furnaces permit the optimization of processing parameters for silicon nitride.
In our investigation, the sinterability and microstructure evolution of various silicon nitride powders is described as a function of the processing variables and the applied temperature/pressure/time-profile. The densification is tracked by means of a dilatometer. It is seen, that the pressure buildup does strongly influence the densification behavior. Furthermore evidence is presented that complete $\alpha \rightarrow \beta$ transition is not required to achieve full densification, e.g. up to 30 vol% of the metastable α-phase may be retained in fully dense materials during short sintering cycles. The mechanical properties of α/β-mixtures hardly differ from those of pure β-silicon nitride. In contrast to sialons, the hardness of $\alpha+\beta$ materials is insensitive to the α-silicon nitride volume fraction. This behavior is attributed to the prominent role of the soft glassy-phase in determining the overall hardness.

BA 25 11.20

SINTERING KINETICS AND DILATOMETRY IN CERAMIC ENGINEERING, A.M.R. Senos, A.P. Moreira, R.F. Silva e J.M. Vieira, Dep.Engenharia Cerâmica e do Vidro, Universidade de Aveiro, 3800 Aveiro, Portugal.

The bases for applying the same rate equations to isothermal CHR sintering, under the practical conditions as to be found in firing of ceramics are reviewed, new procedures for analysis of sintering and hot-pressing kinetics being established. A summary of the theoretical developments concerning the dependence of sintering stress and grain size on porosity, pore segregation and agglomeration and on pore/particle size distributions was prepared, the sintering systems being tentatively classified accordingly to the mathematical expression of these dependencies. The dilatometric analysis, coupled with microstructural observation, becomes a practical tool not only for assessing the effects of sintering aids and atmosphere on densification, but also for screening of raw materials and of powder processing techniques and to introduce computer assisted design of firing schedules whenever optimization of the microstructure or of the engineering properties of ceramics is sought.

BA 26 11.40

THE PRODUCTION OF CERAMICS AND THE GASIFICATION OF CARBON, F.K. van Dijen,
DSM Research, P.O.B. 18, 6160 MD Geleen,
Netherlands.

Ceramic powders and green ware often contain carbon. The carbon in the powder originates from the powder processi-g route, for instance carbothermal reaction or pyrolysis of polymeric precursors. The carbon in the green ware originates either from the powder or from aids used in shaping the powder. These shaping aids are often organic materials or polymers. Upon heating these aids form gases and carbon.

The carbon can be removed by a chemical reaction: Csolid + gas = Cgas (+ gas). Several gases can be used as a reactant. Models which originate from coal gasification are applied on the removal of carbon. The models describe the reactivity of the carbon, the kinetics of the chemical reaction, etc. It will be shown that the models can be applied succesfully to describe the removal of carbon from powder or green ware.

BA 27 10.00

EVALUATION OF GREEN BODIES RELATED TO THE FORMING TECHNIQUE.

C.Galassi* and E.Roncari
Research Institute for Ceramics Technology - CNR, Faenza, Italy

The dipendence of the green body characteristics on the starting powders properties and on the processing parameters were evaluated for a ZTA material. Different forming techniques produce green texture, density and defect state which is dependent on the homogenization route, additives and technique of compaction. Green bodies obtained by slip casting, injection molding and cold isostatic pressing were compared and green density, pore size and pore size distribution, ZrO_2 dispersion were evaluated.
Correlations are drawn among green body properties and solid phase amount, type and quantity of additives and processing parameters.

BA 28 10.20

DISPERSION OF CERAMIC POWDERS IN WAX APPLICATION TO INJECTION MOLDING,

P. Vivier* and B. Calès,
Céramiques Techniques Desmarquest,
78190 Trappes, France

Injection molding is the most suitable technique for the manufacturing of complex ceramic parts. It requires the use of a well controlled injection part with a good dispersion of powder in the wax medium. However, the dispersion of ceramic powders in wax has not been extensively studied up to date. The objective of this study was to develop a procedure to evaluate the degree of dispersion of various oxide and nitride powders in different waxes and to determine the influence of inorganic surfactant on the dispersion of these powders. The wetability of powder/wax systems has been studied as a function of temperature with a special apparatus. The role of mineral additives in the powder or of inorganic surfactants in the wax on the wetability of the powder/wax systems has been analyzed. The results have been correlated to the rheological properties of the different powder-wax mixtures and to the characteristics of the molding process (injection pressure, temperature...) and of the injected parts (green density...).

BA 29 10.40

DEBINDING INJECTION MOULDED CERAMICS,

M.J. Edirisinghe,
Department of Materials Technology,
Brunel University, Uxbridge, Middx. UB8 3PH, UK.

Injection moulding ceramic-polymer suspensions offer an attractive mass production route for the fabrication of technical ceramics. Research on the systematic development of the injection moulding process has been in progress in this department during the past four years. Over fifty different formulations have been compounded using a variety of ceramic powders and polymeric binders. Criteria for injection moulding have been developed and the formulations that satisfy these have been used to produce macro defect free thick section rotor shapes (1).
Binder removal from ceramic bodies depend on several factors: (i) Characteristics of the ceramic powder. (ii) The composition of the polymeric binder. (iii) Thermal decomposition characteristics of the polymers used which depend on the debinding atmosphere.
Using experimental evidence gathered during debinding polypropylene based formulations the above aspects of binder removal will be illustrated and general guidelines for successful debinding will be discussed.

Reference
1. M.J. Edirisinghe and J.R.G. Evans, Proc. E-MRS Conference, May 1988, France.

BA 30 11.00

RHEOLOGICAL BEHAVIOUR OF SIC-SI AQUOUS MIXTURES.

German J. Piderit*, P. Toro, E. Croquevielle.
Universidad de chile, Dept. of Materials Science, Plaza Ercilla, Casilla 1420, SANTIAGO DE CHILE, CHILE.

The rheological behaviour of aquous Si and SiC and its mixtures was studied. Potentiometrical measurements of individuals suspensions of Si and SiC showed the point of zero charge (p.z.c.) at pH 7,0-8,5 and pH 3,5-4, respectively.
The p.z.c. of mixtures (15% and 30% Si) is modified to a greater pH-range.
The Si-particles sizing was coarser than the SiC-particles with 100% under 20u and 35,3% under 5u.
The Bet-specific area of SiC was 1,1 m^2/g.
The viscosity variations (60% solids) decreased proportionally with increasing alcalinity in the pH-range 3-12 and the negative zeta potential did not change aprecially. The zeta potential equal zero was not reached.
The weak acid (pKa) nature of the SiC-surface inhibits a stronger effect of the pH on the zeta potential.

BA 31 11.20

DRY-PRESSING OF CERAMIC POWDERS,
A.P.S. Reymer*, M. Lont and M. v.d. Acker,
TNO Ceramics Department, P.O. Box 513, 5600 MB Eindhoven and TNO Metal Institute, Apeldoorn, The Netherlands.

Research capabilities into dry-pressing technology at the TNO Ceramics Dept. have recently been enhanced. A high speed MTS testing machine with full electronic control of the head and die cylinders and automatic data-processing is used for pressing ceramic powders. Ferrite granulates are pressed into 50 mm discs, wall tile granulates into 50 x 50 mm tiles. A filling device allows study of filling rate and filling conditions. Output consists of displacement-time and load-time curves of both punch and die and printed data incl. pressure-drop during holdtime(s). Products are characterized on density, porosity, expansion, strength, etc. Acoustic methods of recording internal density distributions of green products are being developed. Effects of speed, pre-pressing, maximum load, die movement and filling conditions on green product quality will be discussed.

BA 32 11.40

DYNAMIC POWDER COMPACTION OF Si_3N_4,
D. Stöver*; H. Hampel, Kernforschungsanlage Jülich, Postfach 1913, D-5170 Jülich; Sur Met, Jülicher Straße 336, D-5100 Aachen.

Dynamic compaction is thought to be of some potential in becoming a possible alternative in the consolidation process of ceramic powders e.g. silicon nitride.
Three different types of Si_3N_4 powders have been investigated. The powders are filled into stainless steel capsules of cylindrical size either under air or vacuum respectively. The vibrating density is around 20-25% and can be increased up to 57-67% by cold pressing. The capsule is completely embedded with explosive of variable power leading to dynamic pressures of up to 10 GPa.
The density of the compacted ceramic is up to 96% of theoretical. An effective evacuation prior to explosion is advantageous. Remaining amounts of non released air seem to be responsible for the sometimes observed post cracking of the ceramic. Microhardness profiles have been determined along the samples radii and showed a more or less pronounced drop depending on powder type used as well as the magnitude of the hardness itself. Microstructural investigations have been conducted on the consolidated parts and will be discussed.

BA 33 12.00

WET PRESSING FOR FORMING ADVANCED CERAMICS,
F.KOOLS * and O.FIQUET
PHILIPS COMPONENTS Corporate Innovation Materials BE 229
5600 MD Eindhoven the Netherlands.

Untill recently , wet pressing was only scarcely used for forming ceramics. An important exception has been since 30 years the wet pressing of anisotropic hard ferrite where pressing is done in a magnetic field to align the powder particles. With the advent of the high tech. ceramics however , forming by wet pressing has become increasingly important because it offers the possibility to achieve a very uniform pressed density.
This paper consists of two parts:
a general one and a specific discussion on pressing of anisotopic hard ferrite.
In the general part the principle of wet pressing are outlined and expressions are derived for pressing time and pressed density distribution.
In the second part some details about the application of wet pressing for the main production of anisotropic hard ferrites are given. In addition the monitoring of differents process parameters and the characterization of the pressing properties are discussed.

BA 34 15.00

A NEW TECHNIQUE TO STUDY PARTICLE COMPACTION DURING SLIP CASTING

L.A. Correia* and R.J.G. Beenen
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands

Slip casting, a colloidal filtration route for ceramic processing, offers the possibility of controlling the microstructure of a compact by manipulating the powder particle interaction in suspension.
However, using highly stabilized suspensions of submicron powders only very thin casts can be made because of the high flow resistance in the compact. By adjusting the water suction power of the porous mould to the flow resistance in the cast a mould is developed enabling slip casting of highly stabilized suspensions. In order to study the filtration process an acoustic technique is introduced measuring the evolution of the thickness of the cast and the suspension level. Using an appropriate filtration model results in the characteristics of the microstructure of the compact that is porosity, mean pore size and tortuosity of the pores. The first results of this study will be presented.

BA 35 15.20

FILTRATION OF LIQUIDS AND COLLOIDAL SUSPENSIONS BY POROUS CERAMIC MOLDS

A.P. Philipse*, B.C. Bonekamp and H.J. Veringa
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands

The kinetics of filtration of a suspension or a liquid by a porous mold sometimes clearly deviates from a linear relation between liquid level and the square root of filtration time. The origin of such deviations is discussed, specifically the influence of the hydraulic properties of the mold and sedimentation of suspended particles or agglomerates.
Phenomenological calculations are compared with new filtration results obtained for alumina and silica suspensions with a controlled degree of agglomeration. This comparison shows that the proposed explanation for the above mentioned deviations is correct.

BA 36 15.40

SLIP CASTING OF ALUMINA BODIES WITH DIFFERENTIAL POROSITIES, A.G. LAMAS, Margarida Almeida, R.M.M. Diz*, Universidade de Aveiro, 3800 AVEIRO, Portugal

Metal-ceramic bonding may require ceramic bodies with differential porosities. The objective of this work was to determine slip casting conditions enabling the preparation of alumina samples to be joined to aluminium metal parts. Rheological and sedimentation studies were used to determine floc structure in aqueous alumina suspensions in the presence of different concentrations of various deflocculants. A slip casting technique was developped to allow fabrication of the bodies by varying the degree of flocculation of the suspensions during the forming period. The porosity and density of the presintered bodies were determined. The results show that the conditions of the starting suspensions influence the density of the bodies and that their variation during the slip casting process enable the fabrication of samples with differential porosities.

BA 37 16.00

OPTIMIZATION OF SLIP-CASTING TECHNIQUE FOR SHORT-FIBRE AND WHISKER-REINFORCED CERAMIC COMPOSITES, J.Lehmann*, B.Müller and G.Ziegler, Deutsche Forschungsanstalt für Luft- und Raumfahrt (DLR), Institut für Werkstoff-Forschung, D-5000 Köln 90, FRG.

Homogeneity and stability of the slurries are critical factors in the formation of short-fibre or whisker-reinforced ceramic composites. Homogeneity and stability are mainly dependent on the selection of suitable organic aids. Damage of thin coatings on the reinforcing components due to tribological effects during the slurry preparation has to be avoided.
The effect of specially selected nonionic surfactants on the rheological characteristics and on the particle mobility is discussed. Based on this optimization the mechanical dispersion can be reduced or even eliminated. Furthermore, the advantage of pressure-assisted slip-casting in various composite systems is shown.

BA 38 16.20

NON-AQUEOUS SLIP CASTING OF ALUMINUM NITRIDE. D. Bernardt*, H. Stadelmann, A. Kranzmann and G. Petzow, Max-Planck-Institut für Metallforschung, PML, D-7000 Stuttgart, FRG

Non-aqueous suspensions of AlN in butylacetate were prepared. Rheological studies proved a good stabilization of these suspensions by steric forces. Green compacts with high packing density were obtained by pressure filtration of highly concentrated, sterically stabilized slips.

The yttria doped AlN was densified by pressureless sintered in nitrogen atmosphere. Microstructure, thermal conductivity and mechanical properties were compared with AlN-ceramics prepared by dry powder processing techniques.

BA 39 16.40

TAPE CASTING AND SINTERING OF AlN, Th. Claassen*, C. Nischik and P. Greil,
Technische Universität Hamburg-Harburg, Arbeitsbereich Technische Keramik, D-2100 Hamburg 90, Federal Republic of Germany.

The development of an AlN slip for tape casting is decribed. The AlN slip consists of an organic solvent and an organic system of dispersing agents, binder and plastisizer. Y_2O_3 is choosed as the sintering additive.
The tapes were cut and stacked to laminated bodies. The organic compounds were vaporized in Ar-atmosphere or under reduced pressure in air. The influence of the organic compounds and conditions of vaporization process on the porosity in the sintered bodies was investigated. The oxidic contamination of the AlN was analyzed after each step of the preparation. Based on these results, the quantity of sintering additives was determined to compensate for the negative influence of Al_2O_3 impurities.
The distribution of SiC-platelets in the AlN-tapes was studied in order to obtain a preferential texture of the reinforcing components. The tapes and laminates were pressureless sintered up to 2000°C. The microstructure and mechanical properties were examined.

BASIC SCIENCE I : Ddensification

Friday 23rd June; 10.20 - 12.40 **Chairman : G. König (FRG)** **Room : Auditorium I**

BA 40 10.20

MICROSTRUCTURE OF GRAIN BOUNDARIES IN CERAMICS, H.K. Schmid
Materials Science and Technology Division, CSIR, Pretoria 0001, RSA

Frequently, the processing of dense and strong ceramics requires the addition of sintering aids resulting in the formation of residual intergranular phases in a liquid-phase sintering process. The materials are therefore composed of various components, normaly a matrix phase plus vitreous or crystalline grain boundary phases.

The microstructure of grain boundaries and the composition of intergranular phases in various ceramic systems were studied by means of analytical scanning transmission electron microscopy (STEM) with high spatial resolution. TEM studies on Ce-TZP, Si_3N_4 and modified $PbTiO_3$ ceramic systems revealed the presence of intergranular phases situated in small pockets at triple grain junctions and in thin films at grain boundaries. EDS results indicated inhomogeneous compositions for the intergranular phases; implications on the crystallization behaviour of grain boundary phases and resulting influences on mechanical properties are discussed.

BA 41 10.40

GRAIN BOUNDARIES DYNAMICS IN CERIA ZIRCONIA CERAMICS, S. Meriani*; E. Bischoff.
Appl. and Ind. Chem. Inst., Trieste, 34127 Italy; Max Planck Inst., Stuttgart, D-7000 FRG.

Grain boundaries are often looked upon as weak spots of most solid systems. In fact, advanced ceramics performance, mainly at high temperature, is largely dependent upon grain boundaries size and properties. It has been recognized that, among other impurities, silica plays an important role because it is an almost ubiquitous contaminant of both oxides and non-oxides ceramics.

During the study of the ceria-zirconia alloys it has been observed that silica containing grain boundaries exhibit a special migration behaviour, strongly influenced by both temperature and environment's atmosphere. The phenomenon has been interpreted through a chemically induced grain boundary migration mechanism.

BA 42 11.00

MICROSTRUCTURAL DEVELOPMENT DURING PROCESSING OF AN Si_3N_4/ZrO_2 MATERIAL, L.K.L. Falk*, Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden; M. Holmström, Swedish Institute for Silicate Research, S-402 29 Göteborg, Sweden

A combination of x-ray diffractometry and analytical transmission electron microscopy has been used to investigate the development of microstructure in an $Si_3N_4/ZrO_2(+Y_2O_3)$ composite ceramic material during formation by pressureless sintering. The Si_3N_4-based ceramic was sintered at 1650 °C, and contained 30 wt% ZrO_2, which was prereacted with 3.3 mol% Y_2O_3, together with 5 wt% Al_2O_3 added as sintering aid. The microstructure of fully sintered material consisted of β-Si_3N_4, ZrO_2 with tetragonal structure, relatively large Si_2N_2O grains containing inclusions of Si_3N_4 and ZrO_2 and an extremely small volume fraction of residual glass.

In order to characterize the detailed sintering process, partially sintered compacts were analysed. An early liquid phase formation during the temperature/time programme used for sintering resulted in a near dense body before the sintering temperature of 1650 °C was reached. Only a small proportion of the α- to β-Si_3N_4 conversion took place during heating. The amount of liquid phase present in the compact was reduced at 1650 °C, and towards the end of the sintering programme Si_2N_2O formed.

BA 43 11.20

CRYSTALLIZATION OF THE INTERGRANULAR PHASE IN SILICON NITRIDE CERAMICS WITH RARE EARTH OXIDE SINTERING ADDITIVES,

M. Peuckert, C. Boberski*, P. Selgert; Hoechst AG, Materialforschung G864, D-6230 Frankfurt/M. 80, F.R.G.

Silicon nitride ceramics have been prepared by pressureless sintering using various rare earth oxides and alumina as sintering aids. The effect of the different kinds of additives on the microstructure and, as a consequence, on mechanical strength and toughness were investigated.
By post-sinter annealing the intergranular glass could be crystallized to different silicates and other phases depending on the rare earth element used. The influence of these different phases on the mechanical properties of silicon nitride ceramics will be discussed.

BA 44 11.40

GRAIN BOUNDARY PHASE ELIMINATION AND MICROSTRUCTURE OF ALUMINIUM NITRIDE

Fumio Ueno*, Akihiro Horiguchi
TOSHIBA Research and Development Center
Komukai Toshiba-cho, Saiwai-ku
Kawasaki, J-210 JAPAN

Aluminium nitride with yttrium oxide additive consolidates by liquid phase sintering to form yttrium aluminium oxides as grain boundary phases. These grain boundary phases were eliminated by firing a powder compact or a full dense ceramic in a carbon housing at above 1800°C. During this process, the yttrium aluminium oxide phases were changing into yttrium oxide and finally no trace of yttrium oxide nor pore was found in the ceramic after several hours. The surface of this pure aluminium nitride ceramic was covered by yttrium nitride. This phenomena interpreted as follows. The grain boundary oxide phase is carbo-reduced to form aluminium nitride and yttrium nitride at the surface of the ceramic. As a result, oxide concentration gradient is developed in the ceramic which is relaxed by the grain boundary diffusion of the oxide phase. Kinetics of this phenomena, relation between microstructure and the thermal conductivity will be discussed.

BA 45 12.00

TWIN-ASSISTED GRAIN GROWTH DURING LIQUID-PHASE SINTERING OF $BaTiO_3$ CERAMICS, G. Kästner*, R. Wagner; V. Hilarius
Institute of Solid State Physics & Electron Microscopy of the Academy of Sciences of the German Democratic Republic, PF 250 Halle DDR 4010;
Kombinat Keramische Werke Hermsdorf, ZFT, Hermsdorf 6530

Solution and growth of grains during liquid-phase sintering can be affected by crystallographic features to some extent. On principle, the laws of crystal growth are assumed to govern more or less the size and shape of grains which can exhibit crystallographic facetes, depending on the sintering conditions. If facetes occur already in the stage of shrinking (densification) they favour distinct orientation relationships of interacting grains. Thus also twins may be formed. This view is supported by transmission electron microscopy (TEM) of $BaTiO_3$ ceramics. Further mechanisms of twinning are known from grain growth during recrystallization of deformed metal crystals /1/.

Twinned grains, in particular those containing a twin lamella, are known to be favoured for preferential, exaggerated growth (abnormal or discontinuous grain growth). In case of $BaTiO_3$ such grains are known as $\{111\}$-faceted platelets if sintering occurs near the eutectic temperature /2/ while at higher temperatures, they tend to attain the $\{100\}$-faceted cube shape /4/. In both cases, preferential growth occurs on those faces where the twin lamella emerges (i.e. on the 6 edge faces of the platelet or on the 6 cube faces).

An explanation of this mode of preferential growth has been derived from TEM observations. No evidence could be found of re-entrant crystallographic facete angles assumed in /2/. The mean orientation of the grain boundary does not alter considerably across the twin lamella. Therefore the latter exposes a boundary crystallographically different from the low-indexed faces of the surrounding matrix (which grow most slowly). This deviation from the orientation of lowest growing speed is considered to be the basic reason for preferential growth induced by the emerging twin lamella /3/.

/1/ A. Berger, Thesis, Universität Göttingen 1986
/2/ H. Schmelz and H. Thomann, cfi, Ber. DKG 61 (1984) 199
/3/ G. Kästner et al., J. Mater. Sci. Lett., in press
/4/ D.Bühling, V.Hilarius, G.Kästner,cfi Ber.DKG,in press

BA 46 12.20

MICROSTRUCTURE EVOLUTION OF CORDIERITE XEROGELS WITH TEMPERATURE, A. Dauger, D. Fargeot, A. Lecomte, H. Vesteghem*, UA CNRS 320, ENSCI Limoges 87065, France.

Cordierite wet gels have been prepared by hydrolysis-condensation of silicon and aluminium alkoxides in an alcohol solution with magnesium nitrate.
In previous papers we reported the hypercritical drying of the wet gels and the thermal behaviour of as obtained aerogels.
This paper is devoted to the study of the microstructure evolution with temperature of cordierite xerogels prepared by classical drying of the same wet gels. This evolution was studied by small angle X-ray scattering measurements, SEM and TEM observations. The dependance of gel microstructure with the drying process is discussed.

BASIC SCIENCE II : COMPOSITES

Monday 19th June; 11.30 - 12.30 **Chairman : D.J. Green (USA)** **Room : Auditorium II**

BA 47 11.30

IN SITU SYNTHESIS OF SILICON CARBIDE WHISKERS IN AN ALUMINA OR ALUMINA/ZIRCONIA MATRIX POWDER, J.-P. Erauw**, F. Delannay, Université Catholique de Louvain, Dépt. des Sciences des Matériaux et des Procédés, PCPM - Réaumur, Place Sainte Barbe 2, B-1348 Louvain-la-Neuve, Belgium.

In situ synthesis of silicon carbide whiskers within an alumina or alumina/zirconia matrix powder was investigated as an alternative to the conventional mixing procedure for the preparation of SiC whiskers reinforced oxide composites.
The synthesis reaction consists in a carbothermal reduction of either silica or zircon in presence of metallic aluminum. It is carried out under neutral atmosphere at 1300-1500 °C.
Operating conditions have been optimized in order to promote both the mutual distribution of the constituents and the obtention of silicon carbide whiskers presenting a suitable morphology in view of the reinforcement expected.
A special emphasis has been laid on the catalytic influence of some additions on the amount, morphology and growth mechanism of the whiskers.
The sinterability of the composite powders has been tested by hot-pressing. Densification kinetics is described. Results about the microstructure and rupture behaviour of the sintered pellets are reported.

° aspirant du F.N.R.S.

BA 48 11.50

Al_2O_3/Al-BASE COMPOSITES OBTAINED BY DIRECTED OXIDATION OF MOLTEN Al ALLOYS, M. Sindel* and N. Claussen,
Technische Universität Hamburg-Harburg, Arbeitsbereich Technische Keramik, D-2100 Hamburg 90, Federal Republic of Germany.

The directed oxidation of molten metals represents an alternative technology for composite fabrication overcoming some of the limitations of CVI and multiple sol-gel infiltration techniques. This work discusses the growth behavior and microstructural evolution for the matrix system Al_2O_3/Al. The filler material, consisting of different α-Al_2O_3 powders, Al_2O_3 fibers, SiC particles and SiC whiskers, is "infiltrated" by the reaction of an aluminum alloy with air, i.e. Al_2O_3 grows from the original metal surface into the filler. The porous filler body, usually formed by conventional P/M techniques, nearly represents the final shape and dimensions of the Al_2O_3/Al-matrix composite. The matrix formation mechanism is discussed with respect to alloy content, temperature and filler type. Some mechanical properties, such as K_{Ic} and fracture strength, are given.

BA 49 12.10

REINFORCED CERAMICS MADE OF SILICON -ORGANIC COMPOUNDS

E.Fitzer,M.Keuthen*,H.Münch,D.Nieder

Institut für Chemische Technik
Universität Karlsruhe
7500 Karlsruhe, FRG

The paper will treat the synthesis and some properties of silanes, carbosilanes and silazanes,followed by their thermal decomposition to different ceramic solids like SiC and Si_3N_4.Many products of commercial interest which are to realize by their pyrolysis will be mentioned by the authors.A very promising example, the production of whisker-,short -fiber- and continous-fiber-reinforced SiC and Si_3N_4-ceramics will be given in details.

BASIC SCIENCE II : MECHANICAL PROPERTIES

Monday 19th June; 15.00 - 17.00 — Chairman : D. Broussaud (France) — Room : Auditorium II

BA 50 15.00

FRACTURE BEHAVIOUR RELATED TO MICROSTRUCTURE IN SiC-SiC AND C-SiC FIBRE COMPOSITES.

G. Navarre*, D. Rouby, G. Fantozzi, INSA, 69621 Villeurbanne, France
J.M. Jouin , S.E.P., 33160 Saint-Médard-en-Jalles, France

The material studied are processed by the Société Européenne de Propulsion in Bordeaux (France).The SiC-SiC composite is bidirectional, consisting of superposed woven clothes of Nicalon bundles with the same warp direction; the Carbon-SiC composite is a non woven quasi-isotropic laminate having also a few carbon fibres parallel to the thickness direction. These materials are densified with a SiC matrix by chemical vapor infiltration technique.
The fracture behavior is conditioned by several microstructural mechanisms involving the fibres, the matrix, and also, the fibre-matrix interface.
On a macroscopic point of view, the fracture behaviour is analysed by means of the crack resistance curves (R curves). The tests are performed at room temperature by three point bending on S.E.N.B. specimens in edgewise orientation (the nocth front is normal to the lamina or cloth plane), and acoustic emission is measured during the test.
On a microscopic scale, the role played by the microstructure is analysed by the observation of the fracture surface by scanning electron microscope. Extended pull-out of fibres is observed, illustrating that the fibre-matrix sliding is an important mechanism. In addition, microindentation tests are performed in order to measure the critical shear stress at the interface.
The shapes of the R-curves are described and details of the R-curves are discussed in relation with the arrangement and size of the bundles (mesoscopic scale). The non linear and non-elastic fracture behaviour is analysed in relation with the microscopic observations. The difference between SiC-SiC and C-SiC materials is discussed with regards to the difference in fibre nature and microstructure.

BA 51 15.20

SEM IN-SITU BENDING EXPERIMENTS ON HIGH PERFORMANCE CERAMICS,

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A new developed 4-point bending device was designed for testing high-strength-ceramics in the vacuum chamber of a scanning electron microscope (SEM). Simultaneous SEM-observation of ceramic specimens during crack propagation under various loading conditions is possible and typical results are presented on a video-tape. Controlled crack propagation processes and their dependence on the microstructure are studied on a modern Sintered Silicon Nitride (SSN).

Characteristic processes such as crack deflection at elongated grains, crack branching at the crack tip and crack bridging behind the crack tip are shown at magnifications up to 20.000 X in situ. With this device it is possible to prove the microstructural models of energy dissipative processes and fatigue mechanisms in advanced structural ceramics.

BA 52 15.40

INTERFACIAL FRICTION & DEBOND STRENGTH OF ALIGNED CERAMIC MATRIX COMPOSITES

N. Shafry*, D.G. Brandon & M. Terasky
Dept. of Materials Engineering, Technion,
Israel Inst. of Technology, Haifa, Israel 32000.

The present work describes a quantitative test for the measurement of interfacial friction stresses and debond strength in aligned fibre- and whisker-reinforced ceramic matrix composites. A lapped and polished disc of the aligned composite cut normal to the reinforcement is uniaxially compressed between a stiff, polished Si_3N_4 tile and a soft, ductile aluminium plate. The Si_3N_4 tile imposes a condition of uniform strain on one surface of the composite slice, while the soft aluminium imposes a condition of uniform stress on the other surface. On loading the specimen assembly the elastic mismatch between the reinforcement and the matrix results in indentation of the aluminium by the reinforcement, the extent of indentation depending on the shear strength of the interface and the applied load. The depth of the indentations and the extent of fibre recovery on unloading the specimen are monitored by optical and scanning electron microscopy, and related to the mechanical properties of the interforce.

BA 53 16.00

MECHANICAL PROPERTIES AND AGING BEHAVIOUR OF HOT ISOSTATICALLY PRESSED Y-ZrO_2 CERAMICS MADE OF HYDROTHERMALLY PRODUCED AND SUPERCRITICALLY DRIED POWDERS,

T.T. Lepistö*, T.A. Mäntylä, Tampere University of Technology, P.O. Box 527, SF 33101 Tampere, Finland; G. Gunnarsson, E.L. Sveinsdottir, Technological Institute of Iceland, Keldnaholt, IS-112 Reykjavik, Iceland; A-K. Westman, ABB Cerama, S-91500 Robertsfors, Sweden.

In this study ZrO_2+Y_2O_3 powders were made by supercritically drying zirconium/yttrium hydroxide, or hydrothermally produced zirconia, in order to minimize agglomerate formation. The powders have good sintering properties and sinter to high densities at low temperatures. Hipping of the powders resulted in a microstructure with a small grain size and high density, with strength values comparable to those of commercial powders. The aging properties of the hipped materials in water vapour atmosphere at 150 °C are very promising, proposing this manufacturing procedure to be a feasible way to improve the structural stability of TZP ceramics.

BA 54 16.20

INDENTATION STRENGTH BEHAVIOR OF COMPRESSIVELY-STRENGTHENED BRITTLE MATERIALS

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The Pennsylvania State University,
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It is well accepted that the introduction of surface compressive stresses can be used to increase the strength of brittle materials that fail from surface flaws. The failure criterion is however not well understood when the compressive layer is less than the surface crack size. The fracture mechanics associated with indentation cracks and the resultant post-indentation strength will be discussed. Recent experiments on the indentation strength of ion-exchanged glasses will be discussed. For the case of thin exchange layers it has been found that the strengthening is dependent on flaw history. It is proposed that this behavior is a result of changes in the crack front shape that occur during stressing. These experiments also indicate that the measurement of residual surface stress using an indentation approach can lead to erroneous results.

BA 55 16.40

INVESTIGATION OF MICRO- AND MACROCRACK PROCESSES IN ALUMINA USING COMPLIANCE AND AE MEASUREMENT METHODS,

G. Kleer*, C. Sklarczyk**, R. Schönholz and W. Döll,
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D-7800 Freiburg, West-Germany;
**Fraunhofer-Institut für zerstörungsfreie Prüfverfahren, D-6600 Saarbrücken, West-Germany.

The crack propagation behaviour of alumina was investigated on double torsion specimens; a part of these specimens was pre-damaged by different treatments. The relation between stress intensity factor and crack speed was determined from the change of the specimens compliance due to crack propagation under the applied loads. A specific property of this evaluation method is that it provides integral crack quantities. In order to get additional information on micro-mechanisms at fracture the acoustic emission (AE) from the tip zone of the propagating crack was analysed. According to the results slow crack propagation occured between K_I = 3.6 and 4.2 $MN/m^{3/2}$. Pre-damageing by mechanical and thermal loading lead to shifts of the crack resistance to lower values. Event rates were obtained in a range between 10^{-1} and 10^3 s^{-1} and were mainly correlated to the speed of the macro crack as evaluated by the compliance method. Influences of micro cracking effects were observed especially in pre-loaded material and will be discussed on the base of available models.

BA 56 09.00

PREPARATION OF SIALONS BY THE NPS TECHNIQUE, I.W.M.Brown*, Chemistry Division, DSIR, Lower Hutt, New Zealand; R.Pompe and R.Carlsson, Swedish Institute for Silicate Research, 402 29 Göteborg, Sweden.

The Nitrided Pressureless Sintering (NPS) technique has been used to prepare sialon compositions in the O'-ß' field, along the Si_3N_4-Al_2O_3 join. Following pre-nitridation at 1250°C, samples were fully nitrided after 6 hours at 1370°C, conditional upon achieving sufficiently high surface areas during milling. NPS Si_3N_4 materials are usually prepared at 1350°C in less than 3 hours. The increased time and temperature conditions for full nitridation of sialon compositions reflect a difference in the reaction mechanism. TG, XRD and dilatometric analyses indicate that the nitridation mechanism involves the formation of a yttrium silicate phase during the pre-nitridation step which is probably consumed in favour of a partial Si_3N_4-SiO_2-Y_2O_3-Al_2O_3 melt below the nitridation temperature. Yttrium aluminium garnet (YAG), whose volume fraction increases with time at temperature and with increasing level of Al addition, is formed promptly under these nitridation conditions. This can be compared with NPS Si_3N_4 in which yttrium silicate phases, including YN-apatite, remain the stable phases upon nitridation.

Sintering of the fully nitrided materials was undertaken at 1770-1830°C under nitrogen. The products of sintering and of subsequent heat-treatment to optimise crystallinity were characterised by XRD. Materials property measurements are reported which relate strength to both preparative and compositional variables.

BA 57 09.20

ON THE REACTION MECHANISM AND MECHANICAL PROPERTIES OF NITRIDED PRESSURELESS SINTERED (NPS) Si_3N_4-ZrO_2 COMPOSITE CERAMICS, *K. Rundgren, R. Pompe, and R. Carlsson, Swedish Institute for Silicate Research, Box 5403, S-402 29 Göteborg, Sweden; K. Kishi and S. Umebayashi, Government Industrial Research Institute, Kyushu, Shuku-machi, Tosu-shi, 841 Saga-ken, Japan.

ZrO_2-toughened Si_3N_4 ceramics has been prepared and evaluated. The Si_3N_4 matrix was made by nitridation of Si:Si_3N_4/ZrO_2 submicron powder compacts (NPS-technique) followed by pressureless or gas-pressure sintering. The reaction between ZrO_2 and Si:Si_3N_4 has been studied and methods to minimize the formation of undesirable intermediary phases, i. e. $ZrSi_2$, ZrN and Zr-oxynitride have been tested. ZrO_2 was alloyed with Y_2O_3 and simultaneously, the Si:Si_3N_4 powder mixture was coated with Al_2O_3 using an Al-alkoxide. By this coating the reaction of Si with ZrO_2 giving $ZrSi_2$ and later ZrN on nitridation could not be sufficiently prevented. The ZrN formed, however, has been shown to disappear on sintering, presumably due to a reaction with ZrO_2 to Zr-oxynitride aided by the presence of a sintering liquid. By the stabilization of cubic (c) ZrO_2 with 10 mol% Y_2O_3 prior to mixing with Si the formation of $ZrSi_2$ was precluded at 1150°C. Preliminary data for not fully densified samples made from Al_2O_3-coated Si:Si_3N_4 powder mixtures with addition of ZrO_2 and Y_2O_3 as colloidal sols showed a fracture toughness of 5.8 ± 0.6 MPa·$m^{1/2}$ and a room temperature flexural strength of 700 ± 60 MPa.

BA 58 09.40

STUDIES OF GELS FORMED IN THE ALUMINA-SILICA SYSTEM, S. Bentsen, J.L. Holm*, and B.A. Øye, Inst. of Inorg. Chemistry, The Univ. of Trondheim, N-7034 Trondheim, Norway

The series of reactions by which kaolinite transforms to mullite is perhaps the most important in the entire field of ceramic technology. It has been studied over a longer period of time than any other single reaction, but nevertheless retains many unsolved problems.

In this work gels of synthetic kaolinites formed from mixtures of very pure metal-organic compounds of aluminium and silicon and with different Al/Si ratios, have been investigated by DTA/TG/DTG up to 1200°C. The weight-losses from the samples as well as the areas of the exothermic peak at 980°C have been determined. The heat capacities of the so-called "meta-kaolin phase", kaolinite heated up to 700°C, and the "mullite phase", kaolinite heated to 1050°C, have been determined by DSC in the temperature range 450-550 K. The composition of the phase formed above the exotherm at 980°C, has been discussed with reference to the wellknown work by Brindley and Nakahira (J. Am. Cer. Soc. 42 (1959) 319).

BA 59 10.00

CRYSTALLIZATION BEHAVIORS OF MgO-Al_2O_3-SiO_2 CLASS-CERAMICS DERIVED FROM ALKOXIDE GELS AND MOLTEN CLASSES, D.C. Fu*and J. Engell, Institute of Mineral Industry, The Technical University of Denmark, DK-2800 Lyngby, DENMARK.
Class-ceramic based on cordierite and enstatite crystals are prepared by heat-treating molten glasses and sintering alkoxide gel compacts. Classes and gels of the same composition do not exhibit the same initial phase evolution processes on heating. Depending on the composition, the molten glasses crystallize metastable high-$quarts_{ss}$ or Mg-petalite phase first, whereas the cooresponding alkoxide gels crystallize aluminous enstatite. At higher temperatures of heat treatment, the crystallized phases approach the same in glasses and gels of the same composition. The addition af TiO_2 into the base composition lowers the crystallization temperature as well as the crystallization activation energy. Moreover, it induces phase separation and bulk crystallization in the glasses and gels, which results in fine-grained microstructure of the final materials. Surface crystallization is the dominant mechanism in TiO_2-free glasses and gels. Fibrous bundles or needle-shaped crystals are observed in the heat treated glasses whereas interconnected pores and inter-locking crystals typify the microstructure of the sintered gel compacts.

BA 60 10.20

EMISSION MIXES FOR HIGH INTENSITY DISCHARGE (HID) LAMPS - A REVIEW, R. K. Datta, General Electric Co., Nela Park, Cleveland, Ohio 44112, U.S.A.

An emission mix in HID lamps is applied as a thin coating on the tungsten (W) electrode to lower its operating temperature and extend useful lamp life. Polycrystalline oxide materials such as alkaline-earth oxides, tungstates, molybdates, rare-earth oxides, etc., are commonly used as emission mix. The interaction at the lamp operating conditions (p, t) between the emission mix, arc material and the electrode (electrode-activation process) is the key to the improved lamp maintenance. All the steps involved in activation mechanisms are not understood; it is believed that low work-function materials (neutral atoms, ions, oxides, etc.) released during activation or by thermal decomposition of the mix migrate to the electrode tip with the formation of a layer of activating species on the electrode surface:

$$Ba_2CaWO_6 + W \rightarrow Ba_{2-x}CaW_1 + \frac{x}{3} O_6 + xBa$$

Based on the suggested activation processes, commercial mixes can be broadly classified as: (1) metal on metal; (2) excess metal on semiconductors, oxidic compounds; (3) bulk semiconductors. Requirements, design, process and activation of common emission mixes will be presented.

BA 61 10.40

PHASE COMPOSITION AND SINTERABILITY OF THE MIXTURES IN THE SYSTEM $CaO-Cr_2O_3-TiO_2$, J. Zborowski* and W. Krönert, Institut für Gesteinshüttenkunde, D-5100 Aachen, FRG

Experiments were carried out to check the ability of TiO_2 to promote the sintering process of calcium chromite ($CaO.Cr_2O_3$). Starting compositions lying within the triangle $CaO.Cr_2O_3$-$CaO.TiO_2$-Cr_2O_3 (CK-CT-K) were fired at 1300 and 1600°C and cooled down naturally with furnace. Apparent and relative density were determined and SEM-observations of the microstructure were carried out. Phase composition was examined using X-ray diffraction and semi-quantitative EDX analysis. Under applied experimental conditions CT-K and CK-CT solid solutions were proven to be coexistent in compositions lying on the respective tie lines. No ternary compounds were found within the examined area which turned out to be mainly a three phase field. Only some compositions lying on the K-CT tie line revealed a good sinterability and reached relative densities over 90% after firing at 1600°C .

BASIC SCIENCE II : PHASES AND REACTIONS

Tuesday 20th June; 15.00 - 17.00 Chairman : M. Backhous Ricoult (FRG) Room : Auditorium II

BA 62 15.00

TRANSPORT PROPERTIES OF THE WUSTITE PHASE

F. Adam, B. Dupré, C. Gleitzer and J. Nowotny*
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The equilibration kinetics has been measured for the wustite phase $Fe_{1-x}O$ in the temperature range 1100-1275 K. The studies have involved both oxidation and reduction runs. Regimes in which different processes may control the gas-solid kinetics will be discussed. At x=0.081 the chemical diffusion coefficient was determined within the bulk diffusion regime:

$\tilde{D} = 3.3 \times 10^3 \exp(-222\ [kJ \times mol^{-1}]/RT)$.

Dilution experiments have indicated that the oxidation kinetics is bulk diffusion controlled. The effect of composition and resulting defect interactions on diffusion are also considered. $\tilde{D}$ decreases by the factor of 4 as x increases from 0.063 to 0.10. Finally, the effect of the near-surface diffusive resistance produced by segregation and resulting electric fields in the boundary layer on the gas-solid kinetics will be discussed.

*/Present address: Max-Planck-Institute for Solid State Research, 7000 Stuttgart 80, FRG

BA 63 15.20

MULLITE-FERRITE INTERACTION DURING THE SINTERING OF MgO-BASED FERRITES.

K.J. Sievewright* and F.R. Salo
Manchester Materials Science Centre, University of Manchester, Manchester M1 7HS, UK.

The chemical reactions and microstructural changes associated with the sticking of mullite saggers during the firing of MgO-based ferrites have been studied using high temperature differential scanning calorimetry, differential thermal analysis, X-ray diffraction analysis and optical and electron metallography. The sticking phenomenon has been associated with the formation of low melting point silicates as silica is rejected from the mullite at high temperature. On rejection the silica reacts with impurities, some of which are present in the mullite and some of which are picked-up during industrial handling. No significant differences have been observed between the behaviour of normal, low alkali and fused mullite saggers. In all saggers a sub-surface zone consisting of glassy-silicate and a variety of needle-like growths and cubic crystals of 2:1 (Al_2O_3 - SiO_2) mullite has been shown to form on thermal cycling. This zone leads to spalling of the surface layers and the ultimate failure of the mullite saggers.

BA 64 15.40

THERMAL EXPANSION STUDY OF ALKALI-SUBSTITUTED CORDIERITES

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ABSTRACT

Structural studies of alkali modified cordierite with $M_xMg_2Al_{4+x}Si_{5-x}O_{18}$ formula (M = K, x = 0.5 ; 1.0 and M = Cs, x = 0.5) were performed between 20 and 825°C using a time-of-flight powder neutron diffraction technique on sintered samples obtained by glass crystallization. The evolution of the relative thermal expansion is analysed as well in terms of both nature and concentration of alkali atoms as in terms of thermal history of the samples.

All the crystal structures of these phases are related to the pure hexagonal cordierite one : full Al/Si disorder is observed, and alkali atoms are located within the hexagonal channels. However, long time annealing always favours some Al/Si ordering.

Evolutions of a and c parameters can be explained by a regularization of the $T(1)O_4$, $T(2)O_4$ and MgO_6 polyhedra and by the corresponding reorganization of the polyhedral network. For the K-substituted materials, the c parameter change mainly depends on the thickness change of the $T(1)O_4$-MgO_6 sheets, whereas the steric effect of cesium is rather predominant for Cs-substituted materials.

A very low value of the mean thermal expansion coefficient ($\bar{\alpha} \simeq 0.4 \times 10^{-6}$ K^{-1} between 20 and 825°C), resulting from an opposite evolution of the a and c lattice parameters, has been obtained for a fully disordered $K_{0.5}Mg_2Al_{4.5}Si_{4.5}O_{18}$ material.

BA 65 16.00

STRUCTURAL INVESTIGATION OF THE PYROLYSIS PROCESS OF COVALENT CERAMICS PREPARED BY POLYMER ROUTE

Florence Babonneau*[1], Gian Domenico Soraru[2] and John D. Mackenzie[3].
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[2]Dipartimento de Ingegneria, Università di Trento, 38050 Mesiano-Trento, Italia.
[3]Department of Materials Science, University of California, Los Angeles CA 90024, USA.

Advanced ceramics such as carbides and nitrides, have recently been prepared from metal organic polymers. This paper will present results concerning SiC and SiC/TiC systems. The precursor for SiC is a usual polycarbosilane while precursors for SiC/TiC composites were prepared by reacting a titanium alkoxide with polycarbosilane. The transformation of the polymeric precursor in final ceramics has been investigated by MAS-NMR. The crystallization process has been followed by XRD and TEM. A comparison of the crystallization of the SiC phase in the pure system and in the composite system will be presented.

BA 66 16.20

HIGH TEMPERATURE REACTIONS AT INTERFACES BETWEEN SILICON CARBIDE AND STEELS,

M. Backhaus, CNRS, 92195 Meudon, France;
K. Ostyn', BIL, 9000 Gent, Belgium.

Solid state reactions between different variants of SiC and stainless steel (Fe-18Cr-8Ni) have been studied in a temperature range of 875-1275K. Experiments with the pure components of the steel or binary alloys, Fe-Ni or Fe-Cr or Ni-Cr, showed the influence of the different elements of the steel on the chemical reactions at the interface. The kinetics of the different reactions have been studied. Chemical composition and structure of the reaction products have been analyzed by X-ray, microprobe, STEM- or SIMS-analyses. Details of the morphology of the phases and interfaces are revealed by electron microscopy studies.
Our experimental results on simple metal-SiC systems will help to predict the structure of complex diffusion bondings between steels and silicon carbide and the evolution of the structure of such joints after long time exposure to high temperatures.

BA 67 16.40

PREPARATION AND CHARACTERIZATION OF SOME NEW NITROGEN GLASS CERIMICS.

D.S.Perera, P.Korgul and D.P.Thompson*,
University of Newcastle upon Tyne, NE1 7RU, UK

Glass-forming compositions have been identified in M-Si-O-N and M-Si-Al-O-N systems which crystallize to give single-phase β"-magnesium sialor, Y_2SiAlO_5N, $MgYSi_2O_5N$ and $LnSiO_2N$ (Ln=La,Ce,Nd) glass ceramics. β"-magnesium sialon requires β'-sialon as a nucleating agent and very rapid quenching is needed to avoid crystallization of Mg_2SiO_4; the resulting β" phase is stable up to ≤1050°C Y_2SiAlO_5N is an α-wollastonite which occurs over a range of compositions near the mid-point of the $YSiO_2N$-$YAlO_3$ join, and is bes prepared at more silica-rich compositions than that of the simple formula quoted above. It is unstable above ~1100°C. $MgYSi_2O_5N$ is a nitrogen pyroxene phase and was first observed during heat-treatment of Si_3N_4 ceramics densified with mixed MgO/Y_2O_3 additions. It has some range of homogeneity by substitution of Al+O by Si +N and is stable up to ~1450°C. $MSiO_2N$ α-wollastonites are well known but whereas $YSiO_2N$ melts incongruently and crystallizes to give mixed products, the La,Ce and Nd derivatives form single-phase glass ceramics.

BA 68 15.00

THE EFFECTS OF CARBON AS A SINTERING AID IN SiC

W. van Rijswijk*, Hoogovens Groep BV, P.O. Box 10.000, 1970 CA IJMUIDEN, HOLLAND
D.J. Shanefield, Rutgers University, Piscataway, New Yersey 08855 - 0909, USA.

Carbon, along with other material such as boron, is commonly used to enhance sintering in silicon carbide. It is generally considered that a silica impurity layer around each carbide particle must be reduced for effective sintering, and carbon could serve that function. By bringing together data from the literature it is shown that carbon also acts as a sintering aid by enhancing the bulk diffusion of SiC. The effectiveness of carbon as a sintering aid in SiC is discussed in the light of these two processes.

BA 69 15.20

DENSIFICATION AND PHASE ANALYSIS OF Y-TZP'S CONTAINING GROUP V OXIDES,

C. Crabbe(*) and T.J. Davies
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The densification, grain growth characteristics and phase composition of a 5wt%Y_2O_3 sub-micron zirconia powder containing group V oxides of niobium, vanadium and tantalum was studied. Particular attention was paid to the effect of time and temperature on the formation of c-ZrO_2 and t'-ZrO_2, and the transformability to m-ZrO_2 on grinding.

BA 70 15.40

COMPACTION AND SINTERING BEHAVIOUR OF NANO-CRYSTALLINE Y-TZP,

A.J.A. Winnubst*, G.S.A.M. Theunissen and A.J. Burggraaf, University of Twente, Faculty of Chemical Technology, Lab. for Inorganic Chemistry, Materials Science and Catalysis, P.O. Box 217, 7500 AE Enschede, The Netherlands.

Y_2O_3 doped tetragonal ZrO_2 powders with a crystallite size of 8 nm are prepared by means of two hydrous-gel precipitation techniques. These methods are the hydrolysis of a metal alkoxide or a metal chloride. The density development and change in pore morphology during isostatic compaction are studied. In this way it could be concluded, that both powders are weakly agglomerated. These agglomerates are all fractured prior to sintering. The "alkoxide" powders also contain strong aggregates.
The change in crystallite size and pore morphology during sintering are also studied. The sintering kinetics are probably determined by the aggregate structure within the green compact, which is different for the investigated powders. A nanoscale ceramic (grain size 55 nm) can be obtained after sintering a "chloride" compact during 6.5 hr at 1045°C.

BA 71 16.00

OXYGEN PARTIAL PRESSURE IN HIP SINTERING ATMOSPHERE FOR ENGINEERING CERAMICS

K. Ishizaki
Dept. of Materials Science and Engin., School of Mechanical Engin., Nagaoka Univ. of Tech., Nagaoka, Niigata 940-21, Japan

The Importance of oxygen partial pressure on engineering ceramic sintering is commonly known. The same aspect on HIP sintering must be even more critical due to the higher pressures applied, however this important aspect is not discussed commonly, because of difficulty to handle this problem in HIPping units, especially in the case of capsul-HIPping.

The author describes a generalized method to approach this problem for HIPping including capsul-HIP process by modifying the free energy of reactions at high pressures. Example cases on silicon nitride at extremely low oxygen partial pressure, as well as super conducting ceramics at very high oxygen partial pressure are discussed.

BA 72 16.20

MICROSTRUCTURE DEVELOPMENT DURING GAS PRESSURE SINTERING OF Si_3N_4,

F. Friedrich*, M. Komac, D. Kolar,
"Jožef Stefan" Institute, Ljubljana,
*"Belinka", Ljubljana, Yugoslavia

Powder mixture consisting of Si_3N_4 and small amounts of sintering additives i.e. MgO, Al_2O_3 and metallic silicon were used to study sintering and microstructure development during the heat treatment of Si_3N_4 ceramic. Samples were sintered under nitrogen gas overpressure to high density (98-99% T.D.) and subsequently annealed at 1400°C different periods of time. Generally, by increasing sintering temperature and/or pressure the coarsening of β-Si_3N_4 grains was promoted, while during thermal treatment anisotropic growth of crystals was observed.

An attempt is made to correlate the microstructural peculiarities with mechanical properties of Si_3N_4 ceramics.

BA 73 16.40

SINTERING OF AlN POWDERS OBTAINED FROM CARBOTHERMAL REDUCTION.

M.P. Corral, J.S. Moya and R. Martinez*.
Instituto de Cerámica y Vidrio (CSIC), Ceramic Department, Arganda del Rey, 28500 Madrid, Spain.

The influence of particle size, particle size distribution and specific surface area of several starting alumina powders on the carbothermal reduction production of AlN powders has been studied. AlN powders have been sintered in N_2 atmosphere, by using additives such as CaO, Y_2O_3, CeO2, etc. In the present work, the effect of starting alumina powders, its reduction process, and the use of additives on the AlN sintering is considered.

BA 74 author present: 11.00 - 12.30

PREPARATION AND CHARACTERISTICS OF ZIRCONIA/ALUMINA CERAMIC POWDERS,

P. den Exter*, T.H.P. Leuwerink, A. Bos, A.J.A. Winnubst, E.B.M. Doesburg and A.J. Burggraaf.

University of Twente, Faculty of Chemical Technology, Lab. of Inorganic Chemistry, Materials Science and Catalysis, P.O. Box 217, 7500 AE Enschede, the Netherlands.

Zirconia/alumina powders are prepared by gel-precipitation and sol-gel techniques. A description is given of the synthesis. The resulting powders are characterized in terms of phase composition, surface area and crystallite size. The effect of powder characteristics on compaction and sintering behaviour is discussed in terms of phase composition and strength of agglomerates. Zirconia/alumina powder compacts are pressureless sintered to dense composites at 1600°C. A homogeneous dispersion of zirconia in the alumina matrix is obtained.

BA 75 author present: 11.00 - 12.30

THE PRODUCTION OF FINE-GRAINED PURE ALUMINA AND ZIRCONIA-ALUMINA COMPOSITES.

A. Bos*, P. den Exter, A. J. A. Winnubst, E. B. M. Doesburg, A. J. Burggraaf

CKKO (Centre for Ceramic and Catalyst Research)
Faculty of Chemical Technology, University of Twente, P.O.Box 217, 7500AE Enschede, The Netherlands

It is aimed to fabricate a very fine-grained alumina ceramic with dispersed stabilised zirconia (ZY5.8), toughened by the martensitic t->m transition.
The various stages of production for the zirconia-alumina (15 wt% zirconia) composite, i.e. powder synthesis, calcination, forming and sintering, are compared with those for pure alumina, with and without the sintering additive MgO. Dilatometer experiments with pressed powder-compacts are performed at various heating rates to study the sintering behaviour and to obtain the optimal sintering temperature for minimal grain growth and optimal densification.
The powders and end-products are characterized by the usual methods (BET, XRD, SEM, XRF a.o.).

BA 76 author present: 11.00 - 12.30

TOUGHENED ALUMINAS PRODUCED BY A SOL-GEL PROCESS,

L.Montanaro (°); B.Guilhot (°°); Ph.Gillard (°°); J.P.Lecompte (°°°); A.Negro (°) (*)
(°) Dep.Materials Science & Chemical Engineering, Politecnico, TORINO, Italy
(°°) Dép.Chimie Physique des Processus Industr., E.N.S.M., St.ETIENNE, France
(°°°) Lab. Céramiques nouvelles, U.A.320,Univ., LIMOGES, France

The toughening of ceramics can be pursued developing composites materials: the particle-reinforced composites and the fiber-reinforced composites.
In this paper, some results obtained in the development of aluminas toughened by the dispersion of zirconia particles or ceramic fibers (SiC whiskers) have been reported.
In both the cases, the possibility of achieving a good dispersion of the toughening agents using a sol-gel technique in the preparation of the powders has been exploited.
Two alumina-zirconia composites, containing 15 and 20 w.% respectively of zirconia, have been prepared.
As regards the SiC whiskers, two fiber-reinforced composites with the 20 and 40 v.% of whiskers have been prepared.
On all the sintered specimens, the mechanical properties (σ_F and K_{Ic}) have been evaluated.

BA 77 author present: 11.00 - 12.30

THE USE OF PLASMA SYNTHESIS AND PIGMENTARY COATING TECHNOLOGY TO PRODUCE YTTRIA STABILIZED ZIRCONIA HAVING SUPERIOR PROPERTIES. **G.P. Dransfield*, K.A. Fothergill and T.A. Egerton,
Tioxide U.K. Ltd., Central Laboratories, Portrack Lane, Stockton-on-Tees, Cleveland. TS18 2NQ.**

Abstract

Zirconia powder has been successfully synthesized from zirconium tetrachloride, using a DC plasma. The powder produced is ultrafine with surface area of ~16 m^2/g and median size of <0.1 um. The powder has high purity with respect to Si, Fe and Na (<100ppm). Pigment coating technology has then been used to add yttria stabilizer via a $YCl_3.6H_2O$ solution. Electron micrographs of the coated product are presented.

Dilatometry demonstrates the excellent sinterability of the coated powder. The product may be sintered at 1350°C to give ceramic test pieces of >97% density. Peak strengths of ~1.4 GPa, when measured by biaxial disc flexure, have been recorded for 2 mole% yttria addition. Since this level of addition falls below that which is normally required, it is believed that a more homogenous product has been achieved. The material also displays superior ageing under water at 180°C. The properties are compared with test pieces from commercially available yttria stabilized zirconias.

BA 78 author present: 11.00 - 12.30

PRESSBODIES AND POWDERED FINE CERAMICS BY SPRAY DRYING

K. Masters, Ph.D.
A/S Niro Atomizer, Denmark

Since many ceramic products are first milled in a liquid medium, dried, and later pressed into the final shape from free-flowing powders, spray drying is the ideal processing technique to produce the powder required. This has been the reason behind the rapid growth in use of spray drying within ceramic manufacturing during the last 25-30 years. Today spray dryers are widely used in the processing of whitewares (tiles, dinnerware), electronics (ferrites, titanates, nitrides) and hard metals (carbides). This growth is set to continue due to the new categories of advanced ceramics. Spray drying will play a leading role in realizing the full industrial potential of these new ceramics, in applications much different from the traditional ceramic products, i.e. in heat engines, mechanical/structural parts for turbines, multi-layer integrated circuits and a great number of other electronic parts, cutting tools. Even artificial bone, joints and heart valves are on the long list of advanced ceramic applications.

Total sales in 1980 for these types of products in the Western democracies has been estimated equivalent to 4 billion USD. This could grow to 12 billion USD in 1990 and 17 billion USD in 1995. Most of the volume is expected to be split initially between U.S.A. and Japan. With Europe making up ground in the 90's. Although the vast number of products and applications makes it difficult to generalize, it is true that many products will use the same basic ceramic manufacturing technique, i.e. mill, dry, press, and fire. In fact, the more sophisticated technical requirements will probably make spray drying even more attractive. There may also be a number of new applications for closed cycle spray drying as many of the products are non-oxides and are degraded by water.

This paper reviews the status of spray drying technology within the manufacture of whiteware, electronic parts, and carbide tooling, and describes the development taking place especially in the area of advanced ceramics.

BA 79 author present: 11.00 - 12.30

INFLUENCE OF ADDITIVES ON THE PRESSING AND SINTERING BEHAVIOUR OF SPRAY-DRIED SUBMICRON Al_2O_3

G.J.J. Beckers
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands

To improve the pressing behaviour of Alcoa A16SG, a submicron Al_2O_3 powder, it has been spray-dried with addition of binders and plastisizers. The resulting product has been pressed into pellets and sintered. Quality of the pellets, green and fired density are determined.
The results of experiments with 13 binders and 5 plastisizers, added in concentration up to 3% weight, will be presented.

BA 80 author present: 11.00 - 12.30

SOL-GEL-SYNTHESIS FOR PREPARATION OF YTTRIUM ALUMINIUM GARNET

J.W.G.A.Vrolijk,* J.W.M.M. Willems and R. Metselaar, Centre for Technical Ceramics, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

Sol-gel-synthesis for preparation of pure yttrium aluminium garnet-(YAG)-powder with small grain size is subject of this ongoing study. To obtain pure YAG ($Y_3Al_5O_{12}$) both pH during hydrolysis and temperature during calcination must be carefully chosen. Presence of water has an adverse effect on the degree of agglomeration. To avoid this the influence of dispersion liquids with increasing non-polar character was studied and this led to optimized conditions for precipitation.
Powder characteristics and sintering behaviour will be discussed.

BA 81 author present: 11.00 - 12.30

YAG POWDER SYNTHESIS FROM ALKOXIDES,

M.Steinmann, Centre for Technical Ceramics, POB 513, 5600 MB Eindhoven, The Netherlands.

The translucent yttrium-aluminium-garnet (YAG) ceramic is of interest because of the use in optical engineering. Sintering to translucency at temperatures below 1800°C, primarily requires special powder charàcteristics. In order to meet these criteria, we investigated the feasibility of the powder synthesis from metal-alkoxides. Based on the hydrolysis of a stoichiometric mixture of $Al(OC_3H,i)_3$ and $Y(OC_3H,i)_3$ we developed a procedure with which ultra-fine mixed oxide particles can be prepared. E.D.X. analysis shows a homogeneous distribution of aluminium and yttrium in the stoichiometric ratio, within the range of the particle sizes, 20-50 nm. Between 800 and 900°C a phase-transformation to the garnet structure takes place. The sinter activity of YAG powders depends on the powder microstructure and the phase-transformation temperature. Nevertheless, we did not succeed in sintering YAG compacts to translucency at temperatures $\leq$ 1800°C.

BA 82 author present: 11.00 - 12.30

EXPERIMENTAL DESIGN APPLIED TO A LOW TEMPERATURE SYNTHETIC ROUTE TO CRYSTALLINE, SUBMICRON BARIUM TITANATE/ZIRCONATE POWDER.

*R.L. Perrier, LCC, Thomson CSF, 21100 Dijon, France;
A. Safari and R. Riman, Dept. of Ceramics, Rutgers Univ., Piscataway NJ 08855-0909, USA.

A new alkoxide precursor synthesis of barium titanate/zirconate is investigated. This method provides the extraordinary property of yielding at temperature below 80°C a crytalline monodispersed (around .5 micron) form of $BaTi_{1-x}Zr_xO_3$ ($0<x<.3$). However the powder obtained by this method without precautions is agglomerated and does not yield the low sintering temperature one could expect. In this study we implement a fractional factorial design to evaluate the effects of the processing variables on the final characteristics of this new powder.

BA 83 author present: 11.00 - 12.30

DCCAs IN SOL-GEL PROCESSING OF GLASS MONOLITHS,

L.Nikolić,L.Radonjić
Faculty of Technology, 21000 Novi Sad,Yugoslavia

Relible production of gel monoliths is necessary to realize many of potential advanteges of sol - gel processing of materials. But in the process of gel drying,since stresses developed,cracking the gel is common. The drying stress is a funcion of many parameters. Recently it was demonstrated the use of organic additives to alkoxide sols,termed drying control chemical additives (DCCA),can control drying stresses. One of possible wau solving the cracking problems in sol-gel processing of moliths is using of DCCA.
The objective of this paper is to study the DCCA influence on sol-gel processing the silica monolith. As additives in TEOS (alchohol and wather) solution, formamide, glycerol and oxalic acid was used. These additives have different influence on gelation time (at room temperature) and stability adainst the cracking of gel, dryed gel and fired gel. Formamid as DCCA decreases the geling time and glycerol and oxalic acid increase the time.It was more difficult to find regularity in influence, the same in the process of drying and fireing. Contrary to the similar experiment in literature presented, these results of investigation do not prove high influence of DCCA on crack development in heating the silica gels.

BA 84 author present: 11.00 - 12.30

SYNTHESIS OF MULLITE AND CORDIERITE POWDERS BY SOL-GEL PROCESS AND THEIR SINTERING BEHAVIOUR,

D. Sporn* and H. Schmidt,
Fraunhofer-Institut für Silicatforschung, Neunerplatz 2, D-8700 Würzburg (Fed. Rep. Germany)

The sol-gel process is a suitable way to achieve pure mullite and cordierite at lower temperatures with higher sinteractivity compared to conventional powders. The effect of variations in chemical synthesis (e.g. precursors, reaction, parameters) and of thermal treatments on the formation and the sintering behaviour of the powders has been studied.
It was found that mullite derived from monophasic gels could be formed at temperatures below 1000 °C but this powder was not suitable for dense sintering at low temperatures. For dense sintering it was necessary to use diphasic gels from boehmite and amorphous silica. Such powders can be densified at temperatures below 1300 °C.
Cordierite could be formed from homogeneous gels without interphases and can be densified at a temperature of 1050 °C.

BA 85 author present: 11.00 - 12.30

PROCESSING AND SINTERING OF BETA-SIC POWDERS,

V.Kevorkijan, M.Komac, D.Kolar
"Jožef Stefan" Institute, Ljubljana, Yugoslavia

Sinterability of beta-SiC powders compacts depends strongly on the chemical and morphological characteristics of the starting powder. In order to evaluate critical characteristics, the sinterability of different beta-SiC powders prepared by carbothermal reduction and processed by sedimentation as well as of various commercially available powders was compared.

It was found that once the level of impurities was sufficiently low, the sinterability of beta-SiC powders apparently depended mainly on particle size distribution rather than average particle size. Thus beta-SiC powders with $d_{50} < 0.5$ µm and $d_{100} < 3$ µm can be pressureless sintered up to 97% of T.D., while beta-SiC powder with $d_{50} < 0.2$ µm but with approximately 10% particles coarser than 3 µm sinters only to 90% of T.D. Based on these results, the correlation between beta-SiC powder characteristics, processing and sinterability are discussed.

BA 86 author present: 11.00 - 12.30

LASER SYNTHESIS AND CHARACTERIZATION OF ULTRAFINE Si/C/N POWDERS, M. Cauchetier, O. Croix, M. Lance and M. Luce *, CEA - IRDI/DESICP - Département d'Etude des Lasers et de la Physico-Chimie, CEN Saclay, 91191 Gif sur Yvette cedex (France).

Si/C/N composite particles in the range 20-50 nm were synthesized by a CO_2-laser induced reaction either between silane (SiH_4) and amine (i.e. CH_3NH_2) or between silane and a mixture of ammonia (NH_3) and hydrocarbon (i.e. C_2H_2). By varying the laser power, the flow rates and ratios of the reactant gases, amorphous Si/C/N particles or mixed $Si/SiC/Si_3N_4$ powders were obtained. The powders were characterized by numerous methods : IR spectroscopy, X-ray diffraction, BET, TEM, chemical analysis. Heating treatments by thermogravimetric analysis were performed under air, argon or nitrogen.

BASIC SCIENCE POSTERS : FORMING
Thursday 22nd June; 09.00 - 19.00

BA 87 author present: 11.00 - 12.30

THE INFLUENCE OF PRESSING AIDS ON THE UNI-AXIAL PRESSING OF ZIRCONIA, P.Koskinen* and P.Vaananen, Technical Research Centre of Finland, Espoo, Finland.

The influence of various pressing aids on the pressing process of ceramic powders and the quality of pressed test bars was studied. The pressing tool used was made from maraging steel and it applied the floating die -principle. The pressing strength was 70 MPa. The powder used was partially stabilized zirconia (TZ-3Y, Toyo-Soda) and the pressing aids studied were Glyco PM 100 (Glyco Inc.), Acrawax ethylenbisstearamide (Glyco Inc.), Zn-stearate (Merck 8865) and polyvinyl alcohol (PVA, moisture 55 %, Fluka 81384). The amounts of additives were 0,5 %, 1,0 % or 2,0 % by weight. A ready-mixed PSZ-powder with 4 w-% acrylate polymer additive (TZ-3YA, Toyo-Soda) was used as a reference material. The additives were mixed with zirconia powder for 18 hours in a ball mill. The characteristics studied were the strength needed to push the test bar out of the tool, the green density, the bulk density, the dimensional changes after sintering and the bending strength (4-point bending).
The additives had clearly noticeable optimum contents with regard to the characteristics studied. These characteristics were, however, worse than those of the reference material. The only positive effect of the additives was that they lowered the stregth needed to push the test bars out of the tool.

BA 88 author present: 11.00 - 12.30

GRANULE STRENGTH AND COMPACTION BEHAVIOUR OF AGGLOMERATED CERAMIC MATERIALS, J. van der Zwan; K.S. Haagsma*
TNO Institute of Applied Physics, Ceramics Department, P.O. Box 513, 5600 MB EINDHOVEN, The Netherlands
* Nederlandse Philips Bedrijven B.V., Central Development Materials Elcoma, 5600 MD EINDHOVEN, The Netherlands.

The mechanisms of compaction, the behaviour of the separate particles of the bulk granulate under pressure, and the properties of the produced products are influenced by the granule properties of the pressing powder. A method to characterize these properties (e.g. granule density, granule strength and breakage under pressure) will be discussed.
A strong relationship exists between granule weight and granule strength, and between granule diameter and granule strength.
Furthermore a qualitative relationship between granule properties, e.g. water and binder content, production process of the pressing powder, and the densification behaviour will be discussed.

BA 89 author present: 11.00 - 12.30

DEVELOPING A PRESSING TOOL FOR THE PREDENSIFICATION OF CERAMIC POWDERS, P.Vaananen* and P.Koskinen, Technical Research Centre of Finland, Espoo, Finland.

The purpose of this work was to plan and prepare a pressing tool which would be suitable for predensification of ceramic powders. The tool was designed for test bars with dimensions of 65 x 9 x 4.5 mm^3 before sintering and of about 49 x 6.9 x 3.4 mm^3 after sintering for 2 h at 1450°C. The material used was maraging steel and the tool applied the floating die -principle. The tool was tested using zirconia powder and the pressing strength of approximately 70 MPa.
The quality of the pressing tool was evaluated by the stregth of the test bars. The value of Weibull modulus was also calculated. The main problem in the tests was to push the test bars out of the tool without causing flaws to them. To avoid these problems some changes were made in order to release the inner tensions of green bodies more evenly and to get the push out -phase under better control. These changes improved the quality of the test bars. The heavy wearing of the pressing tool was, however, problematic.

BA 90 author present: 11.00 - 12.30

CIP MOLDING OF LONG THICK WALLED CERAMIC TUBES, N. Duarte, J. J. Fernandes, P. Silva, Dep. Tecnologia de Materiais - LNETI, Lisboa, Portugal.

CIP is an important ceramic moulding technology that can be applied to may different geometries with some advantages.
We have develloped some experience in what concerns mould design an powder preparation wich are important steps for a sucessful fabrication.
During the fabrication of long tubes buckling of core rod can led to the fracture of the compacts. This problem is studied using different length to bore diameter and thickness.

BA 91 author present: 11.00 - 12.30

COMPUTER SIMULATION OF A CIP'ED BODY AND EVALUATION OF ITS PACKING FRACTION AND COORDINATION NUMBER, Yoshiaki HAMADA* and Kozo ISHIZAKI

(Department of Materials Science and Engineering, School of Mechanical Engineering, Nagaoka University of Technology, Nagaoka 940-21, Japan
*Present address : Nisshin Flour Milling Co., Ltd.)

A Cold Isostatic Pressed (CIP'ed) body was simulated by a computer. There have been many reports on computer simulation of unidirectional packing, but none of them on isotropical packing to simulate CIP or HIP processes, so far the knowledge of the authors.

A relationship between the mean coordination number and the packing fraction of a CIP'ed body were evaluated.

Theoretical packing behavior, simulated uniaxial compaction models, and the isotropically densified bodies of the present work are compared to each other. Two assumptions were used to simulate a CIP'ed body. They were (a) all particles were rigid spheres of same size, and (b) they were moved initially toward to the center to contact three other particles.

The results were as follows :
(1) The packing fraction and the mean coordination number are the highest at the center of the compacted bodies, and decreased toward to the surfaces.
(2) The mean coordination number of an isotropically packed body is higher than that of an unidirectionally packed one.
(3) The packing fraction and the mean coordination number of a CIP'ed body are higher than those of a simple cubic and lower than those of a hexagonal prismatic model.

BA 92 author present: 11.00- 12.30

FERRITE POWDER COMPACTION WITH ULTRASONIC ASSISTANCE
E. EMERUWA, J. JARRIGE, J. MEXMAIN
Laboratoire de Céramiques Nouvelles, CNRS UA 320, Université de Limoges, FRANCE

The properties of ceramic bodies are known to be highly dependant on their processes of fabrication before firing, especially on the stage of powder compaction.
Recently, the ultrasonic assistance was introduced at this stage to optimize the properties of metallic and ceramic bodies. An increase of their density, their Weibull modulus and a decrease of the force of compaction were observed.
We have tried to determine the best conditions for the application of ultrasounds in a compaction process. The behavior of a ceramic powder (ferrite) can only be improved by ultrasonic assistance when ultrasounds are used at pressures lower than a critical value Pc. This critical pressure is related to the limit of mobility of the powder grains under ultrasonic vibrations. Its value depends on the caracteristics of the powder, as well as those of the ultrasounds : frequency, amplitude, time of application...
The intrinsic curve of ultrasonic assistance of compaction is also drawn. It is absolutely necessary to draw the intrinsic curve of ultrasonic assistance which includes the critical pressure. The interest of compaction with ultrasonic assistance depends imperatively on the knowledge of ultrasounds and their field of intervention.

BA 93 author present: 11.00 - 12.30

POWDER PROCESSING EQUIPMENT IN THE PRODUCTION OF ZIRCONIA TOUGHENED ALUMINA COMPOUNDS SUITABLE FOR INJECTION MOULDING TECHNICAL CERAMIC COMPONENTS,
N. Theilgaard. Dept. of Plastics Technology, Technological Institute,
2630 Taastrup, Denmark

A method whereby Yttria stabilised tetragonal zirconia is mechanically dispersed into alumina by means of a high speed fluidising mixer and a twin-screw compounding extruder will be described. A comparitive evaluation of the resulting dispersions will be made with a dispersion produced by a chemical precipitation method using SEM analysis.

4-pt bend strengths, Weibul moduli and X-ray diffraction results will be presented and discussed. The possibilities of using this technique in commercial applications will be considered.

BA 94 author present: 11.00 - 12.30

RELATIONSHIPS BETWEEN FABRICATION, MICROSTRUCTURE AND MECHANICAL PROPERTIES OF INJECTION MOULDED Si_3N_4,
P. Lemaitre*,R. Gilissen, A. Smolders; J. Koenen°.
Studiecentrum voor Kernenergie (SCK/ CEN),Mat. Dev. Dept., Boeretang 200, B-2400 Mol, Belgium
°DSM Research BV, Postbus 18, 6160 MG Geleen, The Netherlands.

Si_3N_4 is one of the most promising ceramic materials. Injection moulding has the potential for high volume, low cost production of components of complex shape. The mechanical properties of Si_3N_4 bars obtained by injection moulding and pressureless sintering were determined. The fracture surfaces were examined in order to correlate microstructure, mechanical strength and processing. Flaws near the surface due to dissociation of Si_3N_4 and evaporization of the liquid phase can easily be avoided by choosing the right sintering conditions. Flaws due to wear of the injection moulding machine can only be eliminated if the parts of the injection moulding machine which get in contact with the ceramic powder mixture are rendered more abrasion-resistant. As compared to similar materials, reported in the literature, the developed material has satisfactory mechanical properties.

BA 95 author present: 11.00 - 12.30

STRUCTURE CONTROLLING OF CERAMICS BY PLASTIC FORMING,
J. Havrda*, F. Oujiří, J. Trávníčková and J. Matoušek,
Department of Silicates, Prague Institute of Chemical Technology, 166 28 Prague 6, Czechoslovakia

Plastic forming was used for preparation of ceramic composites. The controlled orientation of fibers in a ceramic matrix during plastic forming in a mouth auger was solved by mathematical modelling of the rate field. A mathematical model for the non-newtonian flow of plastified ceramics is proposed. The model solution requires the data for the constitutive equation of plastic material. This constitutive equation was determined experimentally by means of capillary tube viscometer method. Velocity distribution at different radii of tubes have been obtained from the model calculations. The model was verified experimentally for plastic forming of Al_2O_3-ZrO_2 ceramics with ZrO_2-Y_2O_3 fibers in the plug auger. The orientation of fibers in the ceramics bodies was obtained from the polished section of the green and sintered bodies by means of optical microscopy.

BA 96 author present: 11.00 - 12.30

OPTIMIZING COMPOSITION OF RAW MATERIAL MIXTURE FOR THE PRODUCTION OF SINTERED CERAMIC TILES BY LINEAR PROGRAMMING METHOD,
Lj. Petrašinović-Stojkanović* and B. Živanović, Material Testing Institute, 11000 Belgrade, Yugoslavia;
S. Despotović,
"ZORKA"- Institute, 15000 Šabac Yugoslavia;
O. Gajić
"ZORKA"- Ceramic Tile Plant, 15000 Šabac Yugoslavia.

Based on the mathematical model comprising total material balance in the mixture as well as particular oxide balances, calculation of optimum composition of starting mixture (share of particular raw material components) for the production of sintered ceramic tiles has been made. The calculation also includes minimizing raw material mixture costs by using linear programming method. Based on calculation results, the possibility of reducing the share of raw materials that are not readily available on the market or those incurring higher costa without affecting the desired quality of sintered ceramic tiles has been studied.

BA 97 author present: 11.00 - 12.30

PROCESSING OF ZrO_2 CERAMICS FROM SPHERICAL POWDERS OBTAINED BY SOL-GEL-PROCESS,

(W.Distler*, G.Tomandl, R.Kohl, A.Stiegelschmitt, Universität Erlangen-Nürnberg, Inst. für Werkstoffwissenschaften III, W-Germany;
G.Rinn, Fraunhoferinstitut für Silicatforschung, Würzburg, W-Germany)

Monodisperse ZrO_2 powders were synthesized by a controlled hydrolysis of dilute alcoholic solutions of zirkonium alkoxides. Y-stabilized ZrO_2 powders were prepared by an emulsion-technique. The powders were characterized by using SEM, thermal analysis, infrared-spectroscopy and X-ray diffraction. Various methods to stabilize the Sol-Gel-derived powders were investigated. The state of powder aggregation in dispersions and powder packing in green bodies strongly affected the sintering behaviour. Uniformly packed powder compacts could not be achieved with these powders. Sintering of non regularly packed green bodies with an average density of 55 % th. d. resulted in finegrained microstructures with more than 97 % th. d. at a temperature of 1550 °C, which is lower than required to sinter conventional ZrO_2 powders.

BA 98 author present: 11.00 - 12.30

SLIP CASTING OF TiO_2

H. Wohlfromm, P. Peña, J.S. Moya,
J. Requena*
Instituto de Cerámica y Vidrio, C.S.I.C
Arganda del Rey, Madrid, Spain

The zeta potential of titanium dioxide (anatase) in an aqueous medium has been established for different defloculant contents.
The viscosity curves of suspensions with varying solid content have been determined for a fixed, optimal defloculant content.
Finally, TiO_2-crucibles have been cast and its wall thickness and green density have been measured.

BA 99 author present: 11.00 - 12.30

PREPARATION OF ALUMINUM TITANATE BY SLIP CASTING,

H. Wohlfromm*, P. Pena, J.S. Moya,
J. Requena
Instituto de Cerámica y Vidrio, C.S.I.C
Arganda del Rey, Madrid, Spain

The zeta potential of Al_2O_3 and TiO_2 (anatase) as a function of pH and surfactant content has been determined. Based on this results aqueous suspensions containing an equimolar mixture of Al_2O_3 and TiO_2 have been prepared and characterized by measuring viscosity curves and wall thicknesses for different solid contents and surfactant concentrations. Finally, Al_2O_3/TiO_2-samples have been cast and heat treated at various temperatures > 1300°C in order to obtain Al_2TiO_5.

BA 100 author present: 11.00 - 12.30

FORMING OF CERAMIC COATINGS BY CROSS FLOW PRESSURE CASTING; A NEW TECHNIQUE

B.C. Bonekamp*, R.A. Terpstra and H.J. Veringa
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands

The forming of thin layers on porous ceramic substrates by colloidal filtration (slip casting) is a well-known technique which is used, for example, for the preparation of ceramic micro- and ultrafiltration membranes. Usually the driving force for the layer growth is the capillary action of the substrate, while extensive shear forces are absent (static filtration).
In this communication we report on and analyse some preliminary results concerning the effect of a tangential (cross) flow field on the build up and composition of ceramic layers by pressure filtration of α-Al_2O_3 ($d_{50} \approx 0.6$ µm) suspensions. We call this new technique: Cross Flow Pressure Casting.
We discuss the effect of substrate properties, filtration pressure, suspension velocity and suspension concentration on the layer thickness, layer morphology and -microstructure.
Finally the possibilities for the controlled forming of ceramic tubular shapes ("thick coatings") are discussed.

BA 101 author present: 11.00 - 12.30

PORE PROPERTIES OF CERAMIC POROUS MEDIA PREPARED BY SLIP CASTING OF STARCH FILLED α-Al_2O_3 SUSPENSIONS

B.C. Bonekamp*, M.J. Schoute and M.J.A.A. Goris
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands

Slip casting on porous plaster and ceramic molds is applied as a forming method for the preparation of coarse macroporous plates.
Suspensions of α-Al_2O_3 ($d_{50} \approx 0.6$ µm) with various potato (10-100 µm particles) starch contents were prepared for the casting experiments. After casting and carefully drying, the plates were slowly calcined in order to burnout the starch without introducing cracks or other major defects and then sintered at 1400°C or 1600°C for one hour.
The emphasis of our research is on the characterization of the resulting pore structures with SEM, Hg-porosimetry, bubble pressure porosimetry and liquid permeability.
From SEM-analysis it was found that the pore structure is of a characteristic void-throat network type. Then it is not surprising that the inadequacy of cylinder pore models for the interpretation of Hg-intrusion (extrusion) curves is more pronounced than for simple particle packings. Further the observation of a percolation threshold for open (connective) porosity is an interesting point to be discussed.

BA 102 author present: 11.00 - 12.30

EFFECT OF ANIONIC POLYELECTROLYTE ON THE AGGLOMERATION PROPERTIES OF FUMED γ/δ ALUMINA AQUEOUS DISPERSIONS

B.C. Bonekamp*, W.H. van 't Veen and H.J. Veringa
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands

Drying, calcining and sintering of aqueous particle gels is a convenient route for the controlled preparation of ceramic porous media with pore sizes in the colloidal range. The pore properties of the sintered product find their origin in (and are controllable by) the way structure formation occurs and kind of structure that is formed in the usually concentrated aqueous dispersions.
In this presentation we will focus on the colloidal stability of dilute and concentated γ/δ alumina dispersions and the effect of anionic polyelectrolyte thereupon.
We found in agreement with others that in fully deagglomerated sols hard agglomerates form the kinetic units.
Further it will be shown that additions of polyelectrolyte enhances the formation of particle gels by cluster-cluster agglomeration.

BA 103 author present: 11.00 - 12.30 withdrawn

BA 104 author present: 11.00 - 12.30

THE EFFECT OF THE GREEN MICROSTRUCTURE ON SINTERING OF ALUMINA

L.A. Correia* and M.J.A.A. Goris
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands

Using ceramic compacts prepared by slip casting, the effect of the green microstructure on the sinter kinetics and on the microstructure of the densified ceramic was studied. The green microstructure is varied by using powders with different particle size distributions ($\bar{d} < 0.7$ µm) obtained by fluid classification and by manipulating the powder particle interaction in suspension by changing the zetapotential using acid.
Sintering kinetics is studied by dilatometry while the evolution of the pore size distribution is followed by Hgporosimetry and the microstructure by SEManalysis.

BA 105 author present: 11.00 - 12.30

CALCIUM SILICATE HYDRATE MOULDS.
Piet Reijnen *, Bekir Kavruk ;
Roel Nelissen,Thijs Gelders
Institute of glass, ceramics and composite materials, RWTH D-5100, Aachen
Koninklijke Sphinx, 6201 BB Maastricht (NL)

Moulds for slip casting are usually made from plaster of Paris. They can be produced at low cost within narrow dimensional tolerance without deformation.Plaster moulds slowly dissolve in water, must be dried below 56 °C and have low strenght when they are wet.
Porous moulds of calcium silicate hydrate can be made from a slurry of reactive silica (waste product) and a hydraulic binder such as tricalciumsilicate.After casting the slurry is solidified in two days by hydraulic reaction. A treatment at 190 °C in an autoclave leads to a strong, porous body, without dimensional change taking place. The moulds are insoluble, even in hot water, and can be rapidly dried at an elevated temperature.
The combination of low cost and excellent properties makes this material a serious candidate to replace the traditional plaster moulds.

BA 106 author present: 11.00 - 12.30

DISPERSION OF SiC WHISKERS IN WATER

K.J. Konsztowicz, National Research Council, Halifax, Nova Scotia, B3H 3Z1, Canada

Colloidal filtration is an important consolidation technique for dense ceramic matrix composites. However, the tendency of short fibers and whiskers to agglomerate is a major difficulty in preparing dense (>50 v/o solids), yet homogenous, suspensions of such fibers with ceramic matrix powders. In preparing composite suspensions by mixing two or more independent slurries, the rheological properties of whisker (fibre) suspension become of primary importance.

In this study SiC whiskers were given a variety of surface treatments, and aqueous suspension of a wide range of pH then were prepared. Sedimentation tests and viscosity measurements were performed. With the proper surface treatments, stable aqueous suspensions of up to 40 w/o could be prepared without deflocculants Values of the electrophoretic mobility of SiC water suspensions are related to the spatial arrangement of whiskers in these suspensions, as assessed by SEM examination.

BA 107 author present: 11.00 - 12.30

PRECIPITATION MIXING IN COLLOIDAL NITRIDE SUSPENSIONS, W. Oroschin and P. Greil,
Technische Universität Hamburg-Harburg, Arbeitsbereich Technische Keramik, D-2100 Hamburg 90, Federal Republic of Germany.

Precipitation mixing of silicon and aluminum nitride powders with various additive systems was studied. Mono- and bimetallic alkoxides of Mg, Y, and Al, respectively, were synthesized and cohydrolyzed in non-aqueous powder suspensions. The nitride powders doped with the hydroxide precipitations were calcined and gas pressure sintered in nitrogen atmosphere. Due to the improved dopant distribution, full density could be achieved with significantly smaller amounts of dopants as compared to conventional mechanical mixing which is important to achieve better high temperature properties in liquid phase sintered nitride ceramics. Statistical evaluation of strength measurements confirmed the beneficial effect of improved chemical homogeneity on the decrease of processing dependent defects.

BA 108 author present: 11.00 - 12.30

CASTING OF SILICON NITRIDE, J. Denissen* and J. Kotte,
Centre for Technical Ceramics,
P.O. Box 513, 5600 MB Eindhoven,
The Netherlands.

Forming of ceramics by casting can be done in two ways: either by slip casting in which a ceramic dispersion is dewatered by the capillary suction of a porous mold (e.g. Plaster of Paris), or by pressure casting in which a non-suction filter is used, and dewatering is achieved by an external pressure. Both techniques will be discussed for two different commercial silicon nitride powders.
The most important step in the casting process is slip preparation. In this step several parameters were investigated, such as: dispersing medium, dispersant and solids content. The prepared slips were characterized by the casting rate and the density of the resulting green body. Also attention is paid to the mold release. Pressure casting experiments were performed in a laboratory unit at different pressure levels. Also the influence of the degree of flocculation was studied.

BA 109 author present: 11.00 - 12.30

ALUMINUM PHOSPHATE $AlPO_4$ VIA SOLUTION ROUTES, Laure Coury*, Florence Babonneau, Marc Henry and Jacques Livage, Chimie de la Matière Condensée, Université Paris 6, 4 place Jussieu, 75005 Paris, France.

Aluminum phosphate $AlPO_4$ is a refractory material with a low chemical reactivity that could have potential applications as ceramic matrix for composites.
$AlPO_4$ has been prepared via solution routes using both mineral and metal organic precursors. The solution, mixture of aluminum and phosphorus percursors, was characterized by ^{27}Al and ^{31}P NMR that already showed the presence of Al-O-P bonds. The transformation process of this solution into the final crystalline ceramics was essentially followed by XRD and ^{27}Al and ^{31}P MAS-NMR. The influence of the precursors on the transformation mechanism will be discussed.

BA 110 author present: 11.00 - 12.30

A RAPID SELF-REGULATING DRYING METHOD,
Piet Reijnen; Michel Plein
Institute of glass, ceramics and composite materials.RWTH, D5100 Aachen
PLEWA-Werke G.m.b.H. D 5522 Speicher-Eifel

The wet green body is placed in a metal box with a pin hole, and put in a drying stove. The temperature can be rapidly raised, say to 150 °C. The weight loss is followed with a self registrating balance. As practically no drying takes place, when the temperature of the body is beneath 100 °C, all the heat absorbed in the beginning is used to raise the temperature of the body. The drying process starts when the surface of the green body has a temperature slightly above 100 °C. We found that the drying rate is constant until the body is practically dry, even for large sized bodies ($\emptyset$ = 5 cm). This proves that the evaporating surface remains at the surface of the body. When the drying rate becomes lower, the evaporating surface has left the surface of the body. When this takes place when the body has still a large amount of water, this leads to the formation of drying flaws. Different drying curves made with different materials in different sizes will be presented and analyzed.

BA 111 author present: 11.00 - 12.30

INFLUENCE OF ZrO_2 IN TAPE CAST LAMINATED ZrO_2-MULLITE COMPOSITES, M. Holmström, Swedish Institute for Silicate Research, Göteborg, 40229, Sweden ; T. Chartier*, P. Boch and J.L. Besson, UA CNRS 320, ENSCI Limoges, 87065, France.

ZrO_2 addition can have a positive influence on both the sintering and the mechanical properties of mullite. In this study, the influence of ZrO_2 in tape cast laminated samples has been investigated. Pressed samples have been compared to cast ones for various amounts of ZrO_2.

α-Al_2O_3, quartz and unstabilized ZrO_2 have been used as starting powders.
The study has concerned all stages of the preparation process : development of the slurry formulation, laminating technique, and sintering.
Nearly dense ZrO_2-mullite ceramics can be obtained for sintering at T < 1600°C. The microstructural features and the main characteristics of sintered materials are given and discussed.

BA 112 author present: 15.00 - 16.30

SINTERING AND PROPERTIES OF Si_3N_4-TiN COMPOSITES FORMED BY SLIP CASTING,

H. Mostaghaci*, National Research Council, Atlantic Research Lab., Halifax, Nova Scotia, Canada, B3H 3Z1;
S.J. Milne, Dept. of Ceramics, University of Leeds, Leeds, LS2 9JT ENGLAND

The forming process, as well as the preceeding powder preparation step, is very important in the manufacture of high temperature ceramics because defects introduced in these stages will normally remain in the product even after a successful sintering process. The use of ultrafine silicon nitride powders for the pressureless sintering of parts with a wide variety of shapes has become a common practice. However, ultrafine powders generally exhibit a poor packing capability, and forming techniques such as pressing, which are based upon the appliction of mechanical force to the particles, are often responsible for the presence of defects in the final microstructure. In this study sintering behaviour and microstructural evolution of colloidally consolidated ultrafine Si_3N_4 and Si_3N_4 composites containing up to 40 volume percent TiN were investigated at tempertures up to 1850° and pressures of up to 2 MPa. Alumina and yttria have been used as sintering aids. The four point flexural strength and fracture toughness in Si_3N_4-TiN composites were significantly improved over monolithic Si_3N_4.

BA 113 author present: 15.00 - 16.30

MICROSTRUCTURES OF Si_3N_4 CERAMICS FORMED BY HIP,

E.M. Knutson* and L.K.L. Falk, Department of Physics, Chalmers University of Technology, S-412 96 Gothenburg, Sweden; T. Ekström, AB Sandvik Hard Materials, Box 42056, S-126 12 Stockholm, Sweden.

Si_3N_4-based ceramic materials containing different additions of Y_2O_3, Al_2O_3 and ZrO_2 have been formed by hot isostatic pressing (HIP). Analytical electron microscopy in combination with x-ray diffractometry has been used to characterize the effect of process parameters (e.g. amount of sintering aids and time and temperature of HIP) on the microstructure of the Si_3N_4 ceramic. These results have subsequently been related to hardness and fracture toughness.

The general microstructure of these ceramics consisted of α– and β-Si_3N_4, Si_2N_2O and a residual intergranular glassy phase. When sufficient amounts of ZrO_2 were added, the ceramic also contained ZrO_2 grains. The volume fractions of the different phases were dependent upon composition, process time and temperature.

Increased additions of sintering aids (particularily Y_2O_3) as well as longer process times appeared to promote the α→β Si_3N_4 phase transformation during HIP. This resulted in a higher fracture toughness, primarily due to a more fibrous microstructure. These samples were also found to contain larger volume fractions of glass which, together with the lower α-Si_3N_4 contents, resulted in a reduced hardness.

BA 114 author present: 15.00 - 16.30

MICROSTRUCTURAL INVESTIGATION OF SILICON NITRIDE WITH CERIA ZIRCONIA ADDITIONS.

J M Nel and A W Paterson
Materials Science and Technology Division, CSIR Pretoria, 0001, RSA.

Ceramics of nominal composition 85% Si_3N_4, 12.5% ceria zirconia and 2.5% Al_2O_3 were fabricated and by sintering under nitrogen at atmospheric pressure using a variety of sintering schedules.

The microstructures of the materials produced were evaluated by a number of techniques including SEM and TEM. Phases present were identified using X-ray diffraction.

It was found that the microstructural characteristics varied as a function of the distance from the specimen surface.

Near surface effects include the formation of ZrN and mass transport that results in agglomerates of zirconium rich grains associated with a glassy phase rich in ceria.

In the bulk the zirconia grains are not reduced but the ceria is expelled from the zirconia lattice resulting in the transformation of the zirconia to the monoclinic phase.

The relevance of these findings to other zirconia-silicon nitride systems and the densification of sintered silicon nitride materials is discussed.

BA 115 author present: 15.00 - 16.30

DENSIFICATION MECHANISM OF Si_3N_4 WITH A NEW AZ-TYPE NON-TOXIC, NON-OXIDE ADDITIVES,

Ge Changchun, Xia Yuanluo, and Chen Limin
University of Science & Technology, Beijing, China

We have found that Si_3N_4 can be highly densified with a new AZ-type non-oxide additives during gas pressure sintering or hot-pressing. In this work densification behavior and mechanism of Si_3N_4 with this new kind of additive were investigated. High densification is attributed to liquid phase sintering in connection with α→β transformation occurred due to the expansion of composition range of liquid phase (LP) region and lowering of formation temperature of LP in Si_3N_4-AlN-Al_2O_3-SiO_2 system with this new kind of additive.

BA 116 author present: 15.00 - 16.30

ENCAPSULATION OF RBSN COMPOSITES FOR POST HIPing, K. Scheel, R. Janssen* and N. Claussen, Technische Universität Hamburg-Harburg, Arbeitsbereich Technische Keramik, D-2100 Hamburg 90, Federal Republic of Germany.

RBSN bodies were coated with different Si_3N_4-containing eutectic powder compositions. On heating, the coating forms a gas-tight layer, the viscosity of which is adjusted by the amount of admixed Si_3N_4 powder. Optimized coating compositions exhibited a high enough viscosity to prevent dripping-off and gas permeability at 1800°C under HIP conditions in nitrogen. The encapsulation properties of the coatings are discussed with respect to phase diagrams of Si_3N_4 alloys.

BA 117 author present: 15.00 - 16.30

PROCESSING AND SINTERING BEHAVIOUR OF 3Y-TZP PREPARED BY A SPRAY PYROLYSIS METHOD

DUBOIS B.*, RUFFIER D., ODIER P.
CNRS-CRPHT 1D avenue de la Recherche Scientifique 45071 ORLEANS, FRANCE.

3Y-TZP monodisperse particles in the range 0.2 to 1.8 µm with a narrow size distribution (standard deviation 1.3) have been prepared by a spray pyrolysis method. An appropriate thermal treatment of the mist of an aqueous solution of mixed zirconyl chloride and yttrium nitrate produced by an ultrasonic nebulizer, allows to obtain slightly micro-porous spherical particles with a well controlled size.
The sintering behaviour of these powders studied with a high temperature dilatometer (SETARAM) shows that the Herring scaling law is appropriate for predicting the potential benefit from particle size reduction. The sintering temperature can be decreased from 1750° down to 1250°C by reducing the particle size from 1.8 to 0.2 µm. The sintering of the different powders compacts results in very uniform fine grained microstructures with 99% of theoretical density and no exaggerated grain growth. The chemical homogeneity has been proved to be excellent by electron microprobe and remain perfectly stable up to 1550°C in agreement with the generally accepted phase diagram.

BA 118 author present: 15.00 - 16.30

SINTERING, MICROSTRUCTURAL DEVELOPMENT AND MECHANICAL PROPERTIES OF CeO_2-TZP CERAMICS.

M.González, C.Moure, J.R.Jurado, and P.Durán
Instituto de Cerámica y Vidrio (CSIC), Electroceramics Department, Arganda del Rey, 28500 Madrid, Spain.

Compositions ranging from 0 to 20 mole% CeO_2 were prepared by a wet-chemical route in the ZrO_2-CeO_2 system. The tetragonal phase stability region as a function of temperature and time of sintering was established, and the best sintering condictions for those compositions retaining tetragonal structure at room temperature were studied. Microstructural development on the sintered bodies and the influence of the grain size on the tetragonal phase stability have also been studied. Finally, the influence of the sintering condictions on the microhardness (H) and fracture toughness (K_{IC}) of the sintered bodies have been studied.

BA 119 author present: 15.00 - 16.30

MICROSTRUCTURE AND PROPERTIES OF Y_2O_3 STABILIZED TZP CERAMICS SINTERED AT LOW TEMPERATURE

Meng Guangyao*; O. Toft Sørensen+
* Dept. of Materials Science and Engineering, University of Science and Technology of China, Peoples Republic of China.
+ Risø National Laboratory, DK-4000 Roskilde, Denmark.

It has been a great aim to produce fully dense fine grain TZP ceramics in order to enhance both their mechanical and electrical properties. In this work commercial TZ3YA, TZ2.5Y and TZ2Y powders were sintered at a temperature ranging from 1100°C to 1600°C. The fully dense specimens could be obtained below 1250°C. Density and porosity measurement, XRD identification, microstructure analysis by SEM with EDAX, AC impedance spectroscopy investigation and mechanical property testing were carried out on specimens. The present paper describes the experimental results and gives a discussion on microstructure development and its relation to properties.

BA 120 author present: 15.00 - 16.30

PROCESS KINETICS AND MICROSTRUCTURE DEVELOPMENT IN THE LOW TEMPERATURE SINTERING OF Y-TZP CERAMICS

Meng Guangyao*; O. Toft Sørensen+
* Dept. of Materials Science and Engineering, University of Science and Technology of China, Peoples Republic of China.
+ Risø National Laboratory, DK-4000 Roskilde, Denmark.

This paper describes the results of a study on the kinetic behaviour of sintering process of chemically prepared fine TZY (3Y, 2.5Y and 2Y) powders at low temperature by using a computerized dilatometer, associated with microstructure analysis and property measurements. It includes:
1) Evaluation of shrinkage behaviour and kinetic parameters from both constant heating rate technique and stepwise isothermal dilatometry, and 2) the microstructure analysis with XRD, SEM and EDAX and investigation by AC impedance spectroscopy technique on as sintered specimens at different stage of the sintering.
A comprehensive discussion is given on the basis of the experimental results.

BA 121 author present: 15.00 - 16.30

MIXED PHASE CARBIDE CERAMICS FORMED BY THE REACTION-BONDING TECHNIQUE,

I Higgins*, A Baxendale, M Turek
UKAEA, Northern Reseach Laboratories - Springfields, Salwick, Preston, PR4 ORR, United Kingdom;

A Whitehead
The University of Newcastle-upon-Tyne, United Kingdom

ABSTRACT

The siliconising route commonly used to produce reaction bonded silicon carbide has been developed to yield a family of novel mixed phase ceramics. Green pellets containing various refractory phases in addition to silicon carbide and carbon have been infiltrated with suitable liquid metals to yield fully dense products. Volume changes on firing are negligible hence complex shapes are readily achievable.

Examples of the microstructures of both titanium- and boron-containing composites are given. The nature of crack propagation and the effect of secondary phases on materials properties are discussed.

BA 122 author present: 15.00 - 16.30

HOT-PRESSING KINETICS OF AN AGGLOMERATED POWDER : INFLUENCE OF MICROSTRUCTURAL PARAMETERS, G. Gauthier and D. Bernache-Assollant*
Laboratoire de Céramiques Nouvelles, UA CNRS 320, Limoges, France
An aluminium nitride powder, composed of large agglomerates (50 µm), was hot-pressed under different experimental conditions, in order to determine the influence of the sample microstructure on the kinetic law : sintering rate versus applied pressure.
The evolution of the sintering rate versus pressure is drawn either from the shrinkage curves under isothermal conditions (continuous), or by modifing the applied pressure during the experiment (discontinuous). For a given pressure and a relative density the sintering rate vary strongly according to the method used. However the linearity of the laws suggests a diffusion process for the limiting step.
The discrepeancy between the continuous and discontinuous methods depends on the temperature. At 1700°C, the pressure must be applied at the starting of the sintering experiment, whereas at 1600°C the pressure must be applied during the experiment.
Similar experiments were performed on a deagglomerated powder. The continuous and discontinuous methods lead to similar values for the shrinkage rate.
Comparison between the kinetic curves for agglomerated and deagglomerated powders allows the calculation of the shrinkage in the agglomerates and between the agglomerates.

BA 123 author present: 15.00 - 16.30

HOT PRESSING OF SILICON CARBIDE, E.Kostić
Boris Kidrič Institute of Nuclear Sciences, Laboratory 170, P.O.B. 522, 11001 Beograd, Yugoslavia

Possibility of SiC powders densification during pressureless sintering in the presence of additives from Al_2O_3-Y_2O_3 and Al_2O_3-Dy_2O_3 systems pointed to the way of further improvement of SiC characteristics. Decreasing of additive amount needed for obtaining fully dense SiC ceramics was reached using hot pressing procedure. 10 mass% additive used during sintering at 1950°C was decreased for several times. Although the optimum additive amount for producing of dense SiC material depended on hot pressing temperature, only about 1 mass% additive was needed at 1900°C. It is obvious that the fully dense material during hot pressing can be obtained using both lower temperatures and smaller additive amounts. Microstructural analysis showed that a fine grain material was obtained during this procedure. Average grain size was 1-2 µm. X Ray analysis did not prove a noticeable changing of starting SiC powder crystalline modification.

BA 124 author present: 15.00 - 16.30

SINTERING OF SIALON PRODUCED BY CARBOTHERMAL REDUCTION OF FLY ASH, F. Blömer, Centre for Technical Ceramics, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

Fly ash with a high alumina and silica content is used as low grade raw material for the carbothermal production of ß'-sialon. Before synthesizing the sialon the ash is subjected to a magnetic and chemical upgrading process.
With milling and cold isostatic pressing green products were produced which were gaspressure sintered between 1600°C and 1800°C.
Mechanical properties and oxidation behaviour will be compared with data from literature.

BA 125 author present: 15.00 - 16.30

MICROSTRUCTURE AND PROPERTIES OF α/ß SiAlON COMPOSITES, S.Bošković, Boris Kidrič Institute of Nuclear Sciences, Belgrade Yugoslavia, K.Nickel, Max-Planck Institute für Metallforschung PML, Stuttgart, FRG

Microstructure of α/ß SiAlON composites was followed as a function of hot pressing temperature and α phase content. Samples containing both α and ß Si_3N_4 crystal structures were obtained by hot pressing between 1600 and 1800°C, using Y_2O_3 and Nd_2O_3 as dopants. Depending on hot pressing temperature, α/ß phase ratio, density, grain size, aspect ratio as well as hardness and toughness were measured. It was found that density increased in the temperature range 1400-1600°C and remained unchanged with further hot pressing temperature rise. α phase content got down as the hot pressing temperature went up, while hardness increased with increasing α phase amount. Density was constant after 60 min of isothermal heating, while mean grain size kept on growing.

BA 126 author present: 15.00 - 16.30

GAS PRESSURE SINTERING OF α'-SIALON CERAMICS, G.Z. Cao*, R. Metselaar and G. Ziegler, Centre for Technical Ceramics, P.O. Box, 513, 5600 MB Eindhoven, The Netherlands.

α'-Sialon ceramics densified via a gas pressure sintering process are an attractive subject at present. A GPS process with three sintering steps specially for the formation and densification of α'-sialon ceramics has been optimized. This investigation indicates the improvement of the characteristics of α'-sialon (including α'-ß'-sialon composites) ceramics by use of a gas pressure sintering process involving the formation of a transient liquid phase.

BA 127 author present: 15.00 - 16.30

HOT PRESSING OF SIALON, E. Kokmeijer* and R. Metselaar, Centre for Technical Ceramics, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

Sialon samples, $Si_{6-z}Al_zO_zN_{8-z}$ with $z=3$ are prepared by hot uniaxial pressing in a graphite die. Al_2O_3, AlN and Si_3N_4 powders are used as starting materials. In this paper we discuss the influence of the hot pressing procedure on the reaction and densification process. In particular we studied the influence of the temperature-pressure-time scheme. The temperature at which the pressure is applied has a considerable influence on the final density of the sample, application of the pressure as early as possible leading to higher densities. The resulting product was characterized by x-ray diffraction, scanning electron microscopy, density and hardness measurements.

BA 128 author present: 15.00 - 16.30

SINTERING OF HEXAGONAL BORON NITRIDE UNDER HIGH PRESSURE OF NITROGEN,

Jerzy Frączkiewicz*, Jan Jun

Polish Academy of Sciences, High Pressure Research Center "Unipress", ul.Sokołowska 29/37 01-142 Warsaw, Poland

The investigation of the process of sintering of the hexagonal boron nitride (hBN) in the high nitrogen pressure conditions is undertaken. Hexagonal boron nitride is a refractory material used in the form of powder or sintered shapes. This graphite - like structure material posseses such properties as high thermal conductivity, low thermal expansion, high electrical resistivity and chemical inertness. It is well known that an addition of small amount of boron oxide promotes sintering of hBN but boron oxide spoils high temperature mechanical properties of sintered material. To avoid this, we can heat the material over 1900°C to evaporate boron oxide, or we can try to transform boron oxide to boron nitride under high pressure of nitrogen. Thermodynamic calculations and results of experiments are presented and disscused.

BA 129 author present: 15.00 - 16.30

Abstract for the 1st European Ceramic Society Conference, Maastricht, June 18–23, 1989

THE PREPARATION AND PROPERTIES OF A HIGH SURFACE AREA SILICON (OXY)NITRIDE POWDER

P.W. Lednor* and R. de Ruiter

KONINKLIJKE/SHELL–LABORATORIUM, AMSTERDAM
(Shell Research B.V.)
Badhuisweg 3, 1031 CM Amsterdam, The Netherlands

High–surface–area inorganic powders or gels are of interest in the fields of ceramics and heterogeneous catalysis. As part of a programme aimed at extending the range of inorganic materials with application in catalysis we have investigated silicon oxynitride. Preparative work includes syntheses in solution, as well as nitridation of various silica phases by ammonia at 1100 °C. From the latter work an Si_2N_2O powder could be obtained with a surface area of ca. 130 $m^2.g^{-1}$. Characterisation has included the use of solid–state NMR, X–ray photoelectron, and FT–IR spectroscopies. Some surface chemistry of the powder will also be reported.

BA 130 author present: 15.00 - 16.30

SYNTHESIS OF AlN FROM AMINOALANES, M.-A. Einarsrud*, Institute of Inorganic Chemistry, Norwegian Institute of Technology, University of Trondheim, 7034 Trondheim, Norway; W.E. Rhine and M.J. Cima, Ceramics Processing Research Laboratory, MIT, Cambridge, MA02139, USA.

Aluminum nitride precursors were synthesized by reacting dimethylaminoalane with ammonia in hydrocarbon solvents. Various reaction conditions were investigated in an attempt to control particle size and morphology. Using an excess of ammonia gave submicron, high-purity aluminum nitride powder having large surface area (118 m^2/g) after calcination at 1000°C. After calcination at 1600°C the surface area decreased to 1.3 m^2/g. The oxygen content of samples calcined at 1200°C was 0.5%. A colloidally processed sample densified to >95% of the theoretical density at 1700-1750°C.

BA 131 author present: 15.00 - 16.30

THERMITE REACTION ASSISTED SINTERING OF TiB_2 UNDER HIGH PRESSURE AND ITS SINTERED PROPERTIES, Shuichi Takeda, Komatsu Ltd. Hiratsuka City, Kanagawa; Tadashi Maruyama*, Tokyo Institute of Technology, Tokyo; Koki Ikeda, Iwate University, Morioka, Iwate, JAPAN

TiB_2 powder compact without additives was sintered to high density by the instantaneous alumino-thermite heating under high pressure(26GPa). The influence of starting powder characteristics on the resultant microstructures and their impurities segregation was examined. The elastic moduli and thermal & elctrical properties of sintered bodies will be also discussed.

BA 132 author present: 15.00 - 16.30

INFLUENCE OF ADDITIVES ON SURFACE AND STRUCTURE STABILIZATION OF GAMMA Al_2O_3, J.Katanić-Popović and S.Zec, "Boris Kidrič" Institute for Nuclear Science, Beograd, Yugoslavia

Nitrate salts of magnesium, aluminum and lanthanum were used as precursors of oxide additives to gamma Al_2O_3. The effect of these dopes in pseudoboehmite or gamma Al_2O_3 powders, compacts as well as sintered samples was investigated. The samples with 0.06 M/Al ion ratio and equimolar ratio additive to Al_2O_3 were analysed. Specific surface area, porosity distribution and density changes were followed. The structure development was characterised by X ray. The specific surface area of sintered doped samples increases compared to pure Al_2O_3, even when porosity decreases. This effect is more pronounced in gamma Al_2O_3 treated with nitrate salts than in the case of doped calcined pseudoboehmite. The Al_2O_3 addition obtained from aluminum nitrate was manifested by physical properties improving and some instabilization of the gamma phase.

BA 133 author present: 15.00 - 16.30

SINTER-HIP DILATOMETRIC STUDIES AT PRESSURES UP TO 200MPa,

A. Kühne, R. Oberacker, F. Thümmler
Institut für Keramik im Maschinenbau, Institut für Werkstoffkunde II, Universität Karlsruhe
Haid- und Neustr. 7, D-7500 Karlsruhe

Up to now dilatometric studies were performed during sintering at flowing atmosphere or slight overpressure. With the present design of these dilatometers no high pressures could be applied. Due to the advantages in materials properties nowadays often high gas-pressure is used during sintering, Post-HIP and Sinter-HIP, but no predictions could be made about shrinkage-behaviour of the samples during pressurization and high-pressure/ high-temperature-phases.

With a newly developed dilatometer for use in a commercial hot-isostatic-press, shrinkage of samples during a complete Sinter-HIP-cycle can be measured. By detecting the stage of closed porosity, the optimum point of time for applying pressure can be defined and pressure automatically be brought up.

The dilatometer with a measuring-range of 5mm and a resolution below 0,5µm yet has been tested sucessfully in vacuum up to 1650°C, pressure up to 200MPa and temperature up to 2000°C in a graphite-heated Sinter-HIP-equipment.

Shrinkage-curves, recorded during Sinter-HIP-treatment of several engineering ceramics will be presented.

BA 134 author present: 15.00 - 16.30

THE EFFECT OF SiO_2 ON GRAIN GROWTH AND DENSIFICATION OF ALUMINA,
Hwan-Kyu KANG and Hai-Doo KIM*
Korea Institute of Machinery & Metals,
66 Sangnam-dong, Changwon, KOREA(ROK)

The effect of SiO_2doping on the sintering and microstructural development of alumina prepared by sol-gel technique has been studied under various conditions. It shows that SiO_2 additive retards not only the initial and intermediate stage of alumina sintering, but also inhibits the onset of the discontinuous grain growth which occurs very often without additive, thus, resulting in the fine-grained(submicron order), theoretically dense alumina.
The grain growth of alumina doped with SiO_2 is further retarded when sintered under N_2 atmosphere.
The theoretical consideration on the effects of SiO_2 and sintering atmospheres are given.

BA 135 author present: 15.00 - 16.30

THE EFFECT OF BARIUM OXIDE ON THE DENSIFICATION AND DECOMPOSITION OF ZIRCON
N.S. Carr and A W Paterson*
Materials Science and Technology Division, CSIR
Pretoria 0001, RSA

The effects of barium oxide, temperature, time and combinations of these factors on the densification and decomposition of zircon were studied using factorial designed experiments. Measurements were made of density, apparent porosity, Young's modulus and relative zircon XRD intensities. The behaviour the barium oxide-zircon system were further elucidated by the use of calcium oxide as a codopant. The results show that barium oxide and calcium oxide have equivalent molar effects on zircon decomposition. The behaviour of calcium oxide in association with barium oxide removes a tendency of the barium oxide to inhibit densification in the concentration range studied.

A microstructural study was also carried out on an interfacial reaction zone prepared from zircon and barium oxide powder compacts. The results show evidence of strong capilliary action and intergranular ionic diffusion resulting in a broad spectrum of phases. These were studied in the SEM using EDS. The phases observed and the factorial effects are interpreted with reference to the $BaO-SiO_2-ZrO_2$ compatibility diagram.

BA 136 author present: 15.00 - 16.30

ALMINIUM TITANATE-MULLITE MATERIALS OBTAINED BY REACTION-SINTERING OF TITANIA-BAUXITE MIXTURES

A. Caballero, P. Pena, A. L. Cavalieri*, S. de Aza
Instituto de Cerámica y Vidrio-C.S.I.C., Ceramics Department, Arganda del Rey, 28500- Madrid, ESPAÑA.

Aluminium Titanate materials have been obtained by reaction-sintering of bauxite-titania mixtures.

Dynamic sintering and phase evolution were analyzed as a function of firing temperature.

The mechanical properties, microstructure and thermal stability of aluminium titanate ceramic materials were also studied.

Finally, the influence of mullite on the coefficient of thermal expansion was determined.

BASIC SCIENCE POSTERS : PHASES AND REACTIONS
Thursday 22nd June; 09.00 - 19.00

BA 137 author present: 15.00 - 16.30

Ca- AND Mg-DOPED YAG - DEFECT CHEMISTRY AND SINTERING, L. Schuh*, R. Metselaar and G. de With, Center for Technical Ceramics, POB 513, 5600 MB Eindhoven, The Netherlands.

Yttrium aluminium garnet ($Y_3Al_5O_{12}$) is a high temperature alkali resistant material, which can be sintered to translucency. We performed sintering experiments and investigated the defect chemistry of YAG ceramics with CaO and MgO as sinter-additives. These dopants act as very effective grain growth inhibitors in concentrations as low as 100 wt. ppm. Electrical conductivity and ionic transport numbers were determined as function of partial oxygen pressure, pO_2, and temperature.

The main native ionic defects are oxygen- and aluminium vacancies. In quenched samples colour centres are present due to hole trapped on oxygen-acceptor pairs like $(Mg'_{Y}O^{\bullet}_{O})^{x}$.

Experimentally observed conductivity vs. pO_2-curves are understood in terms of a model describing the defect concentrations over the entire range $10^{-12}<pO_2<10^{5}$ Pa.

BA 138 author present: 15.00 - 16.30

THE INFLUENCE OF THERMAL TREATMENT ON THE CRYSTALLIZATION OF HIGH - QUARTZ IN ZnO - MgO - Al_2O_3 - B_2O_3 - SiO_2 SYSTEM,

E.Tkalčec, H.Ivanković*; and B.Gržeta, Faculty of Technology, University of Zagreb, and Institute " R.Bošković " Zagreb, 41 000 Zagreb, Yugoslavia.

The influence of thermal treatment on the crystallization of high-quartz solid solution in the system ZnO - MgO - Al_2O_3 - B_2O_3 - SiO_2 with Al_2O_3/ZnO =1 ratio and with MgO up to 6.22 mol% has been studied. ZrO_2 and ZrO_2+TiO_2, respectively, have been used as nucleating agents. The temperature of crystallization has been determined by DTA. Gahnite, $ZnAl_2O_4$, and t - ZrO_2 are the first crystals to form from the droplet-shaped separated phase, enriched in Zn, Al, Zr, which was revealed by SEM and EDX. The temperature range of crystallization and stabilization of high-quartz depends on MgO.

BA 139 author present: 15.00 - 16.30

PHASE TRANSFORMATIONS IN Y-TZP-CERAMICS UNDER BOILING VATER, V.P. Lintula* and T.A. Lepistö; Tampere University of Technology, P.O. BOX 527, SF-33101 Tampere, FINLAND.

The mechanism of low temperature degradation phenomena is studied by means of X-ray diffraction, SEM+EDS and TEM+EDS. Lattice constants and peak profiles were measured before and after various treatments in boiling water. TEM-specimens were exposed to same treatments to study the phase transformation during treatment. Yttrium contents and distribution were studied before and after treatments. Different factors affecting the kinetics of phase transformation in commercial TZP-materials are discussed.

BA 140 author present: 15.00 - 16.30

THE ROLE OF ALUMINA IN CERIA-ZIRCONIA COMPOSITE ALLOYS, C. Schmid*, S. Meriani; H. Schubert
Appl. and Ind. Chem. Inst., Trieste, I-34127 Italy; Max-Planck-Institut für Metallforschung, PML, D-7000 Stuttgart, FRG.

Materials scientists and engineers are paying increasing attention to the ceria-zirconia alloys (Ce-TZP) because they exhibit promising properties for both mechanical and electrical applications. In target of this investigation was the correlated preparation, microstructural development and the mechanical properties of Ce-TZP with Al_2O_3 additions. The Al_2O_3 grains were found to have a strong effect on the transformability of the tetragonal grains and the formation of the process zone. The comparison of the microstructure and the mechanical properties of samples prepared from four different starting powders will be reported.

BA 141 author present: 15.00 - 16.30

THE ROLE OF MINERALIZERS ON THE DISSOCIATION OF ZIRCON,
S.M.Naga, I.S.Ahmed Farg And D.M.Ibrahim*
National Research Centre

The effect of small addition of different fluorides on the dissociation reaction of Zircon was studied by X-ray diffraction analysis. Thus NaF, LiF, AlF_3, CaF_2 and mixture from NaF and Lif were added in the range of 2 to 12%. LiF and AlF_3 alone did not affect the dissociation reaction in the temperature range between 1200° to 1450°C. An optimum percentage of 8% NaF and a mix of 6% NaF and 6% LiF were found to give the best dissociation product 59.25 and 65.5 at 1200° and 1350°C respectively.

The D.T.A. showed an early dissociation process starting at about 400°C and is accompanied by gradual loss in weight up to 8% at about 1350°C.

The activation energy was determined for the dissociation process for the different mixes. It was found that low concentration and high temperature did not favour the reaction and led to the volatilization of the fluoride added.

The activation energies calculated for 8% NaF mix in the tempreture ranges between 1200 to 1350°C and 1350 to 1450°C were 9.133 and 71.63 cal/mol. respectively. Meanwhile that for the mix 6% NaF + 6% LiF was 11.56 cal/mol. compared with 406.829 cal/mol. for the mix 10% NaF + 6% LiF in the teperature range between 1350 to 1450°C.

BA 142 author present: 15.00 - 16.30

TETRAGONAL ZIRCONIA POLYCRYSTALLINE IN THE SYSTEM $ZrO_2.TiO_2.CeO_2$,
V.C. Pandolfelli*, M. Rainforth and R. Stevens
Division of Ceramics, School of Materials, Leeds University, Leeds LS2 9JT, England.

Tetragonal zirconia polycrystal ceramics occurring in the $ZrO_2.TiO_2.CeO_2$ system have been prepared using zirconium and titanium alkoxides, and cerium nitrate precursors. The change in microstructure with sintering in the temperature range 1300-1600°C is presented. Theoretical final density has been achieved after pressureless sintering at 1350°C for 2 hours. Full densification is only attained with the aid of a liquid phase, rich in Ce, Ti, which forms above 1350°C. Sintering at temperatures > 1450°C results in a loss of stabilizer from the matrix, by formation of $ZrTiO_4$ and Ce, Ti, rich glass. The c/a ratio of the tetragonal zirconia in this system is higher than in the $ZrO_2.CeO_2$ and $ZrO_2.Y_2O_3$ systems. The martensitic t ⇄ m transformation takes place only after ageing over 50 hrs. at 1350°C.

BA 143 author present: 15.00 - 16.30

FORMATION AND STABILITY OF Y-x-SIALON CO-existing WITH B'- SIALON,YOSHIO UKYO* and Shigetaka Wada, Toyota Central Research and Dev. Lab., Inc., Nagakute, Aichi, 480-11, Japan.

SI3N4 ceramics containing Y-x-Sialon were produced by hot-pressing the mixures of SI3N4,Y2O3 and AlN powders at 1750 to 1850 °C under a pressure of 200 kg/cm^2 for 0.5 to 10 hours. X-ray diffraction analysis indicated that hot-pressed bodies were composed of Y-x-Sialon was increased with increasing amount of Y2O3 and AlN. The lattice constant (solubility) of x'-Sialon depended on the amount of Y2O3 and AlN, while that of B'-Sialon did not. The amount of x'-Sialon was decreased with increasing sintering time and temperature. This phenomenon was observed when SI3N4 ceramics containing x'-Sialon were heated at higher temperatures for a long time. From these results, it is concluded that x'-Sialon co-existing with B'-Sialon is a meta-stable phase at higher temperatures.

BA 144 author present: 15.00 - 16.30

REACTION ENGINEERING PARAMETERS OF THE CARBOTHERMAL PRODUCTION OF ß'-SIALON FROM KAOLIN, A.M. van Neerven, F. Blömer, R. Metselaar
Centre for Technical Ceramics,
P.O.Box 513, 5600 MB Eindhoven,
The Netherlands

The reaction engineering parameters of the carbothermal production of ß'-sialon from kaolin will be presented. These parameters can be used for reactor design, upscaling and process control applications. The overall reaction is known to proceed through a complex, reversible reaction mechanism with a reaction rate which depends on the partial pressure of carbon monoxide. In a first approach, one reaction step is assumed to be rate controlling. Szekely's grain model appears to be an appropriate reaction engineering model.
At a reaction temperature of 1400°C, pore diffusion can be neglected when the pellet size is below 1 mm in diameter. Above this size, pore diffusion shows a substantial influence on the overall reaction rate.

BA 145 author present: 15.00 - 16.30

PRIMARY PHASE FIELD OF MULLITE IN THE Al_2O_3-SiO_2-MgO SYSTEM*
A. L. Cavalieri** , P. Pena, S. de Aza
Instituto de Cerámica y Vidrio-C.S.I.C., Ceramics Department, Arganda del Rey, 28500- Madrid, ESPAÑA.

The aim of this work is to clarify some aspects of the discussion on the nature of the mullite melting.

The location of the boundary line which separates the primary phase fields of crystallization of mullite and corundum, in the system Al_2O_3- SiO_2- MgO, has been determined by establishing two isoplethal sections at 50 and 55 wt% alumina content.

Also, the tie-triangles where alumina (s.s.), mullite (s.s.) and a liquid phase coexist were determined at 1600 and 1650 C by firing and quenching selected samples.

The results are discussed in relation to the melting behaviour of mullite.

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*Work supported by the "Consejo Nac. Inv. Científicas y Técnicas" of ARGENTINE.
**Permanent address in CETMIC-CONICET-CIC La Plata, Pcia. Buenos Aires, ARGENTINE.

BA 146 author present: 15.00 - 16.30

PHASE RELATIONS IN THE CaO-Cs_2O-Al_2O_3 SYSTEM, J.A.M. van Hoek*, F.J.J. van Loo and R. Metselaar, Centre for Technical Ceramics, P.O.BOX 513, 5600 MB Eindhoven, The Netherlands.

In both thermionic energy converters and MHD generators, cesium vapour is in contact with ceramic materials at high temperatures. Although pure Al_2O_3 has a high Cs resistivity, sintered alumina is attacked at the grain boundaries. CaO is often present as an impurity or as a sintering aid. We therefore studied the influence of CaO, residing primarily at the grain boundaries in alumina, on the corrosion behaviour. To this end we examined the phase relations in the system CaO-Cs_2O-Al_2O_3 at 900°C. Since all calcium aluminates react with Cs_2O to a new stable compound we conclude that calcium has a negative influence on the cesium resistance of alumina. A new compound was found and described. The lattice parameters and other properties of this compound have been determined.

BA 147 author present: 15.00 - 16.30

THE $Y_3Al_5O_{12}$ REGION OF THE PHASE DIAGRAM $Y_2O_3 + Al_2O_3 + MgO$

M. Bolech, H.A.J. Oonk; A.J.H.M. Kock* and J.J.C. Oomen*, Department of Chemical Thermodynamics, University of Utrecht, Padualane 8, 3584 CH Utrecht; Philips Lighting B.V., P.O. Box 80020, 5600 JM Eindhoven, The Netherlands

Yttrium aluminium garnet (YAG), sintered to translucency only a few years ago, appears to be a promising material for application in high-pressure sodium discharge lamps. While technologies for powder preparation and sintering were being developed, the knowledge of the phase diagrams of the systems $Y_2O_3 + Al_2O_3$ + sinter dope lagged behind. For that reason, a thermodynamic analysis was made of the system $Y_2O_3 + Al_2O_3 + MgO$ (MgO being an effective sinter aid) for compositions approximating the YAG composition. In the present analysis both literature data and new experimental (liquidus) data are incorporated.

BA 148 author present: 15.00 - 16.30

A PRELIMINARY STUDY ON CuO-BASED CERAMICS

A. de Pretis; D. Minichelli; L. Podda* and F. Ricciardiello,
Università di Udine, Udine, Italy.
Università di Trieste, Trieste, Italy.
Università di Palermo, Palermo, Italy.

Seven ternary phase diagrams based on high-melting oxides, alkaline and earth-alkaline oxides and copper oxide were investigated. No previous data on these diagrams are reported in literature.
The considered oxides were: Y_2O_3, CeO_2, BaO, SrO, CaO, K_2O and CuO.
The equilibrium phases were investigated and identified by means of X-ray diffraction and optical microscopy techniques; thermal analyses (DTA, TGA/DTG) were carried out on the powders in order to optimize the production cycles.
On the most interesting products electrical conductivity measurements at high temperature (400-800°C) were carried out.

BA 149 author present: 15.00 - 16.30

THERMAL DECOMPOSITION OF ALUMINIUM HYDROXYCHLORIDE.

M. Sopicka-Lizer, Institute of Materials Science and Engineering, Katowice, Poland.

Aluminium basic salts are of interest as precursor materials for the production of alumina fibres as well as for the formation of alumina. Thin films of aluminium hydroxychloride were formed by solution drying, calcined and then examined using FT-IR, XRD, DTA, TG, TEM and SEM. The drying process takes place in two stages leading to solvent-water removal and solidification in the form of amorphous material. Dried specimens contained significant amounts of hydration water which can be removed below 200°C without catastrophic breakdown of the structure. At temperatures in the range 300-400°C decomposition of polymeric species Al-13 result in high porosity materials, however the complete dehydroxilation was observed after heating at 600°C. γ-Al_2O_3 has been detected as a first crystalline phase. TEM study revealed that material transformed from polycrystals of γ-Al_2O_3 to single, porous crystals of γ-Al_2O_3.

Acknowledgements: The author is very grateful to the British Council for the stipend and Prof. A. Hendry at Strathclyde University, Glasgow for support and help.

BA 150 author present: 15.00 - 16.30

THERMODYNAMICAL ANALYSIS OF BOTH PHASE AND CHEMIMICAL TRANSFORMATIONS IN CERAMIC SYSTEM

M.Djurić, Z.Zavargo, J.Ranogajec, Lj.Petrašinović-Stojkanović*, B.Živanović
Inst.for Petrochemistry, gas, Oil and Chem.Eng., Novi Sad, Yugoslavia; Inst. of Mat.Examination, Beograd, Yugoslavia

A method, and based on it computer program, has been proposed for precise calculation of thermodynamical parameters which describe chemical as well as phase composition at equalibrium.

Physical and chemical transformations should be described by a general chemical reaction associated with the set of accompanied reaction concerning the particular products and their further transformations. However, the equalibrium mass (or molar) fractions of particular compounds are so affected by equilibrium temperature as the mass and energy balance equations should be solved simultaneously following the procedure which will be introduced.

As the results of the method applied, both equalibrium temperature and composition of a reacting system will be obtained, which form the data basis for every engineering calculation (simulation, design, optimization, etc.).

BA 151 author present: 15.00 - 16.30

ELABORATION OF ALUMINA-ALUMINIUM OXYNITRIDE FROM VARIOUS NITRIDED POWDERS,

Sappei J.*, Goeuriot D., Thévenot F; Laurent Y., Guyader J., L'Haridon P; et Al.
Ecole Nationale Supérieure des Mines de Saint-Etienne
158, cours Fauriel F 42023 SAINT-ETIENNE Cédex 2
Université de Rennes I. Laboratoire de chimie des matériaux
Campus de Beaulieu. Av. du Général Leclerc
F. 35042. RENNES Cedex

Aluminalon is an alumina based ceramic composite material, containing up to 30 v/o of γ spinel aluminium oxynitride. The first generation of this material was obtained by reaction bonding of mixed alumina and Starck aluminium nitride.
Starting from alumina, a new nitridation process, at low temperature (about 1200°C), has led to pure (carbonless) and more reactive AlN powder.
From this process, we have elaborated a partially nitrided alumina powder containing γAlON, and a pure γAlON powder.
This study deals with elaboration of Aluminalon from three different ways. The first two use mixed powders : mixed Al_2O_3 and AlN powders, and mixed Al_2O_3 and γAlON powders. The third way uses a partially nitrided alumina powder (about 1w/o of nitrogen). The materials were prepared by hot-pressing within the range of temperature going from 1550°C to 1700°C. These materials were analysed by scanning electron microscopy and X-ray diffraction. Density, room temperature mechanical properties (toughness, strength, hardness), high temperature mechanical properties (toughness, strength), and tribological properties were mesured.
The properties of these new composite materials are compared with those of the first generation.

BA 152 author present: 15.00 - 16.30

STRUCTURE RELATIONSHIPS DURING PYOLYSIS OF PRECERAMIC POLYSILAZANES, R. Lundberg*, Swedish Institute for Silicate Research, Göteborg, Sweden, P. Goursat and D. Bahloul, L.A.CNRS 320, Univ. of Limoges, France, A. Dauger and A. Lecomte, E.N.S.C.I, Limoges, France

Polysilazanes, which are of interest both as a fibre and a matrix precursor for ceramic matrix composites were studied. Polymerisation of octamethylcyclotetrasilazane using a $KOCH_3$ catalyst was performed to yield polymers with varying oligomer content. A model for the molecular architecture of the polymers was proposed based on small angle x-ray scattering (SAXS) results. The changes in structure during pyrolysis, crystallisation and oxidation were studied using thermogravimetric analysis, ESCA and mass spectrometry in combination with SAXS. An optimized polymer with respect to bloating during pyrolysis was synthesized. This polymer gave a relatively dense amorphous Si-N-C ceramic in 80% yield and was successfully used as a matrix precursor to produce SiC (Nicalon) fibre reinforced ceramics.

BA 153 author present: 15.00 - 16.30

CATALYTIC EFFECT OF FLUORIDE ON CRYSTALLIZATION AND PHASE TRANSFORMATION OF SOME SILICATE SYSTEMS, Samia, N. Salama, National Research Centre, Cairo, Egypt.

X-ray and DTA techniques were used to follow the effect of fluoride on the crystallization and the associated phases formed in silicate glasses of various subsystems belonging to $Li_2O(Al_2O_3)$-MgO(CaO,Zno)-SiO_2 system. Both the crystalline phases and microstructure of the materials should be controlled by addition of fluoride. A suspended phase of high fluoride content developed which crystallizes to simple or complex fluoride-containing phase. Fluorite-CaF_2 and high stable fluor-tremolite, $Ca_2Mg_5Si_8O_{22}F_2$, were detected in fluoride-containing materials depending upon the CaO and MgO content.
Fluoride remarkably improved the nucleation process and facilitated the ionic diffusion in the glasses to such an extent that the structurally more complex silicates like spodumene and $Li_2Ca_3Si_6O_{16}$ can take place. The crystallizing systems have better chance to approach thermodynamic equilibrium in comparison with those free of such catalyst. Therefore, the fluoride enhanced the disintegration of some metastable phases like Mg-wollastonite into wollastonite and diopside and assisted the formation of willemite, Zn_2SiO_4.
Conditions favouring formation of specific phases are discussed.

BA 154 author present: 15.00 - 16.30

$Pb(Sc_{2/3}W_{1/3})O_3$ - NEW COMPOUND WITH THE PYROCHLORE - PEROVSKITE TRANSFORMATION, M. Petrič, D. Suvorov, University of Edvard Kardelj, Ljubljana, "Jožef Stefan" Institute, Jamova 39, Ljubljana, Yugoslavia

Phase relations, reaction mechanism and development of the microstructure in the system PbO-Sc_2O_3-WO_3 were investigated by means of XRD, SEM and TEM. A ternary compound $Pb(Sc_{2/3}W_{1/3})O_3$ with a characteristic pyrochlore - perovskite transition was identified. During firing the oxide mixture at - 350°C $PbWO_4$ is formed. $PbWO_4$ reacts then with the excess of PbO into Pb_2WO_5 at - 500°C. Low temperature form of $Pb(Sc_{2/3}W_{1/3})O_3$ is pyrochlore phase, which is formed at 650°C. The transformation into the perovskite form is diffusive over the temperature range from 750° to 800°C. At 970°C $Pb(Sc_{2/3}W_{1/3})O_3$ melts incongruently into Pb_2WO_5 melt and Sc_2O_3.

BA 155 author present: 15.00 - 16.30

"EVOLUTION OF SPECIFIC SURFACES in SOLID STATE REACTIONS IN CERAMIC BODIES".

GIORGIO USAI DIPARTIMENTO INGEGNERIA CHIMICA E MATERIALI .UNIVERSITA' DI CAGLIARI p.zza D'Armi19 09123 CAGLIARI-I

"The evolution of the sintering reactions between the Components of Ceramic Materials-solid solid and solid liquid Phase reactions-is strictly joined with the development of the contact surfaces during the firing of green materials. In this note are referred the results of some experimental researchs on the evolution of specific surfaces of materials as Alumina & Silica at temperatures from 900°C to 1200°C,obtained by nitrogen adserption and deserption techniques with automatic testing apparatus. A relation between the specific surfaces of alumina & silica phases and the rate of firing reaction is finally proposed".

BA 156 author present: 16.30 - 18.00

USE OF THERMAL METHODS FOR CERAMIC CHARACTERISATIONS

P. LE PARLOUER SETARAM, 69300 CALUIRE/FRANCE

The fabrication of ceramics is linked with thermal treatment (heating, firing, sintering ...). Their applications at high temperature are more and more investigated. In both cases, the thermal analysis methods provide a very interesting tool for the simulation of their heat transformation, of their use at high temperature, for the determination of thermal parameters (specific heat, dilatation). Among the thermal methods adapted for such characterisations : thermogravimetry (TGA), differential thermal analysis (DTA), evolved gas analysis (MS, FTIR), differential scanning calorimetry (DSC), high temperature calorimetry, high temperature dilatometry.

BA 157 author present: 16.30 - 18.00

DETERMINATION OF THE THERMAL CONDUCTIVITY OF POLYCRYSTALLINE ALUMINA AND YTTRIUM-ALUMINIUM GARNET

C. Wijenberg, Philips Lighting B.V., P.O. Box 80020, 5600 JM Eindhoven, The Netherlands

The Thermal Conductivity (TC) of polycrystalline alumina (pca) and yttrium-aluminium garnet (yag) has been determined by means of the Ångström method [1] at temperatures from 300 to 1500 K. The aim of the investigation is to collect accurate high-temperature data allowing thermal modelling of the tube-shaped translucent discharge envelope as applied in high-pressure sodium lamps.

TC data are reported for pca and yag tubes of well-defined geometry and light-transmittance. The TC of pca was determined to be 10±1 J/mKs at 1300 K. The TC of yag at 1300 K was found to be 3.0±0.4 J/mKs. The present results will be discussed and compared with literature data.

[1] K.D. Maglic, A. Cerzailiyan, V.E. Peletsky, "Compendium of thermophysical property measurement methods", New York, Plenum Press, 1984

BA 158 author present: 16.30 - 18.00

CHARACTERIZATION OF ALUMINA-ZIRCONIA COMPOSITES REINFORCED WITH SILICON CARBIDE WHISKERS, A.G. Solomah* and W. Reichert, Institut für Chemische Technologie(ICT) and Zentralabteilung für Chemische Analysen (ZCH), Kernforschungsanlage, KFA-Jülich, D-5170 Jülich, Federal Republic of Germany.

Alumina-zirconia composites reinforced with different contents of silicon carbide whiskers were characterized using x-ray diffraction(XRD), scanning electron microscopy(SEM) and transmission electron microscopy(TEM). Hardness and fracture toughness were determined using Vicker's indentation and single edge notched beam technique. Flexural strength was measured by a means of four-point bending test. High-temperature annealing in air and vacuum were carried out to determine the stability of tetragonal zirconia in such ceramic composites. The annealed and fracture surfaces were examined to understand the toughening mechanisms responsible for the high toughness values measured for such ceramic/ceramic composites. The results will be presented and discussed in the light of different toughening mechanisms.

BA 159 author present: 16.30 - 18.00

THERMAL FATIGUE CHARACTERIZATION OF ZIRCONIA BASED THERMAL BARRIERS.

A. MOUGHIL, G.FANTOZZI, A.VINCENT
Q. SAIF, D. TREHEUX*
Groupe d'Etudes de Métallurgie physique et de physique des Matériaux UA 341 INSA Bât 502, 69621 Villeurbanne Cedex (France)
*Laboratoire Métallurgie physique Matériaux, UA.447, Ecole Centrale de Lyon
B.P. 163, 69131 Ecully Cedex (France)

Thermal barrier coatings were optimized with the aid of various testing methods such as thermal shock fatigue tests with acoustic emission study, ultrasonic imaging and tensile tests.
The aim of the present work is to promote techniques and analysis both in the field of coating characterization and that of bonding testing.
After an experimental and theoretical study of interference effects occuring in the coating, the conditions used to reveal bonding defects which are produced during thermal cycling are described.
The behaviour of plasma sprayed zirconia coating with bond layers produced by Aluminium based slurry coating and with NiAl plasma sprayed bond layers is studied. In particular the effects of additional elements and thermal post -treatments ares specified.

BA 160 author present: 16.30 - 18.00

CHARACTERIZATION OF PURE ZrO_2 POWDERS PROCESSED FROM REACTIONS IN MOLTEN SALT MIXTURES

R. Ravelle-Chapuis*, M.G. Blanchin;
M. Jebrouni+, B. Durand+,
Département de Physique des Matériaux,
U.A. 172,
+Laboratoire de Chimie Minérale III,
U.A. 116,
Université Lyon I, 43 Bd du 11 Novembre 1918,
69622 VILLEURBANNE Cedex FRANCE.

Ultrafine powders of pure zirconia ZrO_2 were prepared by chemical reaction at low temperatures in molten salt mixtures of nitrates (KNO_3,$NaNO_3$).The reaction product was then crystallized by calcination at increasing temperatures. The structure of the phases present in the powders were identified by X-Ray diffraction spectrometry and electron diffraction.The basic product prepared at 260°C contained both amorphous and monoclinic phases (with traces of tetragonal phase).At increasing calcination temperatures the percentage of tetragonal phase proved to increase and then decrease until the powder became entirely monoclinic at about 1000°C. The powder particles were characterized by conventional transmission electron microscopy (CTEM) and high resolution TEM.Those observations revealed agglomerates and agregates of ultrafine primary particles (mean diameter < 50 nm).

BA 161 author present: 16.30 - 18.00

HREM OF INTERFACES IN STRUCTURAL CERAMICS,

S. Hagège.
ENSCP- 75231 Paris and CECM- 94400 Vitry, France.

Transmission electron microscopy under the high resolution mode (HREM) is a very powerfull technique to reveal the true atomic structure of interfaces in ceramic materials. Despite severe restrictions (orientation of the grains, thickness of the specimen, resolution, interpretation ...) an atomic image can provide new insights on the geometry and the chemistry of an interface and thus the physical and thermomechanical properties of the material.
As an example results on aluminium nitride (AlN) and silicium carbide (αSiC and βSiC) will be presented:
Aluminium nitride is very sensitive to the presence of oxygen in its lattice and faulted interfaces are easily produced within the grains. HREM micrographs can demonstrate that the nucleation of these interfaces is related to the oxygen impurities and that the complex configurations of these interfaces originate in the interaction during growth of an original defect.
HREM micrographs of CVD βSiC exhibits particularly well defined multiple twin interfaces which have been analysed using a coincidence modelisation and a high resolution contrast simulation. In the case of a hot pressed bicrystal of αSiC a large amorphous interlayer has been detected and the migration of the interface reveals a αSiC / βSiC transformation.

BA 162 author present: 16.30 - 18.00

STRUCTURAL DEFECTS IN AlN CERAMICS USING TEM,

S. Hagège* ; Y. Ishida.
ENSCP- 75231 Paris and CECM- 94400 Vitry, France;
IIS-University of Tokyo, Tokyo 106, Japan.

Aluminium nitride (AlN) ceramics are well known for their thermal conductivity and potential transluscence. Several materials of different purities and different conditions of preparation have been studied by Transmission Electron Microscopy. The microstructure of hot pressed, pressureless sintered and CVD materials will be critically compared with respect to the nature and the density of structural defects.
The microstructure of hot pressed AlN is mainly affected by its oxygen content inducing polytypoidic phases and "dome-like" faulted defects. The cumulative effects of these surface defects induced by the impurities and the density of dislocations are detrimental to the properties. If the oxygen content is reduced and the material pressureless sintered, the resulting material can reach very acceptable values of thermal conductivity and be fairly translucent.
In the case of CVD material, impurity content is maintained to a minimum value and, by controlling the parameters of the deposition, high quality material almost defect free are obtained. Furthermore subsequent heat teatment on the CVD material (annealing and/or HIP) drastically increase the performance by redistributing the structural defects.

BA 163 author present: 16.30 - 18.00

TEM STUDIES OF SINTERED SILICON NITRIDE (SSN) SURFACES AFTER MACHINING,

R.Haushälter*, H.Frei, G.Grathwohl
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An optimized cross-sectional preparation technique was used to investigate surface and subsurface areas of ceramic materials.
Type and density gradient of crystal defects generated by different mechanical surface treatments were studied by transmission electron microscope. Fine diamond polishing, technical diamond grinding and ultrasonic machining provided different types and extensions of induced surface defects and resulted also in different strength values of machined bending specimens. Amorphisation and the generation of dislocations and microcracks are the predominant defects in the outermost layer below the machined surface of SSN.

BA 164 author present: 16.30 - 18.00

CHARACTERIZATION OF SILICON NITRIDE POWDERS BY WATER DESORPTION ACTIVATION ENERGY,

Mitsuru Kawamoto*, Kozo Ishizaki and Chanel Ishizaki,
Nagaoka University of Technology, Nagaoka, Niigata 940-21, Japan.

The surface properties of silicon nitride powder are great important factors for powder preparation, forming and sintering. Characterization of silicon nitride powder surfaces by temperature programed desorption (TPD) is described in this work. The TPD spectra were measured by a 4 poles mass spectrometer in an ultra high vacuum system (2×10^{-9} Torr).
Two kinds of silicon nitride powders, i.e., A(by imide decomposition) and B(by nitriding silica using carbothermal reduction), were evaluated. From the TPD spectra, the following results were obtained. (1)Water and ammonia were the major adsobates on both powders A and B. (2)Powders A and B have different active sites for both water and ammonia. (3)Activation energy of water desorption water from the powder A was greater than that from the powder B.

BA 165 author present: 16.30 - 18.00

ELECTRONIC STRUCTURE AND CHARACTERIZATION OF TiN_x COATINGS,

E.Beauprez*,S.Harel, J-L.Derep, Centre de Recherche et d'Etudes d'Arcueil, ETCA, F-94114 Arcueil; N.Moncoffre, J.Tousset, IPN, Univ.Claude Bernard Lyon-I, F-69621 Villeurbanne; J-M.Mariot, C.F.Hague, Laboratoire de Chimie Physique, Univ. Pierre et Marie Curie Paris-VI, F-75231 Paris

Vacancy concentrations in TiN_x ($0.57<x<1$) CVD coatings have been measured by nuclear reaction spectroscopy (NRS) and x-ray diffraction (XRD). The information provided by each technique is compared and dicussed. The electronic structure probed by x-ray emission spectroscopy (XES) shows the presence of a strong vacancy induced peak in the Ti K emission band (1). Combining the NRS and XRD data with the XES data has enabled us to show that there is a linear relationship between the intensity of the vacancy peak and the vacancy concentration for $0.7<x<1$. For higher apparent vacancy concentrations the intensity of the peak falls off. Using transmission electron microscopy (TEM) we are able to trace this deviation from a linear relationship to the presence of extrinsic stacking faults in samples with $x<0.7$.

(1) E.Beauprez, C.F.Hague, J-M.Mariot, F.Teyssandier J.Redinger, P.Marksteiner, P.Weinberger, Phys. Rev. B34 886, 1986

BA 166 author present: 16.30 - 18.00

HIGH TEMPERATURE MECHANICAL SPECTROMETRY ON WC-Co CERMETS

M.Gordon, S.Etienne, G.Fantozzi.
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Widely used, as cutting tools, cermets are subjected to severe mechanical stresses at relatively high temperature (800-1000°C).

Mechanical spectrometry which is very sensitive to microstructural effects is particulary suited for the study of microplasticity phenomena which modified the macroscopical properties of this composite material.

In order to study the microstructure, an inverted torsional pendulum working in forced oscillations in the very low frequency range which can reach 1000°C has been designed.

Internal friction spectra have been performed as a function of temperature. They are mainly composed of a relaxation peak around 630°C and a complex phenomenon above 800°C superimposed to a background increasing exponentially with the temperature.

Thermomechanical treatment (grinding, annealing) induced modifications on the internal friction spectra.

* When the material has been abrased the first peak attributed to a brittle-ductile transition [1] is located at 680°C and after annealing at 800°C the peak shifts towards lower temperatures (630°C). It is in agreement with the hypothesis of the formation of an ε'(hcp) phase inside the binder phase of WC-Co [2].

* By thermal treatment at increasing temperatures the ε'(hcp)-->γ(fcc) transformation temperature has been determined using the above hypothesis.

* The temperature of the complex second phenomenon is very sensitive to the thermal history of the material and in particular the spectrum exhibits an hysteresis between heating and cooling.

[1] R.Schaller et al, J. Physique 46 C10-387 (1985).
[2] H.Suzuki et al, J. Japan Inst. Met. vol.32 993 (1968).

BA 167 author present: 16.30 - 18.00

CHARACTERIZATION OF POROUS CERAMIC FUEL CELL COMPONENTS

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Netherlands Energy Research Foundation, ECN
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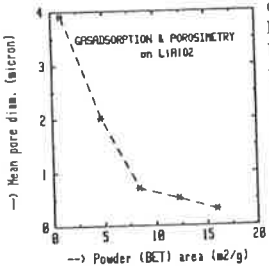
ECN is involved in molten carbonate fuel cell (MCFC) research since 1986. The MCFC consists essential of an anode of Ni-$LiCrO_2$ and a cathode of NiO separated by an electrolyte matrix of $LiAlO_2$. All components named are porous. Suspensions used for tape casting are characterized with static light scattering technique. The sintering behaviour is simulated by extensiometry and differential thermal analyses.
Data on pore size distribution and specific surface are obtained from mercury porosimetry and nitrogen gasadsorption. All mentioned techniques give rise to the insight essential for component development.
Pore size distribution can be tuned by blending two powders of the same material but with different specific surfaces.
As illustrated the required mean pore size of the $LiAlO_2$ matrix material (< 1.0 micron) can be obtained by mixing low and high surface area powder.



BA 168 author present: 16.30 - 18.00

HIGH RESOLUTION SOLID-STATE NMR STUDIES OF SOME NITRIDE AND OXYNITRIDE CERAMICS

M.J.Leach, R.K.Harris; and D.P.Thompson*
University of Durham, DH1 3LE, U.K. and
University of Newcastle upon Tyne, NE1 7RU,UK

^{27}Al and ^{29}Si magic angle spinning NMR spectra have been obtained for a variety of crystalline nitride and oxynitride ceramics. The results for the four La-Si-O-N oxynitrides are broadly similar to equivalent Y-Si-O-N phases and are consistent with crystal structure information where this is available. The effects of simultaneous Si→Al and N→O substitution on the peaks in the NMR spectrum are discussed and spectra for other La-Si-Al-O-N and Y-Si-Al-O-N phases are presented.

NMR spectra are also given for LiSiNO, $LiSi_2N_3$, $MgSiN_2$, $MgAlSiN_3$, $LaSi_3N_5$ and a calcium α'-sialon. From the results obtained, correlation of ^{29}Si chemical shift values with structural variables such as nearest neighbour and next-nearest neighbour coordination and bond angles is discussed.

BA 169 author present: 16.30 - 18.00

MEASUREMENT OF STRENGTH AND DEFORMATION BEHAVIOUR OF GRANULATED CERAMIC PRESS GRADE POWDERS

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Institut für Keramik im Maschinenbau, Institut für Werkstoffkunde II, Universität Karlsruhe
Haid u. Neustr. 7 D-7500 Karlsruhe

The strength of agglomerates is very important in ceramic powder processing: Agglomerates have to be disintegrated during moulding for achieving a homogeneous arrangement of the primary particles in the green compacts. A method for a direct characterization of agglomerate strength by measuring load-deformation behaviour in single granule compression test will be presented.
The measuring system, which is based on a Piezo loading unit, was recently developed and will be described in detail. Practical application of the method is feasible down to granule diameters of 100µm. Measurements of load-deformation behaviour were carried out on model spheres, as well as on granulated ceramic press grade powders. The model experiments are used to get some insight in compressive load-deformation characteristics of spheres, depending on their viscoelastic behaviour. The load-deformation curves of the press grade powders will be analyzed on the basis of these results. The role of granule strength is discussed for the different types of curves observed.

BA 170 author present: 16.30 - 18.00

Toughness and Crack Propagation Resistance in Non Phase Transformation and Transforming Ceramic Materials

M. SAADAOUI*, G. ORANGE, G. FANTOZZI
*Ecole Mohammadia d'Ingenieurs, Agdal-Rabat (Maroc)
INSA Lyon (GEMPPM), Bât. 502, 69621 Villeurbanne (France).

The fracture toughness of Alumina, Zirconia-toughned Alumina (ZTA), Partially Stabilized Zirconia (Mg-PSZ), and Tetragonal Zirconia Polycrystals (Y-TZP) were evaluated by different techniques and as a function of the microstructure of the materials (grain size, metastable phase content).
Crack Resistance Curves of the different materials were investigated by 3 point bending tests. The crack propagation was monitored by compliance measurement and Acoustic Emission Signals detection. In case of phase transformation materials, a deviation to linearity is observed on load-displacement curves, which is not only due to crack propagation.
Experimental results indicate energy absorption processes as the crack propagates through the materials in Alumina or ZTA, with a rising R-curve. In case of Mg-PSZ, a falling or a maximum of the R-curve is observed. Results are discussed according to the stress induced phase transformation and subcritical crack growth mechanisms.

BA 171 author present: 16.30 - 18.00

Effect of Electronic Defects and Oxygen Vacancies on Mechanical Behaviour of Oxyde Ceramics

K. M. LIANG*, G. ORANGE, G. FANTOZZI
INSA Lyon (GEMPPM), Bât. 502, 69621 Villeurbanne (France).
*Tsinghua University, Beijing (China)
M. GAUTIER, J. P. DURAUD, C. Le GRESSUS
CEA-IRDI-CEN Saclay, 91191 Gif S. Yvette (France).

The dependence of ceramic mechanical properties on microstructure has been well studied: effect of porosity, grain size, grain boundary.... This work deals with the change in fracture properties of yttrium oxide with microscopic defects such as those induced by a non-stoichiometric state or by treatment under an electric field.
Oxide ceramics with different stoichiometry (oxygen vacancies) are obtained after heat treatments in vacuo or in air. For an oxygen deficient Y_2O_3 material, a decrease of K_{IC} is observed from 3.5 to 2.3 $MPam^{1/2}$ whereas no significant dependences are measured with the Vickers hardness. Similar effects are observed after treatment of Y_2O_3 specimens under electric field: K_{IC} decreases as point defects are increased in the material. Fracture properties are restored after annealing treatment.
These results are discussed in terms of the evolution of the atomic bond with the stoichiometry (electronic polarization). The electrostatic energy stored in a brittle material containing charged defects seems to play an important role in the energy balance controlling the crack propagation.

BA 172 author present: 16.30 - 18.00

THERMAL EXPANSION OF MULLITE

H. Schneider*, Forschungsinstitut der Feuerfest-Industrie, D-5300 Bonn, E. Eberhard, Mineralogisches Institut der Universität Hannover, Germany.

Pure, chromium (Cr_2O_3: 1.5 wt%), and iron doped (Fe_2O_3: 0.3 wt%) sinter-mullites, and pure fused-mul-lite+ were used for thermal expansion measurements. The sinter-mullites were produced by annealing powder compacts while fused-mullites were crystallized from melts using the Czochralski technique+. Structural expansions of mullite between 25 and 900 °C were determined by high temperature X-ray diffraction Guinier runs.

All mullites display strongest thermal expansion parallel to the crystallographic b axis with expansion coefficients ranging between about 5.2 and 6.2 x 10^{-6}. Expansion coefficients along c are slightly lower (5.4 x 10^{-6}), while those along a are considerably lower (3.5 - 2.6 x 10^{-6}) than those parallel b.

The investigations show that the volume expansion with respect to pure sinter-mullite in chromium doped sinter-mullite is lowered to about 15 %. On the other hand the anisotropy $\propto b / \propto a$ decreases from about 1.9 in pure sinter-mullite to about 1.5 in fused-mullite.

*Presenting author.

+We thank Prof. Guse (Hamburg) for performing fused -mullite single crystals.

BA 173 author present: 16.30 - 18.00

THERMAL COEFFICIENTS OF HIP SINTERED SILICON NITRIDE.
Koji WATARI and Kozo ISHIZAKI.
Nagaoka Univ. of Tech., Kamitomioka, Nagaoka 940-21, Japan

Thermal diffusivity and conductivity as well as specific heat of capsule-HIP sintered silicon nitride were measured at different temperature ranging from 100 to 1300K. Yttria and alumina additives with a total amount of 6mol% were used.

For a given additive percentage, specimens of higher beta phase fraction had higher thermal diffusivity and conductivity, as expected at room temperature. However, samples with higher yttria additive had higher thermal diffusivity and conductivity in spite of a lower beta phase fraction than those with more alumina additive. The highest thermal conductivity was 70W/(m·K) with 6mol% yttria additive alone at room temperature. The reason is that aluminium and oxygen ions are soluble in beta-silicon nitride particles, in the case for alumina addition. Also oxygen presented as an impurity had a profound effect on the thermal diffusivity and conductivity. higher oxygen contents reduced the thermal diffusivity and conductivity. This may be due to the higher amount of grain boundary glassy phase.

The specimens with higher thermal diffusivity and conductivity at low temperatures were those with higher beta phase fraction, larger particle size of raw silicon nitride and rich yttria additive. For these specimens the thermal diffusivity and conductivity showed a larger temperature dependence. Within the temperature range studied, the phonon - phonon interaction was not a dominant factor for the thermal diffusivity, but the phonon - oxygen defect interaction was.

The isobaric secific heat Cp of sintered bodies was 0.67 ± 0.02kJ/(K·g) at room temperature. The crystalline structure (alpha or beta), additive composition, and raw material particle size did not show any effect on the specific heat.

The isobaric specific heat Cp agreed with the isochoric specific heat Cv calculated by the Debye's theory, assuming that silicon and nitrogen atoms are lattice dynamically equivalent. The Dulong-Petit rule applied well to sintered silicon nitride at high temperatures and Cv = 25J/(K·mol). The glassy phase quantity could be estimated by the difference of the measured specific heat and calculated specific heat at low temperature.

BA 174 author present: 16.30 - 18.00

TRANSFORMATION PROPERTIES AND TOUGHENING MECHANISM OF ZIRCONIA,
Tingkai Li, Suxing Wu, Zishang Ding, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, China

The stress-induce transformation of Y_2O_3 metastable zirconia powder, the effective transformable volume fraction and the volume fraction and width of transformed $ZrO_2(t)$ in the cut and fractured surface have been measured by X-ray diffraction. Studies of HREM of transformation process of $ZrO_2(t)$ and measurement of size of the ZrO_2 transformation zone at crack tip have been made. It is found that there exist metastable $ZrO_2(t)$ which transformation are controlled by energy barrier forming nucleation in unconstrained condition in ZTC. The transformation of the $ZrO_2(t)$ grains electively take place around deflects. Hence the $ZrO_2(t)$ grains have greater contribution to toughening. Base on above a new equation of toughening is derived and new mechanism that the crack deflection toughening caused by grains and whiskers having high modulus could strengthen the transformation toughening of ZrO_2 have put forward, and the TZP ceramic with K_{1c}=21.3MPam$^{\frac{1}{2}}$ and σ_f=1578MPa has obtained.

BA 175 author present: 16.30 - 18.00

GAMMA DENSOMAT - A NEW QUALITY CONTROL INSTRUMENT IN CERAMICS,
G. Schlieper*, V. Arnhold, Sintermetallwerk Krebsöge GmbH, P.O. Box 5100, D-5608 Radevormwald, West Germany.

The determination of the density is an important part of quality control in ceramics, as many other properties are influenced by porosity. Conventional methods of density determination are often tedious and time consuming, require skilled laboratory personnel and the tested parts are usually destroyed. The Gamma Densomat provides a tool to non-destructively determine local densities in short times with high accuracy. The measurement is based on the absorption of gamma radiation in the tested material. Green compacts and fired components can be tested with equal precision. Applications for this instrument are in the field of technical ceramics, refractories, magnets, grinding and friction materials, cemented carbides, powder metallurgy.

BA 176 author present: 16.30 - 18.00

MICROWAVE PROPERTIES OF ZrO_2-TiO_2-SnO_2 CERAMICS,
D M Iddles* A J Bell; A J Moulson[2]
Cookson Central Research Labs, Englefield Green, TW20 OJZ, UK
[2] Division of Ceramics, University of Leeds, LS2 9JT, UK

Abstract

Ceramics whose compositions lie in the solid solution region of the ZrO_2-TiO_2-SnO_2 phase diagram are finding commercial application in filters using microwave frequencies. Such applications include hand-held telephones, satellite communications and radar.

A number of papers have been published, concerning the correlation of microwave dielectric properties with composition. However, no study has yet addressed the issue of what controls dielectric losses at microwave frequencies. Thus, the paper reports the correlation of microwave dielectric properties with microstructure, fired density and dopants. The study has demonstrated that if samples are of density > 90% of theoretical, it is the dopants added and their influence on second phase formation and the defect chemistry of the bulk material, which determine the loss characteristics of ZTS ceramics.

BA 177 author present: 16.30 - 18.00

THE ALUMINUM MONO-OXYCARBIDE Al_2OC IN THE REVISED BINARY SYSTEM Al_2O_3-Al_4C_3 AND IN THE TERNARY SYSTEM Al_2O_3-Al_4C_3-AlN; THERMODYNAMIC AND MECANICAL PROPERTIES,

J.-M.Lihrmann; T.Zambetakis and M.Daire, Université Paris XIII,LIMHP, 4 Av.J.B. Clément,F-93430 VILLETANEUSE (France); EHICS,DSM,4 Avenue B.Pascal, BP206 F-67 008 STRASBOURG (France)

The Aluminum Mono-Oxicarbide Al_2OC can exist in a stable as well as in a metastable condition. In the first case it decomposes to Al_4O_4C and Al_4C_3 at 1715°C according to the reaction

$$4\ Al_2OC \longrightarrow Al_4O_4C + Al_4C_3\ ,$$

and the stable phase diagram Al_2O_3-Al_4C_3 should be reviewed to include this transformation.
In the latter case, when reheated above 1200°C Al_2OC undergoes T.T.T. transformations into Al_2O_3 and Al_4O_4C, as is normally expected from metastable components; the reaction is

$$Al_2O_3 + x\ Al_2OC \longrightarrow (1-x)Al_2O_3 + x\ Al_4O_4C$$

Additions of AlN to Al_2OC create a solid solution which strongly improves its stability at high temperature.
The mecanical behavior of these components is also briefly discussed.

BA 178 author present: 16.30 - 18.00

SINTERING OF SILICON NITRIDE WITH LITHIUM-ALUMINOSILICATES, J.M. Sacramento*, P.N. Correia, A.T.S. Fonseca and J.L. Baptista,
Dep. Eng. Cerâmica e do Vidro e Centro de Cerâmica e do Vidro (INIC), Universidade de Aveiro, 3800 Aveiro, Portugal

The pressureless sintering of silicon nitride was studied using additions of SiO_2, Al_2O_3 and Li_2O in different proportions. The effect of the composition of the liquid phase, present at the sintering temperature, on the formation of α and β solid solutions and on densification is reported in this paper. For some compositions almost complete densification can be achieved with negligible formation of β silicon nitride whereas for other compositions α and β solid solutions were formed during the densification process. Recrystallization of the residual liquid phase is also reported. The results are discussed taking into consideration the composition of the liquid phase present during the sintering process.

BA 179 author present: 16.30 - 18.00

CARBIDE

D. GOSSET * and B. KRYGER
D.TECH/SECS/LMA - CEN S - 91191 GIF S/YVETTE - FRANCE

Boron carbide is used as a neutron absorber material in the control rods of the nuclear power plants, due to the high neutron capture cross-section of the ^{10}B isotope. The B-C diagram indicates that the boron carbide phase is a solid solution ranging from the composition B_4C (80 at % B) to $B_{10}C$ (91 at % B). However, the industrial processing of the boron carbide powders leads to a product whose composition is always B_4C+C_F (containing a little excess of free carbon). Unfortunately this composition presents some drawbacks for the nuclear application above mentioned (insufficient boron content and presence of an excess of free carbon).

In order to improve the nuclear behaviour of the boron carbide, studies have been undertaken and we present results we have obtained concerning the elaboration and the characterization of boron rich (B_9C) boron carbide pellets :

- processing : hot pressing into a graphite die protected with a tantalum shroud.

- properties : microstructure, cell parameters, thermal properties...

An irradiation test of this material is in progress in the PHENIX french reactor.

BA 180 author present: 16.30 - 18.00

FORMATION OF TiN FROM TiO_2,

G. V. White,* K. J. D. MacKenzie, and J. H. Johnston, Chemistry Division, DSIR, New Zealand; Victoria University of Wellington, New Zealand.

The kinetics and mechanism of TiN formation by nitridation of TiO_2/carbon mixtures at 1050-1250°C have been studied by X-ray diffraction for a number of fine, pigment grade TiO_2 samples. The results show that TiN is formed by stepwise reduction to Ti_3O_5 which then nitrides.

BA 181 author present: 16.30 - 18.00

Microstructure and composition of the fiber-matrix reaction zone in SiC/LAS composite

M. Lancin[1], J. Thibault-Desseaux[2], P. Trebbia[3], M. Parlier[4]

1. LPM, CNRS, 1 Pl. A. Briand,F-92195 Meudon
2. DRF, CEN, 85X, 38041 Grenoble, France
3. LPS, Paris-Sud, 91405 Orsay Cedex, France
4.OM,ONERA,29,Av.Div.Leclerc,F- 92322 Chatillon

SiC Nicalon fibers / LAS matrix composites are realized by ONERA. During the process, grows a complex interfacial zone which consists of three layers labelled L1 to L3 from the fiber to the matrix. Their microstructure and phase composition have been determined by HREM and EELS/STEM-Vg . L1 and L3 are mainly composed of amorphous carbon. L2 which is also amorphous, contains only a small amount of C; it is mainly made up of Si and O which are likely involved in SiO or in SiO_2 bondings. Beyond the reaction zone, the diffusion of the matrix elements into the fibers which has been revealed by SIMS does not induce any microstructural change in the 202 Nicalon fibers detectable by HREM.

BA 182 author present: 16.30 - 18.00

HREM characterization of the interface in SiC/SiC composites

N. Lob[1] , M. Lancin[2] , J. Thibault-Dessaux[3], M. Parlier[1]

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2.LPM, CNRS, 1 Pl. A. Briand, F-92195 Meudon
3.DRF, CEN, 85 X, F-38041 Grenoble

2D.SiC Nicalon fibers/SiC CVD matrix have been prepared by the SEP for aerospace applications. The fibers were coated by 100 nm C-CVD prior to the infiltration in order to increase the composite toughness. Depending on the processing, the composites exhibit either a high or a low failure strain. TEM (200 kv) and HREM (400 kv) studies have been carried out to characterize the microstructure of the interfacial zone. Distinct microstructures have been revealed which are likely accounted for the differences in the mechanical behaviour.

BA 183 author present: 16.30 - 18.00

THE SINTERING AND OXIDATION BEHAVIOR OF ALUMINIUM NITRIDE

P. Barthelme, F. Ansorge, M. Kulig, T. Hofmann*, C. Rüssel
Universität Erlangen-Nürnberg,Institut für Werkstoffwissenschaften III (Glas und Keramik),
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Commercially available ultrapure aluminium nitride powders, doped with yttria were pressureless sintered under nitrogen atmosphere in a carbon tube furnace. At temperatures higher than 1800 °C a theoretical density of >98% was reached. Depending on the sintering conditions several different yttria containing phases appeared in the microstructure. The aim of this treatment was to localize all oxygen contaminations of the aluminium nitride starting material at separated phases at the grain boundaries or in the triple points.
Aluminium nitride powders and compact aluminium nitride ceramics were oxidized in different gas atmospheres like dried and wet air. At sintered ceramic a dense layer, solely composed of aluminium oxide, was observed. Aluminium oxynitride phases could not be detected at all temperatures investigated. Depending on temperature, a linear or square route rate law could be observed. The influence of different gas atmospheres is discussed.

BA 184 author present: 16.30 - 18.00

The crystal structure refinement of ß-pollucite in a high temperature,Y.Ochi, Yokohama,Kanagawa,Japan

A powder sample($CsAlSi_2O_6$),which had the pollucite structure,was synthesized by a gel method.
With CuKdradiations,4501 powder X-ray diffraction data were collected for the powder compound by a step scan method with a step interval 0.02° in 2θ between 50°C and 900°C.
The crystal structure had been refined with the intensity data by using of a Rietveld program PFLS which was assumed the peason-7 type function as a peak profile model.
The angles of inter-tetrahedral framework were changed with a temperature between 50°C and 150°C. The cell dimensions were incleased with these structural behavious.
However,above 300°C,there were not indicated the change of the inter-framework angles.

EN 1 11.30

STRUCTURAL RELIABILITY ANALYSIS OF CERAMICS,
J. Lamon, Battelle-Geneva, Switzerland.

Ceramics are highly sensitive to minute microstructural flaws. As a consequence, the mechanical strength properties vary to such a degree that a statistical treatment is required. Moreover, the location of the critical flaw is unpredictable among the large quantity of preexisting defects. This renders the fracture of ceramics a probabilistic event.

The Weibull statistics are the most widely used, primarily for routine analysis of test data. Significant inconsistencies were observed when comparing multiaxial failure data with predictions from strengths measured in uniaxial conditions.

A fundamental fracture model (the Multiaxial Elemental Strength Model) which combines fracture mechanics concepts with the statistical Elemental Strength Approach has been devised by Lamon and Evans, and proved to be an improvement over the Weibull method for treating polyaxial failure. Based upon this model, the CERAM computer code has been developed for the structural reliability analysis of ceramic components.

The present paper discusses the Multiaxial Elemental Strength Model and the CERAM computer code. Several practical examples are treated. Finally important implications for the structural design of reliable ceramic components are discussed.

EN 2 11.50

ASPECTS OF DESIGN AND STRESS CALCULATIONS IN ENGINEERING CERAMICS.

Dr.Ir. S. Sinnema

Hoogovens IJmuiden, P.O. Box 10.000, 1970 CA IJmuiden, The Netherlands.

It has been recognized that the strength of ceramics is a statistical quantity sensitive to volume and stress-state effects. For an appropriate design for ceramics these concepts, opposed to conventional concepts used for metallic components, should be taken into account. Moreover, ceramic material can only bear high compressive stresses. Therefore, for the reliability one should try to avoid tensile stresses i.e. the material must be unstressed or kept under compression as much as possible.
For adequate design, stress calculations using "Finite Element Methods" adapted for ceramics are used.
Aspects of design and stress calculations in ceramics will be illustrated with examples from process industries.

EN 3 12.10

FRACTURE OF COMPOSITE CERAMICS,

R.G. Cooke, School of Materials Science, University of Bath, Bath BA2 7AY, UK

Results will be presented on strength, toughness and acoustic emission measurements for carbon-carbon and silicon carbide fibre reinforced borosilicate glass. Results obtained elsewhere will be reviewed. Analysis of inter-relationships between the measured parameters and the structures of the systems will be made and a discussion of the appropriateness of fracture theories that rely on a single critical quantities will be given. It is proposed that more probabilistic predictions, summing over many sub-critical events should be used. Comparison with such methods that have been developed for graphites and heterogeneous ceramics will be presented.

EN 4 15.00

FRACTOGRAPHIC STUDY OF SiC AND Si_3N_4 CERAMICS,
M. K. Ferber* and V. J. Tennery, Oak Ridge National Lab, Oak Ridge, TN 37831-6062 U.S.A.

Commercially available SiC and Si_3N_4 ceramics were fractured in 4-point flexure at room temperature as part of an Annex II Agreement round robin study involving the United States, Federal Republic of Germany, and Sweden. U.S. participants included Sohio Engineered Material Company, NASA Lewis, Garrett Turbine, Allison Gas Turbine, and GTE Laboratories. Participants from Germany supplying data were ESK, KFA, MAN Technologie, KFK-University of Karlsruhe, Bosch, IWM Freiburg, and Daimler-Benz. Participating laboratories in Sweden were Swedish Silicate Research Institute, Asea Cerama, and Sandvik. For each specimen set tested, the bars were ranked by strength and then divided into 3 groups consisting of the 5 highest strength bars, the 5 lowest strength bars, and 5 bars nearest the mean of the strength distribution. Nature, location, and size of the defects responsible for failure were determined. The results were used to examine the applicability of strength-flaw size relationships. Reasonable correlation between the strength and defect size could only be obtained by including a residual stress term in the strength-flaw size expressions.

Research sponsored by USDOE as part of the CTAHE Project of the Advanced Matls. Devlpmt. Prog., under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

EN 5 15.20

STRENGTH-VOLUME-GEOMETRY: QUANTITATIVE RELATIONS FOR VARIOUS COMPONENT DERIVED STRENGTH TESTS,
L. Weiler* and V. Hoffesommer,
Asea Brown Boveri Forschungszentrum,
D-6900 Heidelberg, FRG.

As strength of ceramics is determined by peculiarities of the production process it would be desirable to the engeneer and to the ceramist to get strength data directly of components under service conditions. But strength data are mostly limited to standard bend tests or preferably to tests on parts of components. Due to the dependence on the stressed volume/surface the strength of the component is then to be extrapolated from the test data via the 'effective volume' (stress volume integral) or the 'effective surface area' (stress surface area integral) of the applied tests.

The effective volume and effective surface area are calculated for various strength tests on the prototype component 'tube', the hoop test, the C-ring test and the cylinder segment bend test on the basis of the Weibull theory. The ratio wall thickness/radius and the size are taken as free parameters. The thus derived theoretical strength values are related to theoretical strength values measured by the tensile test and the standard bend test.
Experimental strength data measured on Na-beta-alumina tubes by the above methods are compared with the theoretically derived values.

EN 6 15.40

Influence of nonlinear elastic effects on the crack resistance of ceramics,

F.E. Buresch
IRW/KFA-Jülich
and
ICA
Pfaffenwaldring 27,
7000 Stuttgart 80

The objective of the present work is to clarify the relationship between the properties of the microstructure of some ceramics and their fracture resistance under mode I loading condition, especially during stable crack growth. Characteristic for a ceramic with a rising R - curve is a nonlinear elastic deformation. Than the crack resistance is related to the energy release rate J_c at crack initiation and the tearing modulus $T_J = dJ/da$ which characterizes nonlinear elastic effects during stable crack growth. The macroscopic parameters J_c and T_J are related to microstructural parameters such as the grain size distribution and the residual strain energy density. Thus the microstructure can be optimized with respect to the crack resistance of a special material.

EN 7 16.00

PROOF TEST FOR ASSURING THE STRENGTH OF CERAMIC MATERIALS, Ichiro Takahashi
1030, Shimoogino, Atugi-shi, Kanagawa, JAPAN, 243-02.
The major difficulty in using ceramics or other brittle materials as strength members such as machine patrs is the larger variation in strength as compared with other structural materials. This variation depends upon the flaw distribution.
Accordingly, many studies have been conducted on the strength based on flaws and the techniques of nondestructive examination. It is, however, difficult to detect flaws of the order 10μm in machine parts with X-ray or ultrasonic test equipment. For rotating parts, the over speed spin test method is used to load stresses to assure the reliability of actual machines. For other structural parts, however, there is no method suitable for loading the necessary stresses.
This report presented a technique for loading an arbitrary stress to establish a proof test method for strength of parts and a method for strength evaluation of ceramic materials.

EN 8 16.20

MECHANICAL PROPERTIES OF CERAMIC LINED PIPES PRODUCED BY A CENTRIFUGAL-THERMIT PROCESS, Osamu Odawara, Dept. Electronic Chem., Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan.

A new technique has been proposed for ceramic lining to hollow metallic body by means of a thermit reaction taking place under the influence of centrifugal force("Centrifugal-Thermit Process"). Since the centrifugal-thermit process proceeds along the inner surface of the hollow body first and then into the layer in the radial direction, the temperature increase of the outer metal pipe is delayed compared to the product layers during the process. Due to the differences in melting point and shrinkage coefficient of the produced ceramic from the metal, the metal layer contracts much more than the ceramic resulting in high compression stress in the ceramic layer. The intermediate metal layer formed by the centrifugal effect would play a role in balancing the residual stress of each layer and giving high resistance against thermal and mechanical shocks.
The outline of the recent R&D on the centrifugal-thermit process and the mechanical properties of the obtained ceramic lined pipes will be described mainly by taking into consideration a role of the intermediate metal layer in balancing the bonding between ceramic and metal layers.

EN 9 16.40

INFLUENCE OF MACHINING ON THE STRENGTH OF HOT-PRESSED SILICON NITRIDE,
A.W.J.J. Gallee*; M. Nakamura; E. Nagy, D. McGarry and S.D. Peteves, Hoogovens Ijmuiden, 1970 GA Ijmuiden, The Netherlands; GIRI Nagoya, Nagoya 462, Japan; Inst. of Advanced Materials, JRC Petten, 1755 ZG Petten, The Netherlands

Machining techniques for advanced ceramics have become increasingly important. To a certain extent a large number of potential applications depends upon the development of efficient, economical and reliable machining processes for these ceramics.
An extensive study has been conducted to determine the effects of cost-effective machining on the strength of hot-pressed Si_3N_4. The creep-feed grinding method was adopted and several machining parameters, including diamond wheel specification and preparation were studied; the grinding forces were also measured during machining. The roles of the machining variables were evaluated on the basis of statistical flexural strength data, fractography and scanning electron microscope observations. The results have been correlated to the machining-induced damage and surface flaws. Based on these results the optimal grinding conditions have been assessed.

ENGINEERING CERAMICS : ANALYSIS OF STRESSES

Tuesday 20th June; 09.00 - 11.00 — Chairman : K. Bär (FRG) — Room : 0.2

EN 10 09.00

X-RAY STRESS DETERMINATION IN ENGINEERING CERAMICS AND CERAMIC-METAL-COMPOUNDS, B. Eigenmann*, B. Scholtes and E. Macherauch,
Institut für Werkstoffkunde I, University of Karlsruhe (TH), Postfach 6980, D-7500 Karlsruhe, FRG

In order to achieve an improvement of the behaviour of technical parts during loading, often ceramics or other hard materials are combined with metals. In this way, high resistance against abrasive wear and considerable strength at high temperatures can be realized together with a sufficient ductility and formability. The materials combinations can be achieved in various ways. In all cases, however, residual stresses occur which are balanced between the individual components. X-ray stress determination has proved to be a reliable method to determine these residual stress states. For the interpretation of X-ray residual stress measurements, one has to distinguish between single-phase materials, multiphase materials ans composites in which solid ceramic parts are joined with metallic components. Typical residual stress destributions in ceramics and ceramic-metal composites will be presented and the influence of residual stresses on the behaviour of materials and components will be discussed.

EN 11 09.20

DETERMINATION OF RESIDUAL STRESSES CAUSED BY GRINDING OF SILICON NITRIDE CERAMICS,
T. Pradell*, P. Glaude, S.D. Peteves; and A.W.J.J. Gallee, Inst. of Advanced Materials, JRC Petten, 1755 ZG Petten, The Netherlands; Hoogovens Ijmuiden, 1970 GA Ijmuiden, Netherlands

The mechanical properties of ceramics are extremely sensitive to surface conditions more than any other class of structural materials. As a result, the useful strengths of these materials are higly affected by surface treatments, such as post-processing machining, which generate a residual stress layer at the surface.
The residual stresses introduced during grinding of ceramics and how these relate to strength is the purpose of the present investigation. An x-ray diffraction technique has been developed for the estimate of residual stresses on the hot-pressed Si_3N_4 surface prepared with several machining routes. The appropriate x-ray elastic constants of the silicon nitride were measured, and the magnitude and depth of the surface stresses, which were all compressive, were estimated. First results on the influence of surface grinding introduced residual stresses on the flexural strength of silicon nitride are presented. These are discussed with regard to the effect of the compressive stress layer on the propagation of surface cracks.

EN 12 09.40

R-CURVE BEHAVIOR AND CRACK SYSTEMS DEVELOPMENT IN DISPERSED-PRESSURE-ZONE CERAMICS, E. Lutz*, M.V.Swain+, and N. Claussen,
Technische Universität Hamburg-Harburg, Arbeitsbereich Technische Keramik, D-2100 Hamburg 90, Federal Republic of Germany,
+CSIRO, Melbourne, Australia.

A microstructural design concept is presented in which dispersed-pressure zones on mechanical loading, generate complex crack systems. As a consequence, an unusual R-curve behavior is exhibited leading to improved thermal shock resistance. The type of R-curve can be controlled by the magnitude of stresses developed within and around the spherical zones. This magnitude depends on composition (essentially volume fraction of monoclinic ZrO_2), zone size and volume fraction of pressure zones. The crack systems developed ahead of the main crack are analyzed using a dye-penetration technique and correlated to the mechanical behavior of the composites. Under certain stress conditions, a crack-branching chain reaction takes place resulting in a concave-up R-curve. The respective composites based on 2Y- and 3Y-TZP exhibit a quasi-plastic deformation behavior with little strength degradation after severe thermal shocks.

EN 13 10.00

EXPERIMENTAL INFLUENCES ON THE R-CURVE BEHAVIOUR OF ALUMINA
K.K.O. Bär*, G. Kleist, R. Spelthann
Institut für Reaktorwerkstoffe, KFA-Jülich GmbH, Postfach 19 13, D-5170 Jülich

A close inspection of published experimental data on R-curve behaviour showed that measured R-curves might be influenced by experimental parameters and applied evaluation method. The material inherent causes for enhanced crack resistance are related to the microstructure, to second phases and to residual stresses. It was felt necessary therefore to perform specially designed fracture mechanics experiments with controlled crack growth using three and four point bending as well as DCB-specimens. An alumina grade of high purity, with low glass phase content, fair density and a mean grain size of about 20 um was used. Specimens of different sizes, heat treated and protected against moisture by silicon oil, where mechanically tested at room temperature while been observed by means of a high resolution microscope. Thus, the measurements values of load P, load displacement u and crack growth a are correlated from controlled experiments with constant u, nearly constant crack velocity a and input rate of deformation energy $U = \partial/\partial t \left(\int P(u)du \right)$ The results are discussed taking into account available information on the microstructure and on microcracks as well as on time dependent effects which were observed in the loading experiments.

EN 14 10.20

INVESTIGATION OF LOAD INDUCED MICROCRACKS IN ALUMINA WITH R-CURVE BEHAVIOUR
E. Babilon*, K.K.O. Bär; G. Kleist
Institut für Reaktorwerkstoffe, KFA-Jülich GmbH, Postfach 19 13, D-5170 Jülich

Some ceramics such as alumina show increasing crackresistance with crack growth (R-curve-behaviour). Explanations refer to energy dissipation effects at the cracktip and in the wake region. This presentation gives results of small angle X-ray scattering (SAXS) experiments on SENB- and DCB-specimens with evidence that stress induced mikrocracks build up a microcrack zone on both sides of a macrocrack. In addition, it is shown that the lateral size of the cracked zone increases with decreasing crack propagation velocity up to 2 x 300 um for DCB-specimens. The preferred orientation of the microcracks is within an angular sector of about 40° with respect to the macrocrack direction. Acoustic emission analysis on DCB-specimens, while being loaded to stress levels investigations indicate the generation of microcracks at the notch root. In situ loading of DCB specimen with alternative SEM- or SAXS-observations give some further insight into the nucleation and growth of microcrack regions.

EN 15 10.40

INFLUENCE OF MAGNESIA ON MICRO-FRACTURE AND R-CURVE BEHAVIOR OF ALUMINA

G. Mundry*
Lehrstuhl für Werkstoffwissenschaften, Universität Dortmund;

R.W. Steinbrech
Kernforschungsanlage Jülich GmbH, F.R.G.

Aluminas sintered with various additions of MgO (0.02 - 2.02 wt %) were studied in SENB fracture tests under conditions of controlled slow crack growth. With increasing MgO content, the mode of microfracture changed sharply from trans- to intergranular and then gradually went back to partially transgranular. The R-curve behavior, the increase in crack resistance with increasing crack extension, was most pronounced for specimens exhibiting pure intergranular fracture and the highest crack resistance was found for alumina containing $\sim$0.05 % wt MgO. The microstructural aspects of this result are discussed.

EN 16 15.00

CORROSION OF ALUMINA IN ACIDS

W. Genthe*, H. Hausner
Institut für Nichtmetallische Werkstoffe
Technische Universität Berlin, FRG

In general ceramics have a high resistance against chemical attack. The corrosion resistance of aluminum oxide in various acids has been investigated. Alumina samples have been prepared from high purity aluminum oxide with different amounts of additional oxides. The sintered material has been leached up to temperatures of 230 °C at varying time intervals. The metal content of the leaching solutions has been determined by ICP-AES and the sintered samples were investigated by REM.
It could be shown that the attack occurs preferentially at the grain boundaries. Sometimes the reaction zone extents very deep into the material so that density and mechanical properties decrease significantly. Obviously cracks and open porosity accelerate this process.
The results of the corrosion experiments of the alumina compositions were compared with those of commercially avaible aluminas, hot-pressed materials and single crystals.

EN 17 15.20

Interphases in PVD-coated-TiN/steel system,
L. De Schepper*, L. Stals*, M. Van Stappen**, J.P. Celis***, J.R. Roos***
* Materials Physics Dept., L.U.C., 3610 Diepenbeek (Belgium)
** WTCM, Division Surface Treatment, 3610 Diepenbeek (Belgium)
*** Dept. MTM, Katholieke Universiteit Leuven, 3030 Heverlee (Belgium)

AISI 304 and ASP 23 coupons have been coated in a Balzers industrial size triode ion plating installation. The coatings deposited are either a TiN layer or a TiN layer on a Ti-intermediate layer. A transmission electron microscope investigation allowed to describe the growth mode of the initial TiN layer on AISO 304 and ASP 23 substrate materials. Further on, the effect of this interphase growth mode could be related to the adhesion of the PVD TiN layer on the substrate. In that respect morphology, crystallographic orientation and behaviour during scratch tests were investigated.

EN 18 15.40

A.T.J. Verbeek*, J.M. Houben,
J.A. Klostermann

Adhesion and ductility of Plasma Sprayed Thermal Barrier Coatings.

A new ring test method for testing the adhesion and the ductility of ceramic coatings is applied on ZrO_2- Y_2O_3 thermal barrier coatings.
Process conditions of plasma spraying were varied in order to obtain different types of structures, porosity and internal stresses. Stresses were calculated by final element analysis. The failure process during loading was analysed with an advanced accoustic emission technique. The results were correlated with observations of developing crack patterns. On the basis of the results an optimized plasma spraying process can be indicated.

Eindhoven Technical University
Den Dolech 2, 5612 AZ Eindhoven, Holland

EN 19 16.00

THE MECHANICAL AND CORROSION PROPERTIES OF THIN FILMS, DEPOSITED BY MOCVD.

R.W.J. Morssinkhof*, T. Fransen, M.M.D. Heusinkveld and P.J. Gellings,
Laboratory of Inorganic Chemistry, Material Science and Catalysis,
University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

The rate of attack of high temperature alloys in sulphur and oxygen containing atmospheres at temperatures of 400 to 650 °C is often very large. In many cases it is probable that other metals or alloys, with the required mechanical properties, are not resistant to these types of atmospheres. This means that under certain conditions non-metallic materials can be considered either in massive form or as a protective layer on metals. As far as this last possibility is concerned superficially applied Al_2O_3 proves to enhance the corrosion resistance very well.
Metal Organic Chemical Vapor Deposition (MOCVD) was used to apply thin Al_2O_3 films on Incoloy 800H and AISI 304. With this technique coatings can be made by varying the process parameters which influence the properties of the films. The most important parameters are the temperature and the gas phase concentration of the reactive compound. The influence of the preparation method on the mechanical and corrosion properties will be discussed. The corrosion properties of the films were measured in atmospheres containing oxygen and sulfur by means of thermogravimetry. The sulphur partial pressure was about 10^{-9} atm. The mechanical properties were tested by constant strain rate experiments (CER). Coatings were examined by optical microscopy, SEM/EDX, XPS and SAM. The properties turned ou to be dependent on the process parameters. The optimalization of the coatings regarding the corrosion and mechanical properties is discussed.

EN 20 16.20

MODIFICATION OF CERAMIC MEMBRANES BY CVD AND EVD FOR CASSEPARATION, CATALYSIS AND SOFC APPLICATION
Y.S. Lin, L.G.J. de Haart, K.J. de Vries, A.J. Burggraaf; Univ. of Twente, P.O.BOX 217, 7500AE, Enschede, The Netherlands.

In this contribution we present results of the mathematical modelling and of the deposition parameters(rate,microstructure, composition homogeneity, spreading extend) of a ceramic oxide layer onto the inner pore walls of a porous ceramic membrane by means of a modified CVD technique. In this technique the ceramic layer is formed as product of the reaction of two gaseous reactants each of which was introduced from an opposite side of the membrane. Modified porous ceramic membranes are optimized for gasseparation and catalysis.
Continuation of the above deposition leads to pore closure and interruption of the deposition reaction of the ceramic product. However in the case of mixed, i.e. ionic and electronic,conductivity of the plug which has led to pore closure layer growth continues. Thus very thin ceramic layer composites can be formed. This is a new development that is also of importance for optimization of ceramic electrochemical reactors as e.g. solid oxide fuel cells (SOFC).

EN 21 16.40

Chemical and mechanical characterisation of W-C:H amorphous layers. W.v. Duyn, B. van Lochem. Philips PMF, P.O. box 218, 5600 MD Eindhoven.
W-C:H layers are made on steel by reactive magnetron sputtering in a gas mixture of argon and acetylene. The chemical analysis was carried out by pyrolysis, XRF, and RBS. This shows that the carbon layers contain 5-10 % W, embedded in a polymer-like matrix. If the W content is higher, the film is carbide-like. The mechanical characterisation shows that the hardness is decreasing, when the carbon content is increasing. The load bearing capacity, as measured with a standard scratch tester, is increasing when the carbon content is increasing. The friction coefficients of these coatings sliding against steel are extremely low. The W-C:H coatings can be applied on cutting tools and cold-forming tools and on bearings where an oil-free state is required.

ENGINEERING CERAMICS : CORROSION AND COATINGS

Wednesday 21st June; 10.00 - 12.00 Chairman : J. Schoonmen (The Netherlands) Room : 0.2

EN 22 10.00

MECHANICAL PROPERTIES AND OXIDATION BEHAVIOUR OF HOT-ISOSTATIC-PRESSED TITANIUM NITRIDE
L. Thémelin, M. Desmaison-Brut ; M. Boncoeur, F. Valin
Laboratoire de Céramiques Nouvelles, CNRS UA 320, Université de Limoges, FRANCE
Commissariat à l'Energie Atomique, CEN/Saclay, FRANCE

Dense titanium nitride has been obtained by Hot-Isostatic pressing at 1600°C and under various pressures.
Improvment was developed by properties optimization through pressure variation. Microhardness evolution, flexural strength, weibull modulus, thermal shock resistance are analyzed and related to the porosity.
Increasing pressure treatment increases strength and microhardness whereas fracture thoughness and grains size remained unchanged.
Fractographs revealed that fracture originated mainly on the tensile face at a grain boundary, generally in regions where biggest grains intersect the surface. In some cases, strength is controlled by the largest microstructural defects near the surface, i.e. pores or titanium inclusions.
The oxidation of titanium nitride in oxygen between 800 and 1400°C is characterized by a parabolic general shape of the kinetic curves. A few undulations may be associated with the sintering of the powdered rutile 'scale which forms a compact outer crust.
By applying a parabolic oxidation model involving a diffusion regime through a scale of variable thickness it has been found that the activation energy of the limiting process was 157 kJ/mole.

EN 23 10.20

INFLUENCE OF HEAT TREATMENTS UNDER OXIDIZING ATMOSPHERES ON THE MECHANICAL PROPERTIES OF DIFFERENT RBSN MATERIALS

P. BELAIR and J. DESMAISON
Laboratoire de Céramiques Nouvelles, UA CNRS 320, 123, Av. A. Thomas, 87060 LIMOGES Cédex, FRANCE
Y. BIGAY
Céramiques Techniques Desmarquest, 2, Av. A. Einstein, 78190 TRAPPES, FRANCE

This work is concerned with the study of four reaction bonded silicon nitrides (RBSN) prepared (by "Céramiques Techniques Desmarquest", France) using different shaping techniques, silicon powders and sintering aids.
An exhaustive characterization of the mechanical behaviour of these materials in correlation with their microstructural properties has been conducted.
In order to strengthen the materials different heat treatments under oxidizing atmospheres have been tested. The results show that it is possible to prevent the internal oxidation usually observed, between 900-1200°C, for these types of products by a "flash oxidation" treatment conducted at 1400°C. In addition, heat treatments at 900°C result in an increase of above 45% of the room temperature strength and in the disparition of the decrease of σ_R traditionally observed near 800°C.

EN 24 10.40

Chromiumcarbide: An oxidation and wear-resistant CVD coating; G.van der Kooi, P. van Rooij; Philips PMF; P.O.box 218; 5600 MD Eindhoven.
Many tools in the glass and electronics industrie are used at higher temperatures where TiN and TiC cannot be used as an effective coating. CrxCy however can be used still at 900 centigrade. The chromium-carbide proces differs from other CVD processes because of the in situ production of CrCl2.
The composition of the chromium carbide produced, has been characterized as one of the following: Cr2C, Cr3C2, Cr7C3, Cr23C6, depending on the process parameters and the substrate composition. The properties of the coatings can be compared with TiN and TiC. Special attention has been given to the oxidation resistance of chromiumcarbide, titaniumnitride, titaniumcarbide and aluminumoxide. The chromiumcarbide coating on a cemented carbide substrate retains its colour and no weight increase or decrease was measured after the oxidation test.

EN 25 11.00

CERTAIN ASPECTS OF THE HIGH TEMPERATURE ENVIRONMENTAL (S_2/O_2) DEGRADATION OF SILICON NITRIDES; J S Gray* P K Datta; C Gill[1].

Surface Eng. Research Group, Newcastle upon Tyne Polytechnic, NE18ST, UK.

[1]Dept. of Mech. & Mfg. Systems, Sunderland Polytechnic, SR27EE, UK.

The high temperature stability of silicon nitride ceramics in aggressive (S_2/O_2) gas turbine and fossil-fuel gasifier environments is significantly dependent upon the formation and survival of a defect-free silica/silicate film. Changes in the morphology of this pellicle, its protectiveness and subsequent corrosion kinetics might be anticipated from the concentration of impurities/additives and the incorporation of environmentally-derived sulphur species within the scale. Furthermore remnant intergranular vitreous phases may restrict high temperature durability by providing conduits for rapid sulphidation/oxidation. This paper considers these aspects and reports certain residual mechanical properties data following the exposure of silicon nitrides to S_2/O_2 ambients at elevated temperatures. Degradation mechanisms are proposed.

EN 26 11.20

OXIDATION OF Si_3N_4 IN CRACKS, K. G. Nickel*, G. Schneider, Z. Fu and G. Petzow,
Max-Planck-Institute für Metallforschung, PML, D-7000 Stuttgart 80, FRG

Oxidation experiments on Y,Al doted Si_3N_4 have been carried out. The specimen investigated were notched and pretreated by a thermal shock to initiate a crack of several mm length.
Subsequently the oxidation experiments were carried out in air under differing loading conditions:
a) isothermal
b) steady state thermal gradients
c) fast thermal cycling.
There are major differences in the rate of oxidation on the free surface of the specimen and on the crack surface depending on the crack width : oxidation scales in the cracks are much thinner than those on the free surface and exhibit a different structure.
The growth of oxidation scales is also strongly dependent on the stress mode (dynamic/static). The differences are shown and discussed in the light of kinetic and thermodynamic calculations.

EN 27 11.40

CVD OF TiB_2 ON TiN
Johanna G.M. Becht*, Paul J. van der Put Joop Schoonman, Delft University of Technology, Laboratory for Inorganic Chemistry, Delft, The Netherlands.

TiB_2 is a very interesting material: it is both corrosion and erosion resistant. However, the deposition of TiB2 with CVD using $TiCl_4$, BBr_3 and H_2 on steel is hampered by the occurence of destructive boronation of the substrate. The application of a diffusion barrier can solve this problem. TiN, a wear resistant material itself, is a good candidate: it is used in the electronic industry as a diffusion barrier, but under much milder boronation conditions. The applicability of TiN as a diffusion barrier under CVD conditions has been established experimentally, using BBr_3 and H_2 at 1000 °C. After 3 hours only a very slight boronation of the substrate has been observed. Similar TiN coatings have been used subsequently as a substrate for the deposition of TiB_2. Depending on the deposition conditions TiB_2 shows a nodular growth or the formation of a closed, smooth film.

EN 28 10.00

EFFECT OF SIC-WHISKER CHARACTERISTICS ON THE INTERFACE AND THE MECHANICAL PROPERTIES OF SILICON NITRIDE MATRIX COMPOSITES

W.Braue*, A.Hölscher, B.Saruhan and G.Ziegler, Deutsche Forschungsanstalt für Luft- und Raumfahrt (DLR), Institut für Werkstoff-Forschung, D-5000 Köln 90, FRG.

Improvement in mechanical properties of silicon nitride through SiC-whisker additions is considered to be potentially possible. Additions of 20 wt.% SiC-whiskers to silicon nitride, in the present study, result in an increase of the fracture toughness by about 30 %. By varying the SiC-whisker type (morphology and chemical composition) no change in this value of fracture toughness was observed. However, the strength of the composites seems to be dependent on the whisker characteristics. A better understanding of the reinforcement mechanisms can be brought about by determining the interfacial relations. Therefore, in the present study, a comprehensive transmission electron microscopy investigation was conducted in order to study the interface and to define the relation between the interfacial characteristics and the mechanical properties.

EN 29 10.20

HIGH TEMPERATURE PROPERTIES OF PRESSURELESS SINTERED SiC-WHISKER REINFORCED Si_3N_4

A. Lutsch*, M.J. Hoffmann, R. Danzer and G. Petzow, Max-Planck-Institut für Metallforschung, PML, D-7000 Stuttgart 80, FRG

Si_3N_4/SiC-composites containing 10 vol.% SiC-whiskers and 15 wt.% sintering additives were pressureless sintered and post-HIPed. The fracture toughness and the strength were measured up to 1570 K. Particular attention was given to an investigation of the creep behaviour. The stress exponent and the activation energy were determined. Microstructural changes were observed using SEM and TEM as an additional means of clarifying the dominant creep mechanism.

The properties of the composite were compared with those of the unreinforced matrix material. The monolithic material was shown to be superior to the composite, a finding which could be explained in terms of the microstructural observations.

EN 30 10.40

Al_2O_3-MULTILAYER COMPOSITES REINFORCED WITH ORIENTATED SiC PLATELETS

T. Claassen* and N. Claussen,
Technische Universität Hamburg-Harburg, Arbeitsbereich Technische Keramik, D-2100 Hamburg 90, Federal Republic of Germany.

Composites of Al_2O_3 and SiC platelets with preferred orientation have been fabricated by tape casting. The green tapes were cut and laminated to bodies consisting of 15 to 30 layers. After burn-out of the organic components, the multilayer composites were sintered in Ar to closed porosity and then HIPed. The platelet orientation was determined by an X-ray texture method. The mechanical properties of multilayer samples were examined both normal and parallel to the basal plane of the SiC platelets. Fracture toughness and 4-point bend strength were compared to those of composites of identical composition and sinter/HIP history, however with random SiC-platelet orientation. These samples were prepared by cold isostatic compaction. Fracture behavior and toughening mechanisms are discussed.

EN 31 11.00

Y-TZP AND Ce-TZP REINFORCED WITH Al_2O_3 FIBERS AND PLATELETS

K.-H. Heussner and N. Claussen*, Technische Universität Hamburg-Harburg, Arbeitsbereich Technische Keramik, D-2100 Hamburg 90, Federal Republic of Germany.

Composites of Yttria- and Ceria-stabilized tetragonal Zirconia polycrystels (Y-TZP, Ce-TZP) with up to 20 vol % Alumina short fibers or Alumina platelets were fabricated by hot isostatic pressing. Among various conditions, also HIPing in a non-reducing atmosphere ("white HIPing") was carried out. Microstructure and mechanical properties of these materials were investigated. The fracture toughness of Y-TZP, measured by the chevron-notch-bending technique at room temperature, was significantly increased by addition of short fibers or platelets, e.g., K_{Ic} of 2Y-TZP from 6.3 MPa$\sqrt{m}$ to 9.5 MPa$\sqrt{m}$ with 10 vol % Al_2O_3 platelets. The 4-point-bending strength, however, decreased from 1100 MPa to 735 MPa in this composite. Such decrease in strength was generally observed in all reinforced Y-TZP material. In contrast to Y-TZP composites, reinforced Ce-TZP exhibited a slight increase in strength and a decrease in fracture toughness when compared to the non-reinforced matrix.

EN 32 11.20

ON THE CREEP BEHAVIOR OF SILICON-CARBIDE WHISKER REINFORCED ALUMINA, K. Y. Donaldson, A. Venkateswaran, D. P. H. Hasselman*, Virginia Polytechnic Institute, Blacksburg, Virginia, 24061 USA; J. F. Rhodes, Advanced Composite Materials Corporation, Greer, South Carolina, 29651 USA.

The creep behavior of SiC-whisker reinforced alumina at 1500°C exhibited typical primary, secondary and tertiary creep. The initial creep rate in the primary regime exhibited a stress exponent of 1.59, typical for polycrystalline alumina. The stress exponent for secondary (steady-state) creep was found to have a value of 2.88. The presence of the whiskers appeared to suppress cavitation or other damage, thereby eliminating any contribution from elastic creep by crack growth or crack-enhanced creep.

An analysis of these results suggested that stress-dependent sliding at the SiC-alumina interface and/or stress-dependent whisker fracture with associated decrease in the average value of aspect ratio appear to be the most likely mechanisms responsible for the high value of the apparent stress exponent in the secondary regime.

EN 33 11.40

PLASTIC DEFORMATION OF Al_2O_3/ZrO_2/SiC CERAMICS.
R. Duclos*, J. Crampon ; B. Cales+,
Université de Lille 1,59655 Villeneuve d'Ascq, France
+C.T.Desmarquest, 78190 Trappes, France

Al_2O_3/ZrO_2 ceramics reinforced with SiC whiskers have been deformed in compression in air between 1250 and 1400°C in a stress range varying from 40 to 300 MPa. Strains up to 25% have been obtained. The main features of deformation are:
1)the existence of a threshold stress, depending on temperature and varying from 50-60 MPa at 1250°C to 30 MPa at 1400°C.
2)the presence of cavities, the density of which is depending upon deformation conditions, generally lengthened in a parallel direction with the compression axis.
The stress exponent value of 1.7, the activation energy of 800-900 kJ/mol and the absence of dislocations inside grains are in agreement with a deformation mechanism where grain boundary sliding is partly diffusion and/or interface controlled and also partly nonaccommodated.
The influence of whiskers on the mechanical properties has been analysed relative to the mechanical behaviour of the Al_2O_3/ZrO_2 matrix.

EN 34 12.00

EFFECT OF TEMPERATURE ON TRIBOLOGICAL PROPERTIES OF Al_2O_3 AND SiC CERAMICS.
P.Boch*,G.Kapelski and F.Platon.
E.N.S.C.I., 87065 Limoges cedex,(France).

This study was devoted to the understanding of the influence of composition and microstructural characteristics on the tribological properties of Al_2O_3 and SiC ceramics, as a function of temperature.
The experiments were performed using a ball-on-disc high-temperature tribometer. They were complemented by SEM observations. The tribological tests concerned both the friction properties and the wear properties. The parameters under study were:
- pressure and velocity.
- temperature (up to 1000°C).
- atmosphere (dry air and air with a controlled humidity).
The experimental results were discussed, using the "third-body" theory which focuses on the role of debris.Therefore,a particular attention was paid to the characterisation of the layer of debris, and on its rheological properties.The microcracking of the wear track appeared to be the main concern. Data suggest that engineering ceramics require the use of solid lubricants for high temperature tribological applications.

EN 35 15.00

TOUGHENING MECHANISMS IN HEAVY-DUTY CERAMICS, W.M. Müller, Hermann-Föttinger-Institut für Thermo- und Fluiddynamik, TU-Berlin, 1000 Berlin 12, Federal Republic of Germany.

From the experimental work of Claussen, Rühle, Hubner and others it is well-known that the fracture toughness of ceramic materials (e.g. Al_2O_3, SiC) can be increased considerably by adding Zirconia and/or SiC-whiskers/fibres.

The various toughening mechanisms (transformation toughening, crack deflection, crack bridging, pull-out) are investigated quantitatively. To that end the interaction between a Griffith crack, a ZrO_2- particle and a whisker is studied numerically.

The stress intensity factors and the corresponding increase in toughness are calculated using the methods of linear elasticity: integral equation technique, Laurent series expansion and FEM.

All results are visualized in a 16 mm computer-animated film .

EN 36 15.20

SENB TOUGHNESS MEASUREMENT OF OXIDE CERAMICS

J. Wang* and R. Stevens
School of Materials, University of Leeds, Leeds, LS2 9JT, U.K.

A range of oxide ceramics, including fine and coarse grained aluminas, transformation toughened ceramics and microcracked ceramics, have been measured for SENB toughness. It is found that the SENB toughness is dependent or independent of notch width, depending on the microstructure. A discussion is made of the relationship between SENB value and the toughening mechanisms. The "dynamic" toughening mechanisms, such as transformation toughening, give a strong SENB toughness dependence on the notch width.

EN 37 15.40

SUBCRITICAL GROWTH OF AS-INDENTED PYRAMID AND KNOOP CRACKS IN SODA-LIME GLASS, Mitsuo Yoda, College of Engineering, Nihon University, Koriyama, 963, Japan.

The indentation cracks closely resemble the natural contact damage that glass surfaces experience during surface finishing and service. Subcritical crack growth data on soda-lime glass subjected to sustained bend stress in water were obtained using the small pyramid and Knoop indentation cracks. To compare the growth of large cracks, the compact type (CT) specimens were also used. The stress intensity factor K_I-crack velocity V curves for the indentation cracks show that there is apparently a small crack effect. The crack velocity is initially high, decreases and thereafter increases with K_I. In addition, the slope of these curves is smaller than that for the CT specimens. However, the annealed indentation crack shows the same trend of growth as that for the CT specimens. The effective stress intensity factor K_{Ieff} was obtained by adding a term describing the state of residual stress after indentation and used to explain this anomalous growth behavior of the as-indented pyramid and Knoop cracks.

EN 38 16.00

ITERATIVE STRENGTH DEVELOPMENT OF SLIPCAST Si_3N_4

K. Linde*, M. Persson, R. Pompe, S. Karlsson and R. Carlsson, Swedish Institute for Silicate Research, Box 5403, 402 29 Göteborg, Sweden

The mechanical properties of four batches of slip cast Si_3N_4 were evaluated. Iterative development of the powder processing, slip casting and sintering techniques led to an increase in average strength at room temperature from 570 MPa for the 1st batch to 790 for the 4th.

Fractographic studies showed how the type and size of fracture origins changed with the fracture strength. For high strength-specimens (>800 MPa) the fractures mainly originated from Si_3N_4-agglomerates (20-70 μm), but also from spherical pores. None of the fracture causing defects were smaller than 20 μm. Elimination of defects larger than 50 μm would probably be sufficient to give strength-values above 800 MPa to all the specimens.

EN 39 16.20

EFFECT OF PRE AND POST-DENSIFICATION HEAT TREATMENTS ON MICROSTRUCTURE DEVELOPMENT AND STRENGTH OF HPSN, G. Wroblewska* and H. Hübner, Technische Universität Hamburg-Harburg, 2100 Hamburg 90

In order to optimize the microstructure of HPSN, the temperature-time cycle during densification was varied using three different temperature routes, i.e. (1) "normal" hot-pressing at 1800°C and 30 MPa during 1 hour, (2) in-situ heat treatment at 1690°C before hot-pressing and (3) post-densification thermal treatment at 1300°C. Using route 2, a more homogeneous material was obtained than by normal hot-pressing. The grain size distribution was considerably smaller and the strength was somewhat higher, demonstrating the effectiveness of the α→β phase transformation prior to densification. Route 3 resulted in a material of exactly the same mean grain size and distribution as was obtained by normal hot-pressing. However, additional crystalline phases appeared in the microstructure which were supposed to form from glass phase residues. Addionally, the distinct strength increase observed was taken as a further evidence of the occurrence of in-situ crystallization of the intragranular amorphous phase.

EN 40 16.40

STRUCTURAL PROPERTIES OF CERAMIC ALUMINA MICROFILTRATION MEMBRANES AS A FUNCTION OF SINTERING TIME AND TEMPERATURE

R.A. Terpstra[1]*, H. Visser[2], A.J.G. Engel[1] and H.J. Veringa[1]

[1] Netherlands Energy Research Foundation, ECN P.O. Box 1, 1755 ZG PETTEN, the Netherlands

[2] Hoogovens Groep B.V., P.O. Box 10.000, 1970 CA IJMUIDEN, the Netherlands

At our institute (ECN) we develop ceramic microfiltration (MF) membranes in close cooperation with Hoogovens Industrial Ceramics. Ceramic membranes possess some superior mechanical, thermal and chemical properties over the more conventional polymeric membranes. They are therefore expected to penetrate the already existing membrane market, but also new applications for instance at high temperature are foreseen. The mechanical strength of our membrane system is provided by a macroporous support tube which is extruded using a water based paste. After careful drying and sintering, the tube is coated with an aqueous alumina suspension. This results after drying and sintering in a smooth thin microfiltration layer. The membrane fabrication route will be presented and the results will be discussed of a study on the influence of the sintering time and temperature on the pore properties of the system, the water permeability, the burst pressure and the MFlayer-substrate bonding.

ENGINEERING CERAMICS : CREEP

Friday 23rd June; 10.20 - 12.40 — Chairman : H. Hübner (FRG) — Room : 0.2

EN 41 10.20

MICROSTRUCTURE AND CREEP OF Si_3N_4 COMPOSITES WITH TiN PARTICLES

J.Crampon*, R.Duclos, B.Cales+,
Université de Lille 1,59655 Villeneuve d'Ascq,FRANCE.
+C.T.Desmarquest,78190 Trappes,FRANCE.

The compression creep behaviour in air of Silicon Nitride sintered with the aid of Y_2O_3 and Al_2O_3, and containing TiN particles was studied in the temperature range T=1260°C-1340°C and stress range 100-300 MPa. The volume fraction Φ of TiN particles was varied from 0 to 40 vol % and two TiN particle sizes 1μm and 2.5 μm were studied.Strain rates versus stress were analysed to determine the stress exponent n ($\dot{\varepsilon}=A\sigma^n$). Changes in the microstructure were studied from observations made by T.E.M of thin foils cutted from samples before and after creep.

The dominant creep mechanism of the pure matrix was viscous creep (n=1) up to 1300°C and 200 MPa . At higher stress and temperature (300 MPa,1340°C) cavitation in the intergranular glassy phase produces an increasing stress exponent up to 1.5 .

The effect of the TiN addition on the creep behavior was marked by a decrease of the creep strength with increasing volume fraction of TiN and decreasing particle size of TiN. In the same way the creep rate was affected by the TiN addition and increased as the ratio Φ/d, that which can be accounted for in terms of the total grain-boundary area of TiN particles.

During creep experiments the grain boundary phase crystallized in part and cracks formation was observed mainly along the TiN-Silicon Nitride interfaces.

EN 42 10.40

CREEP CAVITY FORMATION IN PURE AND VITREOUS BONDED ALUMINA, J. Stark* and H. Hübner, Technische Universität Hamburg-Harburg, 2100 Hamburg 90, FRG

The effect of stress and strain on creep cavity formation was studied in two different types of alumina, a vitreous bonded material and an essentially pure material, by measuring the density changes induced by creep deformation in bending. Additionally, small angle neutron scattering (SANS) was used to get informations about the size and density of the cavities in dependence of strain. For both materials it was found that the creep porosity P increased linearly with creep strain ε. Thus, a creep cavitation sensitivity $\omega=\Delta P/\Delta\varepsilon$ could be defined which differed markedly for the two aluminas at same stress levels. The ω value of the vitreous bonded material was about 20 times that of the pure material, demonstrating the proneness of the glass phase to creep damage formation. SANS results and electron microscopy observations revealed that in the two-phase material the cavitation process was dominated by the nucleation of new pores, in contrast to the glass free material where cavitation was controlled by the growth of existing pores.

EN 43 11.00

CYCLIC FATIGUE OF SILICON NITRIDE

A.-P. Nikkilä* and T.A. Mäntylä, Tampere University of Technology, Institute of Materials Science, P.O. Box 527, SF-33101 Tampere, Finland.

Cyclic fatigue properties of silicon nitride were studied. To avoid the difficulties of fatigue test of brittle ceramics in pull-push test, a special 4-point bending jig was constructed. The tests were made at room temperature. Effects of different loading types were studied using three different fatigue test modes: 1) sinusoidal R=-1 (tension-compression), 2) sinusoidal R=0 (tension) and 3) positive half sinusoidal R=0 (tension); negative part of the loading cycle is cut off. Theoretical crack propagation differences of three fatigue modes were calculated and compared to measured values. Results will be presented and discussed.

EN 44 11.20

CREEP OF Y_2O_3 FULLY-STABILIZED ZrO_2 SINGLE CRISTALS

J. Martínez*, M. Jinénez, A. Domínguez, R. Márquez; A.H. Heuer+.
Dpto. de Física de la Materia Condensada, Apdo. 1065, Sevilla, Spain.
+ Department of Materials Science, Case Western Reserve University, Cleveland (Ohio), USA.

Fully stabilized cubic ZrO_2 single crystals containing 9.4 mol% of Y_2O_3 oriented for single slip on (001)|110|, have been deformed in compression under nominal stresses betwen 120 and 160MPa, at temperatures between 1300°C and 1550°C and two oxygen partial pressures (PO_2), 0.2 and 10^{-5} atm. The data were analysed using the equation for recovery-controlled creep. The strees exponent is close to 7, the creep rate is PO_2 independent and the activation energy is 7.3± 0.1 eV at 1300°C and 6.2± 0.3 eV betwen 1400°C and 1550°C. These data suggest a change in the mechanism controlling the creep of the fully stabilized ZrO_2.
The dislocation substructure both in the primary (001) and secondary (111) and (100) planes, in the samples deformed have been studied by transmision electron microscopy. Sustantial cross slip and climb of dislocation ocurred during deformation depending in temperature, in agreement with the change in the creep mechanism suggested.

EN 45 11.40

FLOW BEHAVIORS AT HIGH TEMPERATURE OF TETRAGONAL ZIRCONIA POLYCRYSTALS (Y.T.Z.P.)

M. Nauer and C. Carry
Laboratoire de céramique, E.P.F.L.
34, ch. de Bellerive, CH-1007 Lausanne

The aim of this work is to show how some variations in the amount of residual impurities can drastically affect the deformation behavior of TZP materials. Samples with different grain sizes (0.3 to 1.5 µm) have been elaborated from two batches of commercial yttria doped (3% mole) zirconia powders which differ only by their residual impurity contents (0.03 and 0.08% weight). These materials are deformed in tension and in compression between 1250 °C and 1450 °C in creep conditions or in traction conditions. For the same grain size (0.4 µm) strain rates differ by a factor ten (10^{-3}/s to 10^{-4}/s) under 20 MPa at 1350 °C from one batch to the other one and flow stresses at 1450 °C are twice higher (11 MPa to 22 MPa for a $3 10^{-4}$/s strain rate) for the material with the lowest impurity content. The stress exponent n ($\varepsilon \alpha \sigma^n$) decreases from 3 to 1.8 when the grain size increases from 0.3 µm to 0.75 µm. The results are analysed to established correlation between macroscopic flow behaviors and microstructures with special attention on the grain boundary glassy phases. Discussion will be based on superplastic models for materials with or without grain boundary liquid phases.

EN 46 12.00

THE ROLE OF THE INTERGRANULAR GLASSY PHASE IN THE SUPERPLASTIC DEFORMATION OF TZ-3Y ZIRCONIA,

T. Hermansson and G.L. Dunlop, Department of Physics, Chalmers University of Technology, S-412 96 Gothenburg, Sweden.

Superplastic hot-forging has for some time been considered a possible technique for the fabrication of complex shaped oxide-ceramic components. This paper will discuss the role of the secondary phase in the superplastic deformation of yttria stabilized tetragonal zirconia polycrystals (Y-TZP). It has been shown that grain boundary sliding (GBS) is the predominant strain providing mechanism in this material. An interesting question is whether GBS is also strain-rate controlling. Is the sliding itself, lubricated by the amorphous glassy phase, the rate-controlling link in the overall deformation process? Measurements of the creep activation energy give values somewhat higher than the activation energy for interdiffusion of cations, which suggests that some diffusional process may be rate controlling. However, some authors argue that the activation energy for diffusion is much lower when the sample is exposed to stress than for the unloaded state.
To investigate these questions Y-TZP bars have been fabricated with various amounts of intergranular glassy phase and their stress and strain-rate relationships have been compared with the predictions of existing creep models. The microstructures after high temperature deformation have been examined by TEM and SEM.

EN 47 12.20

PLASTIC DEFORMATION OF STABILIZED ZrO_2 SINGLE CRYSTALS BELOW 1000°C

P. Teracher, H. Garem and J. Rabier*
Laboratoire de Métallurgie Physique,
U.A. 131 CNRS
Université de Poitiers
86022 POITIERS

Fully stabilized cubic zirconia (ZrO_2 + 9.4% mol Y_2O_3, ZrO_2 + 14.9% mol CaO) single crystals were deformed in the temperature range 250°C - 600°C at constant strain rate $\dot{\varepsilon} = 2 10^{-4}\ s^{-1}$ in a Griggs apparatus. The compression axis <112> was chosen to favour the (001) [110] glide system. Slip trace analysis confirms the activation of this system ; furthermore cross-slip is evidenced. TEM observations show that the deformation substructures are mainly built with glide loops elongated in the screw direction. {111}<110> glide systems have been also found to be activated. Numerous dipoles resulting from jog dragging by screw dislocations or double cross-slip confirms the occurence of cross-slip at the macroscopic level. These substructures will be discussed as a function of the deformation temperatures.

EN 48 author present: 11.00 - 12.30

EFFECTS OF LAYERS ORIENTATION ON THE CRACK PROPAGATION BEHAVIOUR OF A C-SiC COMPOSITE MATERIAL
M. Gomina, LERMAT-URA 1317, 14032 CAEN Cedex FRANCE

The mechanical behaviour of a laminated 2D-woven composite material made of carbon fibres and SiC matrix was investigated. Fracture mechanics analysis were applied to three point bending specimens to check the crack propagation behaviour using different orientations of the material.

It is shown that depending on the relative orientations of the notch and the layers plane, the failure criterion is the maximum stress in the remaining ligament or the critical stress intensity factor.

In this last case, optical crack length measurements were performed during the loading sequence. These crack lengths were compared to predicted values before using them to work out crack resistance parameters.

EN 49 author present: 11.00 - 12.30

CONTROLLED FRACTURE EXPERIMENTS ON SIC-WHISKER REINFORCED ALUMINA,

C.Plappert*, H.Frei, G.Grathwohl
Institut für Keramik im Maschinenbau, Institut für Werkstoffkunde II, Universität Karlsruhe
Haid- und Neustr. 7, D-7500 Karlsruhe

A miniaturized 4-point bending device is used to study crack propagation in a SiC-whisker reinforced Al2O3/ZrO2-ceramic under simultaneous observation in a light microscope and a scanning electron microscope.

The device is shown to provide a new tool for the investigation of material's behaviour upon loading under various conditions. Crack resistance measurements and their interpretation using photographs of the microstructure under load are presented for modern ceramics.

EN 50 author present: 11.00 - 12.30

SiC WHISKER REINFORCED CERAMIC COMPOSITES
WIA Pei*, ZHOU Wanchun and ZHANG Zinsong
Inst. of Metal Research, Academia Sinica
2-6 Wenhua Road,110015,Shenyang, P.R.China

ABSTRACT
SiC whisker reinforced Si_3N_4,ZTA,TiC and TiB_2 ceramic composites were investigated. It was found that for ZTA-SiCw and TiB_2-SiCw composites both strength and fracture toughness were increased with the SiC whisker loadings; for Si_3N_4-SiCw and TiC-SiCw composites,however, the fracture toughness was increased and the flexure strength was a little decreased by the addition of SiC whiskers. Microstructure and interface of the composites were observed in TEM. And fractography of the composites was analyzed in SEM. The toughening and strengthening mechanism was also discussed.

EN 51 author present: 11.00 - 12.30

MECHANICAL PROPERTIES OF Y_2O_3-ZrO_2-Al_2O_3-SiC-WHISKER COMPOSITES, M. Shiomi,
Tosoh Corporation, Tokyo Research Center,Japan

It is well known that Y_2O_3-ZrO_2-Al_2O_3 compsites have the highest fracture strength, but a lower fracture toughness.
It was tried to increase the fracture toughness by addition of SiC whisker in those composites matrixs. The composite samples which contains 20 wt. % SiC whisker were prepared by hot-pressing under 400 kg/cm^2 in Ar atomosphere at the temperature 1500-1600°C.
The mechanical properties, fracture strength, fracture toughness and hardness, of thus obtained samples were studied.

EN 52 author present: 11.00 - 12.30

MECHANICAL RESPONSE OF SHORT CERAMIC FIBRE PREFORMS

J.C. Longchampt, S. Bengtsson and R. Warren*
Chalmers University of Technology, Göteborg, Sweden

Short alumina fibres are currently used as reinforcement in metal matrix composites. The composites are generally prepared by infiltration of silica-bonded fibre preforms by the molten matrix alloy. Here, the response to compressive loading of such preforms with from 5 to 20 vol.% fibres has been studied.

The preforms exhibit reversible elastic response up to a critical pressure corresponding to the failure of the binder and/or the crushing of fibres. This lies between 0.5 and 2 MPa depending on the binder content, binder strength (determined e.g. by firing temperature) and fibre fraction. Beyond the critical pressure and up to a level between 2 and 3 MPa, the preforms suffer significant, permanent deformation associated with a sharp decrease in average fibre length to about 30 μm. During this stage the preforms attain densities (fibres + binder) of 30-40%, presumably as a result of fibre rearrangement. Beyond this stage, they exhibit a sharply increasing resistance to crushing and permanent deformation, behaving like a powder and with little further reduction in fibre length.

EN 53 author present: 11.00 - 12.30

THERMOMECHANICAL BEHAVIOUR OF A STRUCTURAL FIBROUS COMPOSITE MATERIAL, M. Gomina, P. Fourvel and M.H. Rouillon, LERMAT-URA 1317, 14032 CAEN Cedex FRANCE

We present high temperature measurements and observations performed using a SiC-SiC composite material.

In air, three point bending experiments on unnotched samples showed deep modifications in the Elastic Modulus (E) and the Flexural Strength (σ_R) evolutions as functions of the test temperature. The modifications of these material parameters were corrolated to optical and scanning electron microscopes observations of the crack paths on polished surfaces and of surfaces of rupture, to understand the mechanisms involved in rupture at high temperature.

Potential energy-derived crack propagation resistance was studied using notched specimens of different dimensions as a function of test temperature.

EN 54 author present: 11.00 - 12.30

RBSN COMPOSITES REINFORCED WITH SiC PLATELETS,

R. Janssen* and Nils Claussen,
Technische Universität Hamburg-Harburg, Arbeitsbereich Technische Keramik, D-2100 Hamburg 90, Federal Republic of Germany.

The effect of dispersed SiC-platelets on the sintering behavior and mechanical properties of RBSN-based composites is evaluated. After nitridation, toughening was only observed when liquid-phase forming components were added, whereas the strength was slightly reduced due to the increased flaw size and macropore formation by the large platelets used. Post-densification of SiC-platelet - RBSN composites with sintering additives by gas pressure sintering (GPS) and hot isostatic pressing (HIP) resulted in high-density samples for platelet additions of up to 20 vol %. The observed sintering retardation due to the SiC platelets can be compensated for by prolonged sintering times. Addition of 20 vol % SiC platelets leads to a fracture toughness increase of up to 50 %. The strength reduction is influenced by the volume fraction and size of the platelets. Microstructure-property relationships are discussed.

EN 55 author present: 11.00 - 12.30

Ageing of an Al_2O_3-ZrO_2-SiC_w composite,

R. Molins, N. De Dave, A. Thorel*, ENSMP, Evry, France; B. Calès, Céramiques Techniques Desmarquet, Trappes, France.

This composite belongs to the new generation of high performance materials devoted to thermomechanical applications. Systematic mechanical testing, performed on three point bend specimens up to 1200°C, shows a constant 1000 MPa fracture strength. The aim of this paper is to investigate the behaviour of the microstructure during long term ageing at high temperature and the consequences on the mechanical properties. The three point bending test shows that a heat ageing treatment debases the fracture strength. Microstructural investigations, before and after ageing, using analytical (EDS, EELS) and high resolution transmission electron microscopy, show that during ageing there are changes at the interfaces, especially between the SiC whiskers and the matrix. It can be inferred that it is mainly the interfacial structure which is involved in the decrease of mechanical properties after ageing. Taking into account the physico-chemical informations at an atomic scale, we give an interpretation of the behaviour of the material during high temperature treatment.

EN 56 author present: 11.00 - 12.30

SYNTHESIS AND PROPERTIES OF SiC-Y_2O_3-Al_2O_3 COMPOSITE, M. Omori* and T. Fukuda; K. Nishiyama,
Institute for Materials Research, Tohoku University, Sendai 980, Japan.
Department of Mechanical Engineering, Faculty of Science and Technology, Science University of Tokyo, Noda 278, Japan.

The ceramic-ceramic composites offer the possibility of providing a useful combination of properties which are not available from one material. A high strength composite is fabricated from SiC, Y_2O_3 and Al_2O_3 powders. The composite has not been prepared from SiC and Y_2O_3 powders, whereas two powders can be combined by alumina. Alumina is reduced by SiC near 2000 C. The sintering temperature must be under 2000 C. The sintered body which loses alumina decomposes gradually at room temperature. The Y_2O_3 body has not been viewed as a structural material. In the composite SiC particle is dispersed in the matrix of yttrium oxide. The difference of the thermal expansion of SiC and Y_2O_3 is not large. The thermal schrinkage of the Y_2O_3 matrix is inhibited by the SiC particle of low expansion, then the internal stress slightly remains. The high strength is assumed to arise from the internal stress.

EN 57 author present: 11.00 - 12.30

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF ALUMINA / ZIRCONIA + (Y2O3,CeO2) COMPOSITES, S. Maschio, O. Sbaizero*, S. Meriani.
Appl. and Ind. Chem. Inst., Trieste, I-34127 Italy.

Alumina is the ceramic which has been used most to serve as a structural material subjected to mechanical loads, even at high temperature, because of its high melting point, Young modulus, hardness and chemical corrosion resistance. Among the means which were proposed to enhance its mechanical properties, up to date dispersed zirconia particles proved to be the most valuable one.

In this investigation a series of Al2O3-ZrO2 composite materials were prepared using either ZrO2 or ZrO2 containing different amounts of Y2O3 or CeO2 for stabilizing its tetragonal form. The mechanical properties (hardness, bend strength and toughness) were measured. The influence of the different microstructures obtained, as well as the amount and effects of the phase transformation, has been assessed.

EN 58 author present: 11.00 - 12.30

ALUMINA-ZIRCONIA COMPOSITES; FABRICATION AND PROPERTIES, T. Rytkönen* and K. Keskinen, Helsinki University of Technology, SF-02150 Espoo, FINLAND ; P. Lintula, Tampere University of Technology, SF-33101 Tampere, FINLAND

Two commercial starting powders were used in the production of Al_2O_3 - ZrO_2 composites in the composition range Al_2O_3 = 0, 20, 40, 60, 80 and 100 vol.-%. Powders were mixed with ball-milling for several hours.

Shrinkage behaviour of uniaxially pressed (100 MPa) composites was studied in an optical dilatometer. A set of the composites was hot-pressed.

Phase structures were analysed by X-ray diffraction and microstructures as well as the mixing homogeneity were viewed by SEM.

Fracture strength of sintered, uniaxially pressed (130 MPa, lubricants added at the final stages of ball-milling) as well as hot-pressed bars was measured by 4-point bending.

EN 59 author present: 11.00 - 12.30

PREPARATION, MODIFICATION AND MICROPOROUS STRUCTURE OF ALUMINA AND TITANIA CERAMIC MEMBRANE SYSTEMES,
W. van Praag*, V.T.Zaspalis, K Keizer, J.G. Ommen, J.R.H. Ross and A.J. Burggraaf,
University of Twente, Department of Chemical Technology, Laboratory for Inorganic Chemistry, Materials Science and Catalysis, P.O. Box 217, 7500 AE Enschede, the Netherlands.

Crack-free ceramic membrane layers of aluminium oxide, titanium oxide and their binary combination, supported on porous plate shaped α-alumina substrates are prepared by the sol-gel technique. These membranes are subsequently modified with silver or vanadium oxide by making use of wet impregnation techniques in order to enhance their catalytic properties. Silver or vanadium oxide are detected only at the membrane layer. The structural properties of the above mentioned systemes are discussed.

EN 60 author present: 11.00 - 12.30

ELECROCONDUCTIVE Si_3N_4-BASED COMPOSITES

A.Bellosi*, A.Fiegna, G.N.Babini

CNR-IRTEC, Research Institute for Ceramics Technology, Faenza, Italy.

Si_3N_4-based composites with 20-40 vol % TiN or TiB_2 were produced by hot pressing. Sintering behaviour and microstructural characteristics have been evaluated. The effect of type and amount of the additives and of the microstructure on the electrical properties (i.e. resistivity vs. temperature and Joule dissipation) were investigated.

Moreover the values of several thermal and mechanical properties (thermal expansion, hardness, flexural strength) and of the oxidation resistance were related to the composition of the composites.

EN 61 author present: 11.00 - 12.30

THE MECHANICAL PROPERTIES OF CORDIERITE-MULLITE COMPOSITES AS A FUNCTION OF TEMPERATURE,

D. Monroe* and J.B. Wachtman, Jr., Rutgers University, Piscataway, NJ 08855, USA; C. Gault, ENSCI, Limoges, France.

The mechanical properties of cordierite-mullite and glass-bonded cordierite-mullite composites for substrate applications were investigated. Mixtures of cordierite-mullite-glass frit powders were sintered below the melting temperature of cordierite. The elastic moduli increased with mullite content. The strength showed a general increase, but dropped off at very high mullite contents due to the poor sinterability of the mullite. Porosity was taken into account by an e^{4P} factor. The 10% glass additions raised the strength, but decreased the elastic moduli. The relative Young's modulus behaved as most oxides do at high temperatures, exhibiting a slow decrease of about 1%/100°C. The compositions with glass underwent an abrupt decrease in Young's modulus at about 1150°C and in strength at about 1000°C due to the softening of the glass. The strength decrease at high temperatures increased with the percentage of cordierite.

EN 62 author present: 11.00 - 12.30

ELASTIC PROPERTIES OF CERAMIC COMPOSITES AT HIGH TEMPERATURES,

R.Wagner* and G.Ziegler, Deutsche Forschungsanstalt für Luft- und Raumfahrt (DLR), Institut für Werkstoff-Forschung, D-5000 Köln 90, FRG.

This paper deals with the elastic properties, Young's Modulus, Shear Modulus, and Poisson's ratio, of whisker and particle reinforced composites, as a function of temperature up to 1500 °C. The properties were measured by the resonance frequency technique using rectangular bars. The study was carried out with ceramic composites based on alumina, silicon nitride and mullite with varying amounts of SiC-whiskers and SiC-particles. Additionally, the size of the SiC-particles was changed. The correlation between the elastic properties and the content and morphology of the SiC-reinforcing components is discussed.

EN 63 author present: 11.00 - 12.30

THERMAL SHOCK OF MULLITE-ZIRCONIA BASED COMPOSITES.

C.Baudín, J.S. Moya

Instituto de Cerámica y Vidrio, C.S.I.C., Arganda del Rey, 28500- Madrid, SPAIN.

The thermal shock behaviour of mullite - zirconia and mullite - alumina - zirconia composites is studied.

The materials have been prepared by reaction sintering of alumina and zircon green compacts with and without sintering aids.

Results are discussed in relation to microstructure and composition of the different materials.

EN 64 author present: 11.00 - 12.30

PROPERTIES OF ALUMINIUM NITRIDE DOPED WITH LANTHANUM OXIDE, J.-P. Bazin*, A. Kranzmann and G. Petzow, Max-Planck-Institut für Metallforschung, PML, D-7000 Stuttart 80, FRG

Because of its high thermal conductivity, AlN is valuable as a substrate material for electronic devices. To trap the oxygen which is always present in commercial powders, the AlN has been doped with La_2O_3 (< 5 wt.%) and pressureless sintered at temperatures lower than 1900°C. The influence of oxygen on the microstructure has been investigated by additional doping with alumina.

Densities higher than 98 % of the theoretical value are obtained. The influence of the microstructure, phase composition and oxygen distribution on the mechanical properties and the heat conductivity of the material has been investigated.

EN 65 author present: 11.00 - 12.30

THE INTERACTION BETWEEN SiC AND METALS,
R.C.J. Schiepers, J.A. van Beek,
F.J.J. v. Loo, and G. de With,
Centre for Technical Ceramics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Diffusion bonding between SiC and metals has been studied from a thermodynamical and kinetic point of view. In solid-state diffusion couples the reaction kinetics have been studied between SiC and Ni, Fe and (Ni, Fe)-alloys in the temperature range 700-1000°C. In SiC-Fe couples the layer consists of Fe_3Si with random carbon precipitates. In SiC-Ni couples the phases Ni_2Si, Ni_5Si_2 and Ni_3Si are formed; the carbon is present as precipitates in regular bands in the Ni_5Si_2 and Ni_2Si layers.
In Fe_xNi_{1-x}/SiC couples ternary compounds are formed. Based on these results and on the analysis of equilibrated alloys isothermal sections of the Ni-Si-C, Fe-Si-C and Fe-Ni-Si-C systems are proposed. If in practical situations the reaction rate has to be reduced, a diffusion barrier is necessary. The effectiveness of various barriers has been investigated.

EN 66 author present: 11.00 - 12.30

JOINING OF ALUMINUM TITANATE WITH NIOBIUM
H. Wohlfromm*, P. Pena, J.S. Moya
Instituto de Cerámica y Vidrio, C.S.I.C. Arganda del Rey, Madrid, Spain;
A.P. Tomsia, G. Thomas
Department of Materials Science and Mineral Engineering, University of California, Berkeley CA 94720, USA

Aluminum Titanate has been joined with Niobium with the aim to study the possible interfacial reactions at the metal/ceramic interface.

The interface has been characterized using scanning electron microscopy, energydispersive X-ray microanalysis (EDS and WDS) and indentation measurements.

An interfacial reaction has been observed involving decomposition of Al_2TiO_5 which resulted in some cases in a strong metal-ceramic bond.

EN 67 author present: 11.00 - 12.30

ELASTIC PROPERTIES AND CRYSTALLIZATION IN SiYAlON GLASSES AND CERAMICS, C.Gault, T.Rouxel*, J-L.Besson, UA CNRS 320-ENSCI Limoges 87065 ; P.Goursat, UA CNRS 320, UFR des Sciences, Limoges 87060, France.

The high temperature mechanical properties of nitrogen ceramics are strongly dependent on the intergranular phases.Crystallizing these phases, which are vitrous after sintering, improves creep resistance.
In order to have a better understanding of the secondary phases, nitrogen glasses* with varied compositions in the SiYAlON diagram are studied.In addition to usual characterizations, the elastic properties are determined using an ultrasonic method.
Young's modulus is very sensitive to structural changes.Its evolution with temperature allows to localize the onset of the glass transition range and the crystallization domains.Isothermal experiments, associated with XRD, bring informations on the crystallization kinetics.The results permit an optimal choice for post-sintering treatments.

*The glasses were elaborated by Dr. S. Hampshire, NIHE, Limerick, Ireland.

EN 68 author present: 11.00 - 12.30 withdrawn

EN 69 author present: 11.00 - 12.30

RESULTS OF THE VAMAS HARDNESS TEST ROUND ROBIN EXERCISE USING ALUMINA CERAMICS, R.Morrell*, D.M.Butterfield, D.J.Clinton, National Physical Laboratory, Teddington, Middlesex, TW11 OLW, UK.

The accuracy and reproducibility of conventional hardness testing procedures has been evaluated in an international round-robin exercise under the auspices of VAMAS (Versailles Project on Advanced Materials and Standards). Participants were supplied with two discs of different high-alumina ceramics which had previously been tested by NPL using Rockwell Superficial HR45N, Vickers HV1.0 and HV0.2, and Knoop HK0.2 methods. They were asked to measure the HV and HK indentations with their own equipment, and then to use this equipment to place their own series of indentations into the discs and measure the indentation sizes (or HR45N hardness no.). The discs and the data were returned to NPL where a data analysis was made to establish the reliability of the participants' measurements compared with those from NPL.
This paper reports the data analysis and provides a basis for generating guidelines for hardness testing ceramics. All methods have limitations of accuracy, but errors in microhardness tests are probably too large for specification purposes.

EN 70 author present: 11.00 - 12.30

THE HARDNESS OF Ce-PSZ MATERIALS OVER THE TEMPERATURE RANGE 20-900C, R. Morrell, S. Blackburn*, P.G. Senhenn and P. Greenwood,
National Physical Laboratory, Teddington, Middlesex; Universal Abrasives Ltd, Stafford, England.

A ceria stabilised TZP produced by the electrorefining route will be discussed in terms of its micro hardness over the temperature range 20-900C. Pseudo plastic behaviour of this material has been observed at room temperature. The degree to which this phenomena develops over the above temperature range will be reported. Where possible comparative data with the Y-PSZ system will also be presented.

EN 71 author present: 11.00 - 12.30

INFLUENCE OF SOME OXIDES ON THE THERMAL CHARACTERISTICS OF STOICHIOMETRIC Al_2TiO_5

P.P. Demaestri, A. Giachello, P.C. Martinengo
Fiat Research Center, Orbassano, Italy

Aluminium titanate is considered an engineering material, where thermal insulation is required. This is due to its special combination of properties, low thermal conductivity, excellent thermal shock resistance and low thermal expansion coefficient, that it make possible to apply components like portliners into cylinder heads directly in aluminium casting process.
The aim of this work is to understand the influence of the addition of some oxides like SiO_2, ZrO_2 and MgO on the behaviour of the material at high temperature expecially respect to the thermal decomposition of Al_2TiO_5 at 1000° and 1100 °C, which are very critical conditions also in actual engine applications.

EN 72 author present: 11.00 - 12.30

THERMOMECHANICAL PROPERTIES OF ALUMINUM TITANATE CERAMIC BETWEEN 20 AND 1000 °C,

B. Freudenberg*[1], E. Gugel[1], H.-A. Lindner[1]; P. Thometzek[2]
1 Cremer Forschungsinstitut, Rödental/FRG
2 Bayer AG, Uerdingen/FRG

One prominent application of aluminum titanate ceramic is the thermal insulation of the exhaust port. In this case, the ceramic liner is integrated into the cylinder head during the metal-casting process. Reliability of such ceramic parts depends on the thermomechanical properties not only at room-temperature, but over the whole temperature range experienced during the metal-casting and in service life.
With this respect, a slip cast reaction-sintered aluminum titanate grade is investigated concerning properties such as bending strength, Young's modulus, thermal expansion and thermal conductivity as a function of temperature. Results are interpreted in the light of the microcrack network, a specific feature of aluminum titanate ceramic.
Based on these data, the shrinkage stress exerted by the cast metal housing on the ceramic tube is calculated and discussed.

EN 73 author present: 11.00 - 12.30

Influence of geometrical and material parameters on the thermal shock behaviour of ceramic components,

A. Dutschk
DFVLR (IBK)
Pfaffenwaldring 38-40
D-7000 Stuttgart 80
and
F.E. Buresch
IRW/KFA-Jülich
and
ICA
Pfaffenwaldring 27,
7000 Stuttgart 80

The present communication deals with the relationship between the distribution of thermal stresses in tubular ceramic components due to rapid heating with their local strength which depends on the fabrication condition. The assignment is based on computational as well as experimental work. The strength distribution in the axial and tangential direction of the components was determined using bend and ring specimens. The results show that besides the material specific parameters such as thermal condentivity and strength most important is the transient heat transfer at the surface.

EN 74 author present: 11.00 - 12.30

CHEMICAL AND PHYSICAL PARAMETERS INFLUENCE ON AlN BASED CERAMICS THERMAL DIFFUSIVITY

MICHELET J.P., HAFIDI A., LECOMPTE J.P., JARRIGE J., BILLY M., MARTIN C., MEXMAIN J.
Faculté des Sciences, Laboratoire de Céramiques Nouvelles (UA 320), 123, Av. A. Thomas, 87060 LIMOGES Cédex - FRANCE

Aluminum nitride ceramics have been extensively studied because of their promising applications as components in heat engines operating at very high temperatures. Now, AlN is also rapidly becoming an important substrate material in electronics. It offers a unique combination of high thermal conductivity, low electrical conductivity, low thermal expansion and low toxicity rating compared to BeO ceramics. Literature data on a single AlN crystal at room temperature gives 320 W/m.K and values obtained on polycristalline ceramics are very dispersed between 50 to 260 W/m.K. This is the reason why we tried to encircle a great number of chemical and physical parameters such as origin of AlN powder, purity (chemical, oxygen content...) as well as the microstructure.
Ceramics have been elaborated through pressureless sintering, hot pressing and hot isostatic pressing with and without additives (CaO, Y_2O_3, BeO...). The measurements were carried out in the temperature range 300-600 K using a laser-flash diffusivity technique, the samples surface being coated with colloidal graphite during the test to avoid laser shine-through.
Discussion will lead to microstructure action and the sintering aid's influence on the characteristics of obtained ceramics.

EN 75 author present: 11.00 - 12.30

INVESTIGATIONS OF THE THERMAL FATIGUE BEHAVIOUR OF HPSN, SIC AND GLASS,

K. Keller[1]; T. Fett[2]; D. Munz[1],[2]

1) Universität Karlsruhe, Institut für Keramik im Maschinenbau, Postfach 6980, 75 Karlsruhe 1, F.R.G.
2) Kernforschungszentrum Karlsruhe, Institut für Material- und Festkörperforschung IV, Postfach 3640, 75 Karlsruhe 1, F.R.G.

Ceramic components are often subjected to thermal cyclic loading. Due to temperature gradients, which lead to thermal stresses, crack growth can occur. A test-apparatus was built to investigate the thermal fatigue behaviour of SiC, HPSN, and glass in different quenching media.

For HPSN and SiC the damage was determined indirectly by measuring the remaining bending strength. The glass specimen were pre-cracked with a Knoop indenter, and the crack growth could be measured directly on the fracture surface.

To predict the remaining strength, the cyclic crack extension was calculated in the following steps: analytical temperature distribution, transient stress distribution, calculation of the stress intensity factor applying the method of weight function, crack growth evaluation from the subcritical crack growth parameters, which have been determined in dynamic bending tests.

EN 76 author present: 11.00 - 12.30

THERMAL CONDUCTIVITY MEASUREMENTS OF FUSED CAST ZIRCONIA BRICKS BY TRANSIENT HOT WIRE METHOD, K.Hayashi*.Wakamatsu, Y.Okamoto, A.Ito** and Shigeo Endo**
Kyoto Institute of Technology, Kyoto, 606
**Toshiba Monofrax Co., LTD. Chiba, 289-02, Japan

The thermal conductivity for fused cast bricks containing various amounts of zirconia was measured by the transient hot wire method ranging from room temperature to 1400°C. The thermal conductivity of the fused cast 94% monoclinic zirconia brick decreased with increasing temperature. With decreasing zirconia and increasing alumina content, these types of bricks represented their thermal conductivitis characteristically in a parabolic curve with increasing temperature.
The relationship between the temperature dependence and the chemical composition of bricks will be discuss in the paper.

ENGINEERING CERAMICS POSTERS : FRACTURE AND NDT
Monday 19th June; 10.00 - 19.00

EN 77 author present: 15.00 - 16.30

HIGH TEMPERATURE MECHANICAL BEHAVIOUR OF DENSE ZIRCON BODIES.

R.Torrecillas*,G.Orange,G.Fantozzi,INSA,69621 Villeurbanne,France

E.Segura,S.de Aza,J.S.Moya,Instituto de Ceramica y Vidrio CSIC,Arganda del Rey, Madrid,Spain

Submicronic zircon powders have been used as starting materials to obtain dense compact bodies (99% th) by pressureless sintering at 1570 and 1630°C.
Bending strengh,fracture toughness and R-curve behaviour have been studied as a function of temperature. The effect of a partial dissociation of zircon on the high temperature mechanical properties is also reported.

EN 78 author present: 15.00 - 16,30

MEASUREMENT OF THE WORK OF FRACTURE USING A MODIFIED CHEVRON NOTCHED SPECIMEN

P. Merckx*, O. Van Der Biest**, P. Virier**, B. Fournel*** and M. Boussuge***

* Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, Belgium
** Desmarquest Technical Ceramics, Trappes, France
*** Centre des Matériaux, Ecole Nationale Supérieure des Mines, Paris, France

Measurements of the work of fracture in ceramics critically depend on the ability to introduce a sharp precrack and to obtain stable crack growth during the test. In this work the modified chevron notched specimen, as proposed by Himsolt et al (J. Am. Ceram. Soc., 70, C133, 1987), has been evaluated for work of fracture measurements. Experimental parameters which have been investigated for a range of silicon nitrides, include : the mode of loading (3 point/4 point), the rate of loading and the temperature of the test. Stable crack growth has been achieved at room temperature under low loading rate for most tests. Causes for instability were studied using fractography and theoretical calculations. At high temperature the maintenance of the sharpness of a precrack during heating remains a critical issue.

EN 79 author present: 15.00 - 16.30

MICROSCOPICAL OBSERVATIONS ON CONTROLLED CRACK PROPAGATION IN POLYCRISTALLINE ALUMINA, K.K.O. Bär*, IRW-KFA, 5170 Jülich, F.R.G.; R. Mergen, IWW, T.U-Clausthal, 3392 Clausthal, F.R.G; and F. Osterstock, LERMAT, U.A 1317, 14032 Caen Cedex, France.

Either frontal process zone or bridging effects in the wake of the crack are actually proposed to describe the R-Curve behavior of polycristalline ceramics.

Specimens have been prepared in order to avoid stress corrosion effects. Controled load or displacement tests have been been run in conjunction with AE measurements and optical observations and recording using a device with very high resolution.

Depending on the loading rate first acoustic emission signals have been registrated just before or at the deviation from linearity. Usually isolated cracks appeared in front of the main crack tip. Propagation takes place by the growth of one isolated crack toward the main crack tip. These observations sustain the model of a frontal process zone.

However in accordance with results of accelerating cracks (constant load) or relaxing cracks (constant displacement), the definition of the crack tip as well as the energetic equilibrium conditions of static and dynamic cracks under inert conditions need to be requestionned.

EN 80 author present: 15.00 - 16.30

STATISTICAL ANALYSIS OF FLEXURE STRENGTH DATA - RESULTS OF AN INTERNATIONAL ROUND ROBIN PROGRAM,

A. Brückner-Foit

Nuclear Research Centre,
P.O.Box 3640, D-7500 Karlsruhe 1, F.R.G.

Within the framework of an research agreement of the IEA (International Energy Agency) an extended round robin program has been conducted on the determination of the flexure strength distribution of advanced ceramics. The results of this program are analyzed with statistical methods in order to determine a common combined flexure strength sample from the results obtained by the various participating laboratories for a given material. In the course of this analysis it is shown how statistically significant deviations can be identified which occur between the test results obtained by different laboratories. A discussion of possible sources for significant deviations is given.

EN 81 author present: 15.00 - 16.30

DEFORMATION BEHAVIOUR OF ENGINEERING CERAMICS,

G.A.Gogotsi

Institute for Problems of Strength of the Ukr.SSR Academy of Sciences, Kiev, USSR

Application of zircinia, cordierite ceramics in machine building testifies for the necessity to take into account not only Hook's law but also the ceramics inelasticity behaviour when studying the mechanical properties. Depending on the inelasticity of ceramimics at room temperature its fracture toughness, acoustic emission, the deformability and subcritical crack growth characteristics appear to be variable in heating. The inelastic ceramics increases its deformability while the elastic one shows a decrease of this parameter when having been subjected to thermal shock. The ceramics mechanical regularities prediction could be made through the brittleness measure parameter earlier proposed by the authors which should be the basis for choosing the fracture toughness evaluation criteria and techniques for testing this type of materials. The novel setups for studying the ceramics bending deformability regularities are described.

EN 82 author present: 15.00 - 16.30

EFFECT OF CREEP STRAIN ON CREEP DAMAGE FORMATION IN HPSN, E. Meßner* and H. Hübner, Technische Universität Hamburg-Harburg, 2100 Hamburg 90, FRG

Creep damage formation was studied in two yttria-doped HPSN materials by creep tests in bending. The creep behaviour differed markedly, one material showing low ductility, a minimum creep rate and tertiary creep followed by creep rupture, the other one being characterized by a stationary creep state, a pronounced ductility and the absence of tertiary creep. The creep porosity of the two materials as determined by the very precise sink-float technique was found to increase linearly with creep strain; thus, a creep cavitation sensitivity ω could be defined. It was shown that (1) ω turned out to be independent of creep strain, (2) the magnitude of ω was strongly dependent on the stress state, i.e. ω in the sample region under tensile stress by far exceeded that in the region under compressive stress, and (3) the ω values of the two materials were quite similar. The latter result is in contrast to the creep behaviour observed, since similar values of the creep porosity should lead to similar shapes of the creep curve.

EN 83 author present: 15.00 - 16.30

MECHANICAL BEHAVIOUR OF OXYGEN-FREE PERFORMANCE CERAMICS IN VARIOUS ENVIRONMENTS

G.A.Gogotsi and Y.G.Gogotsi

Institute for Problems of Strength of the Ukr.SSR Academy of Sciences, Kiev, USSR

Oxygen-free ceramics changes its mechanical properties in high-temperature oxidation and this is normally neglected in testing.
The data is generalized for the authors' studies on the strength, fracture toughness and other characteristics dependences for reaction-sintered and hot-pressed Si_3N_4, reaction-bound B_4C and hot-pressed SiC tested in air, argon and vacuum at temperatures up to 1400°C, as well as the relation is found between their resistance to oxidation and mechanicalal behaviour regularities. The data and fractographic evidences obtained made it possible to single out origins and mechanisms of ceramics fracture in various environments showing the possible reduction in strength to be by 50%.

EN 84 author present: 15.00 - 16.30

CYCLIC FATIGUE OF ALUMINUM OXIDE IN BENDING,

T. Fett[1]; D. Munz[1,2]

1) Kernforschungszentrum Karlsruhe, Institut für Material- und Festkörperforschung IV;
2) Universität Karlsruhe, Institut für Zuverlässigkeit und Schadenskunde im Maschinenbau,
Postfach 3640, 75 Karlsruhe 1, F.R.G.

The delayed failure of mechanically loaded ceramic components at temperatures below the creep range can be caused by subcritical crack growth as well as by a real fatigue damage. If the stresses are constant or change moderately with time subcritical crack extension is responsible for crack extension. In cyclic test an additional cyclic fatigue effect occurs. Such an effect can be concluded by comparing cyclic lifetimes from experiments with predicted lifetimes based on static tests.
Experimental results are obtained for alumina in air at room temperature. The tests are performed in a cantilever bending test under pure alternating load with R=0 and a frequency of 50Hz for natural cracks as well as for artifical Knoop cracks. From these tests a real cyclic fatigue effect can be concluded. Also first results obtained for sintered silicon nitride will be reported.

EN 85 author present: 15.00 - 16.30

INFLUENCE OF ATMOSPHERE AND ANNEALING TIME ON MICROSTRUCTURAL AND MECHANICAL PROPERTIES OF MULLITE - ZrO_2 - TiO_2 COMPOSITES,

M. F. Melo*, Dept. Mater. Techn., LNETI, 1699 Lisboa Codex, Portugal; J. S. Moya, Inst. Ceram. y Vidrio, CSIC, Arganda del Rey, Spain; and M. O. Figueiredo, C. Cryst. Miner., IICT, 1000 Lisboa, Portugal.

Annealing effects in mullite / zirconia composites with TiO_2 additions (0.25 and 1.0 mol) have been studied under helium and air atmospheres at sintering temperatures (1500 and 1550 °C).
Differences in grain growth, solid solution conditions and mechanical properties were observed, either influenced by the atmosphere and / or the titania content. The results are explained in terms of changes in grain boundary micro-Chemistry as a consequence of distinct PO_2 conditions.

EN 86 author present: 15.00 - 16.30

HIGH TEMPERATURE UNIAXIAL ALTERNATING FATIGUE OF ENGINEERING CERAMICS,

D. Bolsch* and J. Bressers,
Joint Research Center of the EC, Petten, The Netherlands.

A testmethod is described, which allows fatigue testing of engineering ceramics under uniaxial alternating load up to a temperature of 1600°C and up to a frequency of 120 Hz in air. A flat, easy to grip sample geometry is selected. Special care is given to achieve a homogenous temperature and stress distribution, and a low bending component. Some results of constant stress amplitude HCF-tests are presented for a monolithic HPSN and a SiC Whisker reinforced SSN Composite.

EN 87 author present: 15.00 - 16.30

FRACTURE OF SINTERED GLASS AS A FUNCTION OF POROSITY, L. Coronel and F. Osterstock*, LERMAT U.A 1317, 14032 CAEN Cedex, France.

Glass samples with porosity ranging from 2% to 37% have been obtained by sintering microspheres at various temperatures for various durations.

This kind of material is very well suited for investigating the influence of porosity on fracture mechanical parameters, because on the one hand residual stresses of the first order can easily be removed and on the other hand residual stresses of the second order arising from the anistropy of the thermal expansion coefficients of the grains does not exist.

The results show that, as K_{IC} decreases continuously, G_{IC} passes through a maximum as poritisy increases. They do not fit with the model of R.C. Rice - shortest fracture path between pores - nor with the model of damage of Katchanov or Lemaitre. They are however in qualitative agreement with some experimental values published by Pabst et al.

Fractographic observations show that deviation of the main crack and lateral microcracking must be taken into account.

EN 88 author present: 15.00 - 16.30

POST-HIPPING OF SILICON NITRIDE-BASED MATERIALS, A. Bellosi, V. Biasini, S. Guicciardi,
Research Institute for Ceramics Technology - CNR, Faenza, Italy

Several silicon nitride-based materials, in the systems Si_3N_4-Al_2O_3-Y_2O_3 and Si_3N_4-MgO-Y_2O_3, have been pressureless sintered in the same conditions (1800°C, 2 hours) starting from different commercial powders. The sintered bodies have been hipped at 1700°C for 1 hour. The dense materials, both sintered and hipped, have been characterized under the point of view of:
-microstructure (grain size, porosity, crystalline phases, type and distribution of secondary phases)
-mechanical properties (hardness, flexural strength, fracture toughness).

EN 89 author present: 15.00 - 16.30

THE EFFECT OF THE GREEN MICROSTRUCTURE ON THE MECHANICAL PROPERTIES OF DENSE ALUMINA
L.A. Correia* and P.P.A.C. Pex
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands

The mechanical properties of ceramics highly depends on the microstructure defects of the dense material, that is intrinsic flaws introduced during compaction of the powder as well as processing flaws not eliminated during densification. In order to study the influence of the green microstructure, compacts of 70 x 70 x 7 mm are made by slip casting using submicron powders ($\bar{d}$ < 0.7 µm) with different particle size distributions obtained by fluid classification and attrition milling. The suspensions are of several degrees of deflocculation with a high solid content. From these compacts densified at the appropriate temperature in air, rectangular bars of 4 x 4 x 50 mm are machined for mechanical testing. Flexural strength is measured using 4-point bending tests while the thoughness is measured on V-notched specimens.

EN 90 author present: 15.00 - 16.30

RELATIONSHIPS BETWEEN GREEN AND FIRED STRENGTH OF Al_2O_3 WITH CONTROLLED DEFECTS.

Bill Bergman,* Kristin Breder and Mats Petersson,
Department of Physical Metallurgy and Ceramics,
Royal Institute of Technology,
S - 10044 Stockholm, Sweden.

Controlled defects in the form of 10µm polymer spheres and powder agglomerates were added to alumina. The evolution of these and their effect on the strength distribution were studied using the diametral compression test. The mean strength and the Weibull modulus were analysed and discussed in relation to density and fractography Material with added agglomerates was shown to fail from the flaws associated with these and the strength scaled well with the measured flaw sizes. Material with added polymer particles failed from connected pore systems. No single critical defect was observed in the material without added defects, and it is believed that arrays of small pores were strength controlling in this case. The material containing agglomerate and the reference material had a lower Weibull modulus in the sintered state than in the green state. In the material containing polymer particles (pores) the Weibull modulus remained unchanged after firing.

EN 91 author present: 15.00 - 16.30 withdrawn

EN 92 author present: 15.00 - 16.30

ACOUSTIC EMISSION FROM THERMAL FRACTURE OF CERAMICS, K. J. Konsztowicz. National Research Council of Canada, Halifax, N.S., Canada.

Although it is recognized that microcracks growth may contribute to failure of ceramics undergoing thermal shock, there is still very little experimental evidence. The contribution of acoustic emission (AE) and SEM observations can provide such evidence at the very initial stage of crack growth. In this work AE data were analysed after rapid quenching of ceramic samples in silicone oil. A thermal shock resistant material, alumina, and a material resistant to thermal damage, zirconia, have been examined. Cracks were detected by analysis of AE amplitudes and durations and their growth was monitored by systematic SEM observations as thermal shocks of increasing severity were applied. Residual strength was determined by three-point bending after quenching. For the first time images are presented showing early stages of crack iniation for temperature differences less that ΔT crit, i.e. where the strength was heretofore believed unaffected by thermal shock. Following thermal shock fatigue tests prove that, once initiated, even the smallest cracks can grow and strongly affect the residual strength of the material.

EN 93 author present: 15.00 - 16.30

APPLICATION OF MICROFOCUS RADIOLOGY AND DYE PENETRANTS IN QUALITY AND FRACTURE TOUGHNESS DETERMINATION OF CERAMIC SAMPLES
H. Kölker and P. Henze
Elektroschmelzwerk Kempten GmbH, West-Germany

The x-ray microfocus technique using image processing is applied to detect flaws and density fluctuations in green and sintered ceramic components. Various problems and recent improvements of the method such as detection limit, contrast resolution capability, and beam hardening are addressed and experimentally investigated. Surface cracks are investigated by capillary flaw inspection using liquid dye penetrants. This method is extended to assess different ways of fracture toughness determination in ceramics.

EN 94 author present: 15.00 - 16.30

CORROSION OF SOME SILICON NITRIDES IN $H_2/H_2O/H_2S$ GAS MIXTURES AT 1200-1300°C,

F. Costa Oliveira, C.E.C., Joint Research Centre, Petten, The Netherlands.

Although many industrial environments have low pO_2 and contain S, little is known about the corrosion of silicon nitride in such gases. Four silicon nitrides sintered with the aid of Y_2O_3 and Al_2O_3 in various ratios were investigated. Corrosion rates varied from 0.03 to 30 mm/year (0.8 to 850 g m^{-2} h^{-1}), depending critically on the gas composition and temperature.

To complement the phase stability diagram, a "volatility map" was constructed for the Si-O-S system to predict the behaviour. Corrosion was fast (and disastrous for some silicon nitride compositions) when a high pSiS is predicted and SiO_2 is not stable. When SiO_2 is stable, a glassy layer forms which blocks SiS evaporation but is gradually converted to SiO gas at a rate limited by transport in the gas phase. Under these conditions a high equilibrium pSiS causes internal sulphidation.

EN 95 author present: 15.00 - 16.30

GASEOUS CORROSION OF SOME SILICON NITRIDES IN SO_2-AIR MIXTURES AT HIGH TEMPERATURE,

J.B. Veyret*, R.J. Fordham, C.E.C., Joint Research Centre, Petten, The Netherlands; and M. Billy, University of Limoges, Limoges, France.

The gaseous corrosion of two hot-pressed and one pressureless sintered Si_3N_4 ceramics was investigated. Corrosion was carried out in the range 800-1400°C for exposure times of up to 100 hrs in 1 and 5 Vol% SO_2 in dry air. The presence of sulphur was evident on all samples up to 1300°C, and analysis using ESCA and EPMA indicated the formation of sulphates on the surface with a maximum in the region 800-900°C for the yttria hot-pressed material and in the region 900-1200°C for the magnesia hot-pressed and yttria-magnesia pressureless sintered materials. The mechanisms of corrosion are explained in terms of the reactivity of secondary phases in the SO_2/Air environment.

EN 96 author present: 15.00 - 16.30

CORROSION OF TECHNICAL CERAMICS BY METAL MELTS,

U. Schwabe, Centre for Technical Ceramics, P.O. Box 513, 5600 MB EINDHOVEN, The Netherlands.

Corrosion of various technical ceramic materials was studied in a number of aluminium alloy melts. Thermodynamical calculations were carried out regarding possible corrosion reactions. Predictions based on theory were compared with experimental results obtained in a temperature range of 800-1000°C. Reaction times up to some 100 hours were used in reducing environments.

EN 97 author present: 15.00 - 16.30

MICROSTRUCTURE OF THE OXIDE LAYERS PRODUCED DURING OXIDATION OF SILICON NITRIDE

J.Echeberría and F.Castro
Centro de Estudios e Investigaciones Técnicas de Guipúzcoa, Barrio de Ibaeta s/n, Apdo. 1555, 20.080 San Sebastián, Spain.

Oxidation of silicon nitride with additions of ceria + alumina, yttria + magnesia and yttria + alumina has been carried out in air at atmospheric pressure for up to 72 hrs at 1100 to 1350 C.Parabolic oxidation kinetics were observed in all cases, although the microstructure of the oxide layers formed, as studied by x-ray diffraction and electron microscopy,were dependent on the initial chemical composition of the specimens,the oxidation temperature and the cooling rate. However, for yttria-containing specimens, the influence of cooling rate is only important for those having alumina, since the formation of enstatite ($MgSiO_3$), in those with MgO additions, which favours in turn the crystallisation of an yttrium-disilicate, seems to be independent of cooling rate.The microstructural changes of the substrate,induced by the oxidation treatment, were also studied by XRD and scanning transmission electron microscopy.

EN 98 author present: 15.00 - 16.30

OBSERVATIONS OF THE SLIDING WEAR BEHAVIOUR OF TRANSFORMATION TOUGHENED CERAMICS,

M. Rainforth*, R. Stevens, J. Nutting.
School of Materials, University of Leeds, Leeds LS2 9JT

Y-PSZ and Mg-PSZ ceramics have been examined under sliding wear conditions, mated against both ceramic and metal counterfaces. The low thermal conductivity of the ZrO_2 was found to dominate the wear mechanism. In those tests where a metal counterface was used, metal oxide was readily formed, which acted as an abrasive to the Zirconia. A TZP (Tetragonal Zirconia Polycrystals) pin slid against a Zirconia Toughened Alumina disc showed evidence of very high flash temperatures at the interface, possibly as high as 2000°C. Under low load conditions, where temperature rises were much lower, transformation of tetragonal to monoclinic can occur at the interface, resulting in an increased wear rate.

EN 99 author present: 15.00 - 16.30

MACHINABILITY CHARACTERISTICS OF TRANSFORMATION TOUGHENING ZIRCONIA CERAMIC IN ULTRASONIC DRILLING

B.L. Anantha Ramu, Research Scholar, R. Krishnamurthy,* Professor, Dept. of Mech. Engg., C.V. Gokularathnam, Asst. Prof., Dept. of Metallurgy, I.I.T., Madras-600 036, INDIA.

The present study concerns with Zirconia ceramic (toughened by precipitation treatment). Ultrasonic machining trials were carried out on LEHFELDT-DIATRON IC ultra sonic drilling machine. The observations comprise geometrical inaccuracy of the drilled hole, surface finish, tool wear, tool materials and influence of working conditions on driling force. The drilling force was measured by using piezoelectric crystal type dynamometer, which has been fabricated specially for this study. Tool penetration rate varied with different tool material. Higher hardness of Zirconia ceramic resulted in more rebouncing of abrasive on to the tool causing more tool wear. Stainless steel tool was better for machining of Zirconia ceramic. During machining while the drilling force was observed to be periodic, exhibiting marginal variation with static load, the surface texture was consistent with minimum distress.

EN 100 author present: 15.00 - 16.30

CONTROL OF SURFACE DAMAGE IN MACHINING OF ENGINEERING CERAMICS,

C.A. van Luttervelt* and J.J. Saurwalt,
Technical University of Delft, 2628 CE, The Netherlands;
E. Lijbrink,
Netherlands Energy Research Foundation (ECN), Petten, 1755 LE, The Netherlands.

The paper bears on an investigation addressing the prime practical conditions applying to a systematic approach of surface quality control in abrasive machining of engineering ceramics.

The important prerequisites for such an approach are:
- knowledge of the basic mechanisms which control deformation and fracture in brittle solids and material removal in abrasive machining of ceramic species;
- availability of relevant information on mechanical and physical properties and structural constitution of the material systems involved;
- availability of serviceable methods to produce lacking specific data accurately and consistently.

This contribution deals with the preparation and results of grinding experiments which were designed to assess significant relationships between resultant surface conditions and
- specific material quality in terms of composition and micro-structure;
- the actual magnitude of the normal force per single abrading particle acting on the ceramic surface during machining;
- characteristic grinding wheel performance as associated with typical cutting behaviour of single crystal vs. polycrystalline diamond particles.

The experiments are conducted as part of a development programme engaged to meet the above-mentioned prerequisites.

EN 101 author present: 16.30 - 18.00

Applications of CVD and PVD thin films.
S. Franklin, G. van der Kooi; Philips PMF P.O. box 218, 5600 MD Eindhoven.

The metallurgical laboratory at the Philips PMF (Plastics and Metalware Factories) has facilities for the deposition of a variety of hard, wear-resistant coatings onto different substrates. Experience has also been accumulated in assessing the practical lifetime and wear performance of coated tools and components and in the characterisation of thin surface layers. A different range of CVD coatings can be deposited on a laboratory and production scale. With the current available equipment it is possible to deposit TiC,TiN,alumina and CrxCy coatings, or combinations of these, at high temperatures (850-1000 Centigrade). The thickness of the coatings can be varied between 2 and 10 microns. These coatings can be deposited on various substrate materials such as steel and cemented catbide for tribological and wear-resistant purposes. An advantage is the good adherence between the film and the substrate.

EN 102 author present: 16.30 - 18.00

Applications of CVD and PVD thin films
W. van Duyn, B. van Lochem; Philips PMF; P.O. box 218; 5600 MD Eindhoven.

Metallic films, made by conventional magnetron sputtering, cab be used for various electric, optical or decorative purposes. TiN coatings can be made by reactive sputtering in a plasma of argon and nitrogen. These coatings have a good resistance against abrasive wear of cutting tools, moulds and dies.
W-C:H films are new types of carbon rich layers which can be made in a plasma of argon and acetylene. The most important property of these layers is their low friction coefficient against metals. Succesful applications are: Cutting tools bearings and cold-formimg tools for metals. Chemical analysis shows that W-C:H films consist of tungsten carbide particles, embedded in a polymer-like matrix. The mechanical properties, hardness, load bearing capacity and friction coefficient depend strongly on the WC content in the layer, which is strongly influenced by the acetylene percentage during the proces.

EN 103 author present: 16.30 - 18.00

PE-CVD OF BN USING ORGANIC PRECURSORS
Johanna G.M. Becht*, Paul J. van der Put Joop Schoonman, Delft University of Technology, Laboratory for Inorganic Chemistry, Delft, The Netherlands.

Thin amorphous films of boron nitride have been deposited on glass, fused silica, silicon and indium phosphide using plasma enhanced chemical vapor deposition. Volatile ternary amine borane complexes have been used as a single reactant containing both boron and nitrogen. Optimal reaction conditions and electrode configurations have been established. The substrate is held at 290 °C. It is found, that an excess of nitrogen in the form of ammonia is required to prepare stoichiometric films. The growth rate of the films is 20 nm/h when using dimethyl amine borane, and 50 nm/h when using triethyl amine borane. The latter films, however, are never stable is air, probably due to an excess of boron in the films. Although the reactants contain carbon, no carbon has been found in these layers with XPS.

EN 104 author present: 16.30 - 18.00

UPGRADING CERAMIC COMPONENTS BY LPCVD,
L.R.Wolff, Centre for Technical Ceramics. POB 513,5600 MB Eindhoven,the Netherlands.

Ceramics, just like glasses, are very sensitive to surface defects. In structural applications, failure is often induced by tensile stresses peaking in the components surface. Surface defects also play an important role in the corrosion of ceramic components.

Using Low Pressure Chemical Vapour Deposition (LPCVD), one can effectively eliminate surface defects. Ceramic components are coated with a thin (6µm) film, either of the same material or a different one. The LPCVD coating is pure, single phase, dense fine grained and essentially defect free.

When the coating composition differs from that of the substrate, the coefficient of thermal expansion difference will create stresses. By carefully selecting the nature of the coating, as well as the deposition temperature, a compressive stress situation can be achieved in the coating under operating conditions. This approach will markedly enhance strength and corrosion resistance as well as the Weibull modulus of these properties for ceramic components.

EN 105 author present: 16.30 - 18.00

A COMPARATIVE STUDY OF THE OXIDATION OF RBSN AND RBSN COATED WITH CVD-Si_3N_4,

A.P.M. Adriaansen, H. Gooijer,
Centre for Technical Ceramics
P.O. Box 513, 5600 MB Eindhoven,
The Netherlands

Oxidation resistance of Si_3N_4 depends strongly on surface porosity, surface cracks and contaminants like sinter additives. These additives can, at high temperatures, diffuse to the surface and decrease the oxidation resistance. By coating a bulk Si_3N_4 material with Si_3N_4 by CVD the surface porosity can be decreased and thus the oxidation resistance increased.
At the centre for Technical Ceramics a research program was initiated in order to systematically assess the potential of this possibility. Several reaction bonded Si_3N_4 (RBSN) samples were tested on oxidation resistance at 1200°C. These results were compared with samples of RBSN coated with CVD Si_3N_4.

EN 106 author present: 16.30 - 18.00

MECHANICAL CHARACTERIZATION OF MACROPOROUS CERAMIC SUPPORT TUBES FOR MICRO/ULTRAFILTRATION

P.W. Bach*, N.P.G. van der Burg and R.A. Terpstra
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands

At ECN microfiltration and ultrafiltration ceramic membrane systems are being developed. For these a macroporous support is needed, which gives a high mechanical strength to the system with a very low hydraulic resistance. The support tubes are produced at ECN by extrusion. After controlled drying the tubes are sintered at temperatures above 1500°C. Also commercially obtained support tubes have been used.

The tubes are mechanically characterized by bursting pressure tests and by C-ring tests. For the bursting pressure test a parameter study (length of the tubes, pressure application rate, clamping load) is carried out. The results of the mechanical tests are compared with microstructural data (poresize and -distribution, permeability) of the tubes.

EN 107 author present: 16.30 - 18.00

MODIFIED SOL-GEL TECHNIQUES FOR THE PREPARATION OF MICROPOROUS CERAMIC MEMBRANE TOPLAYERS ON MACROPOROUS ALUMINA SUPPORTS,

M.H.B.J. Huis in 't Veld*, R.J.R. Uhlhorn, K. Keizer and A.J. Burggraaf
University of Twente, Department of Chemical Technology, Laboratory for Inorganic Chemistry, Materials Science and Catalysis, P.O. Box 217, 7500 AE Enschede, the Netherlands

Crack-free mesoporous γ-alumina membrane layers, supported on plate or tube shaped α-alumina (multilayer) substrates, are prepared by a sol-gel technique. Modifications of this membrane layer with silica and magnesia are performed to decrease pore size and influence the chemical characteristics of the membrane surface, in order to enhance gas separation properties. Magnesia is introduced by the use of a wet impregnation technique. Modification with silica is performed through a sol-gel route (acidified TEOS/ethanol solution), and yields a microporous membrane ($d_p < 2$ nm) with high permselectivities (CO_2/CH_4 = 30). The structure and the distribution of magnesia and silica within the membrane layer will be discussed.

EN 108 author present: 16.30 - 18.00

THE CALCINATION AND THERMAL STABILITY OF CERAMIC Al_2O_3 MEMBRANES FOR GAS SEPARATION

H.M. van Veen*, J.P.B.M. Tol, R.A. Terpstra, A.J.G. Engel and H.J. Veringa
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands

The three layer tubular ceramic membrane system prepared by ECN, consists of an alpha-alumina substrate, an (alpha-alumina) intermediate or microfiltration layer and a gamma-alumina top layer. The microfiltration layer is applied by a film coating technique while the top or ultrafiltration layer is obtained by slip casting. The top layer has a narrow pore radius distribution in the nanometer region, a thickness of about 3 microns and it has segregative properties for gases.
With the recently developed carrier system it is now possible to produce an almost defect-free gas separation membrane. In this paper various calcining procedures for the top layer will be compared and it will be shown that relatively fast calcining has no influence on the pore properties while a smooth layer without cracks is formed.
In order to study the thermal stability of the top layer, the membranes are first calcined at 600°C and then exposed to different temperatures for up to 600 hours. The membranes are then characterized by nitrogen adsorption/desorption and X-ray diffraction.

EN 109 author present: 16.30 - 18.00

ALUMINA MEMBRANES: APPLICATIONS, ADVANTAGES AND DISADVANTAGES

by

F. MUILWIJK * ; J.P.P. THOLEN

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The Netherlands

An overview of the possible applications of alumina microfiltration and ultrafiltration membranes is presented. The advantages and disadvantages of alumina membranes versus polymer membranes and other separation techniques are described.
The first test results of the Energieonderzoek Centrum Nederland-Hoogovens Groep membranes, used in oil-emulsion water separation are given.

The Hoogovens Groep approach for the industrial production of these membranes is highlighted.

EN 110 author present: 16.30 - 18.00

FABRICATION OF MILLIPOROUS CERAMIC SHAPES

A.P. Philipse, F.P. Moet, P.J. van Tilborg
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands

Ceramic shapes containing a continuous pore structure with pore sizes of the order of one millimeter are of considerable importance because of their divergent applications, for example as catalyst carriers and as filters for the high temperature filtration of liquids and gases. Fabrication techniques for such milliporous shapes are being investigated at our institute. An overview of these investigtions will be presented with emphasis on new developments in the preparation and application of ceramic foams and related structures.

EN 111 author present: 16.30 - 18.00

The Type Al_2O_3-ZrO_2 Ceramic Exloitation on the Engine Cam Follower.

J.Zemánková et al.,ÚVMV,Praha,ČSSR:

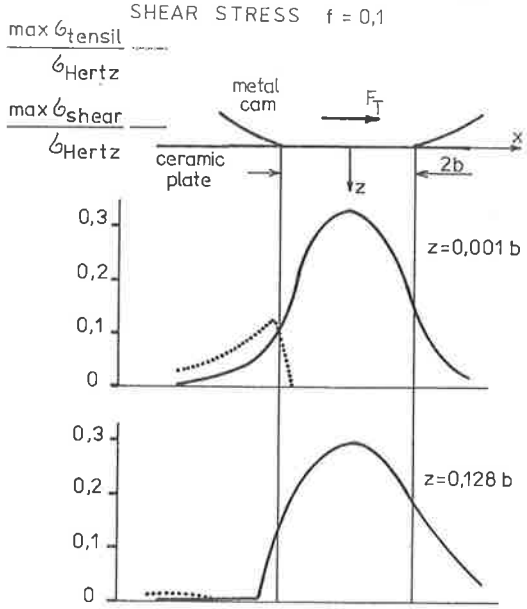
Intensive wear of the engine cam follower sorfaces decreases a life of this parts.
The high hardness and the wear resistance is from this reason used on the cam followers. The metal cam sliding in contact with a follower exerts except the normal load also the tangential force and consequently the tension stress.Therefore is necessary to chosse for a contact surface the ceramics with a good fracture thougliness. For the cam followers of ŠKODA 742 car was selected the Al_2O_3-ZrO_2 ceramic (fy DIAZ Turnov) with the following characteristics at a room temperature:
Youngs modulus of elasticity,E..350 MPa
4-point MOR, Rm .....580 MPa
Fracture toughness, K_{IC} ....4,5MPa $m^{1/2}$

The numerical computation of a stress (analytical solution / 1 / for a automotive loading system shous,dangerous part of a stress quickly decreases with the distance onder surface(Fig.1) it appears thet the decreas is higner with a lower coefficient of friction f in the system metal cam- ceramic follower surface.However, ther arises also

high perts of the shear stress,and they could play an important role in the mechanism of surface damaging. They could, with the shearing off, separate the parts of ceramics between the crachs going from the surface andupright to it. These crachs, tecanse of a low strain energy, cannot grow deeply under the surface. The mentioned imagination has been confirmed by the experimental watching on the cam followers of an engine of the ŠKODA-742.
The ceramical plates were fixed to the metal followers by means of the adhesive, and this trought some problems. Nevertheless , till the present time, these followers passed 4500 km of the road drive upon which the wear of the cam has been minimal and that of the ceramics was so small,thet it was impossible to measure.
The test continues up to this time.

References:
1. Richerson,D.W.-Finger,D.B.-Wimmer,J.M.:Analytical and ExperimentalEvaluation of Biaxial Contact Stress.Fract. Mech.of Cer,Vol.5,1983,p.163
2. Zemánková,J.-Novotná,J.-Vacek,R.-Ninger,V.: Keramické destičky zvedáků ventilů. Výzkumná zpráva ÚVMV Z-77/87, Praha 1987.

Fig.1.MAX. TENSIL STRESS AND MAX. SHEAR STRESS f = 0,1



EN 112 author present: 16.30 - 18.00

CERAMICS FOR HEAT-FLUX APPLICATIONS IN FUSION DEVICES

J.G. van der Laan, P. Groot
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands
M. Dvorak, M. Mack, ISOT-Dortmund, FRG

The in-vessel components of a fusion plasma experiment are exposed to high heat fluxes. For the Next European Torus (NET) the design heat loads are up to 0.5 MW/m² during normal operation. Heat fluxes due to off-normal events may have energy densities up to 10 MJ/m² in a period lasting 0.1-20 ms. An unprotected stainless steel vessel suffers from cracking, melting and erosion under such conditions.
For protection thick (0.5-1 mm) titanium carbide coatings are being developed in a joint programme of ISOT and ECN. Coatings have been produced by plasma spraying at atmosperic pressure (APS) and low pressure (LPPS). Microstructural analysis of these coatings includes Electron Probe Microanalysis (EPMA), X-ray diffraction, gas-chromatography, neutron activation analyses, texture analysis and optical and scanning electron microscopy. Thermo-mechanical evaluation includes thermal fatige tests and short pulse laser heat flux tests. Experimental results will be interpreted using a detailed numerical transient heat flow model. The performance of the coatings will be compared to those of dense monolithic titanium carbide and carbon materials. The latter are presently considered to be superior.

EN 113 author present: 16.30 - 18.00

Facilitated transport through molten salts immobilized in ceramic membranes.

J.L. Bakiewicz, K. Keizer, A.J. Burggraaf
University of Twente, Department of chemical Engineering, Laboratory for Inorganic Chemistry, Materials science and Catalysis.
P.O. Box 217; 7500 AE Enschede; the Netherlands

α- and γ-alumina membranes have been modified with low melting point salt ($LiNO_3$) and salt mixtures (KCl-CuCl). These salt (mixtures) are able to adsorb O_2 reversibly. Aim was creating a LIM (liquid immobilized membrane) in which a molten salt was captured in the pores and using this system for the separation of O_2 from an O_2/N_2 mixture.
In this contribution the conditions for and the preparation of liquid immobilized membranes based on porous alumina ceramics are presented.

EN 114 author present: 16.30 - 18.00

PRODUCT AND MOULD DESIGN FOR SANITARYWARE PRODUCTS BY NUMERICAL METHODS.

Schins*,W.[1], Smeets,M.[1], Dortmans,L.[2],
1) N.V. Koninklijke Sphinx, P.O. Box 1050, Maastricht, The Netherlands.
2) Centre for Technical Ceramics, P.O. Box 595, Eindhoven, The Netherlands.

Upon firing of cast sanitaryware products the simultaneously occurring processes of anisotropic shrinkage and visco-plastic flow result in large geometrical product distortions. Without having a tool for accurate predictions of dimensional changes available, product and mould design is principally based on iterative trial and error methods. Development times for moulds might be reduced considerably by using a Finite-Element-Modelling technique coupled with CAD-CAM equipment, a CNC fraising machine and a measurement unit for geometrical checks. In order to perform the necessary numerical calculations constitutive equations describing the material behaviour should be assessed. The Finite-Element software to be used should be able to combine both physical and geometrical non-linear behaviour under dynamical working conditions (transient thermo-mechanical loading).

EN 115 author present: 16.30 - 18.00

ZIRCONIA TOUGHENED CORDIERITE,

I. Wadsworth*, J. Wang and R. Stevens
School of Materials, The University of Leeds, Leeds LS2 9JT, England.

Zirconia-cordierite composites were fabricated by hot pressing cordierite and zirconia powders at 1350°C/20 MPa for 10 mins. Both the fracture toughness and fracture strength are enhanced by the zirconia addition. Such improvements are due to the stress-induced transformation toughening and residual stresses caused by the thermal expansion mismatch of the two phases. Microcrack toughening is unlikely to occur in the composite as a consequence of the large thermal expansion mismatch. The transformability of zirconia inclusions in cordierite matrix is higher than in an alumina matrix although the inclusions are rounded in morphology, as a result of the presence of a liquid phase at the hot pressing temperature.

EL 1 10.00

FERRITE MAGNETIC COMPONENTS AND MINIATURISATION
J.L. ROLLAND,
THOMSON - LCC Ferrites Dpt 21200 BEAUNE

Trends in soft Ferrite magnetic components are here examined from the miniaturisation point of view.

Compared to active and other passive components like capacitors, volume is still a main limiting factor for magnetic ones.

We shall try to compare the evolutions of different types of components, in a given electronic function, and connect this evolution to the progress in soft ferrite materials.

EL 2 10.20

WET CONSOLIDATION OF FERRITES PREPARED BY DIRECT PRECIPITATION, A. Noordermeer* and M.M.E. Vantilt.
Philips Research Laboratory Eindhoven
P.O.Box 80.000, 5600 JA Eindhoven, The Netherlands.

Wet chemically prepared ferrites were compacted, out of suspension by a combination of sedimentation and filtration.
The ferrite powders were prepared by a direct precipitation method. The particle sizes ranged between 0.05 and 1.0 µm depending on the process conditions and on the composition of the ferrite and had a dispersity of 20 to 25%.
Stabilization of the particles in the suspensions was realized by electrostatic and/or steric repulsion.
The effect of the electrostatic repulsion has been investigated with suspensions of different basicity using different hydroxides. Steric repulsion in these aqueous suspensions is introduced by using long chain amines. The effects, of the size of the counterion, of the pH, of the presence of small concentrations of a different electrolyte and of the particle size on the porosity and on the packing characteristics of the compact will be demonstrated. The size of the counterions has a significant influence on the density reached. Densities up to 63% were realized.
The effect of pure steric repulsion was studied by coating the ferrite particles with carboxylic acids of different chain length. Organic liquids with different dielectric constants and/or viscosity were used to stabilize the suspensions of these coated particles. The effect of these parameters and of the chain length on the porosity and on the packing will be discussed.
A comparison between the combination of electrostatic and steric repulsion, and steric repulsion only will be made.

EL 3 10.40

THE SOLID SOLUBILITY OF SILICA AND CALCIA IN MNZN-FERRITES, J.J. Roelofsma* and F. Kools,

Philips Components Div.,Corp.Innov.Mat.,Bdng. BE-2, 5600 MD Eindhoven, The Netherlands.

It is well known that silica and calcia have an important influence on the properties of MnZn-ferrites [1]. Previous investigations have shown clear enrichments of Si and Ca in the grain boundary region [2]. These enrichments may originate from a liquid grain boundary phase, or via the precipitation/segregation from solid solution. In this respect it is interesting to know the solid solubility of Si/Ca.
Samples of a MnZn-ferrite with different amounts of SiO_2 and CaO were presintered to the desired Fe^{2+} content, and to a grain size which allowed EPMA. Samples were then reheated, and soaked to allow dissolution of Si and Ca, and finally quenched in order to avoid segregation upon cooling. The solid solubility was derived from EPMA measurements (integral and local spot) and X-ray diffraction analyses.
The solid solubility of SiO_2 appears to be dependent upon CaO content and soaking temperature. Hence, at 1300°C, respective values are 0.05 wt% SiO_2 for zero CaO, and 0.02 wt% SiO_2 for CaO levels greater than 0.2 wt%.

[1] T.Akashi, Tr.Jap.Inst.Metals 2 (1961),171.
[2] L. Laval,J.de Phys.,Tome 47,(1986),C1-329.

EL 4 11.00

THE ROLE OF THE REFRACTORY ON THE SINTERING OF Li CONTAINING MgZn-FERRITE, J.G. Boerekamp
Philips Components, Corp. Innov. Mat., BE-222, 5600 MD Eindhoven, The Netherlands.

LiZn and MgZn-ferrites are used for high ohmic, soft magnetic applications. When sintered on refractory support materials (e.g. mullite or alumina), there is marked chemical reaction between ferrite and refractory. The nature of these reactions is investigated. Sintering of Li substituted MgZn-ferrite on mullite results in a deterioration of magnetic properties compared to those obtained for sintering on pure alumina refractory. The explanation for this deterioration is given by Ridgley et.al.[1]. However the quantity of Li that is lost during sintering appears to be mainly dependent on the specific refractory used. Whereas van Arkel et.al.[2] showed Li evaporation to occur at higher temperatures in water containing atmospheres, this study indicates that oxygen, rather than H_2O, atmospheres seem to influence Li loss.
In the mullite refractory, crystallization of Zn-aluminate occurs, and is enhanced by Li or Cu present in the ferrite. It appears that the liquid phase, which results from the presence of Li or Cu, accelerates the Zn loss.

1. D.H. Ridgley, H. Lessoff, J.D. Childress, J. Am. Ceram. Soc. 53(6), 304 (1970).
2. A.E. van Arkel, U. Spitsbergen, R.D. Heyding, Can. J. Chem. 33, 446 (1954).

EL 5 11.20

ULTRAFINE Mn,Fe AND Fe,Co SPINEL OXIDES PREPARED FROM MIXED CARBONATES, J.M. Jimenez Mateos, J. Morales and J.L. Tirado* Dept. Quimica Inorganica e Ingenieria Quimica. Facultad de Ciencias. Universidad de Cordoba. Spain.

Mn,Fe and Fe,Co mixed oxides prepared as powder or ceramic bodies are important materials for many applications. Recently, it was reported that ultrafine ferrites prepared by precipitation reactions sinter to almost theoretical density. In this work, the preparation and properties of ultrafine spinel oxides from mixed carbonates are studied.

Monophasic mixed carbonates were prepared by direct precipitation with $nCO_3^=$ solutions while passing CO_2. For the $Fe_{1-x}Co_x$ system, nine samples were prepared from x=0 to 1. The thermal decomposition of these carbonates in air at 300°C leads to single-phase spinels with decreasing the a unit cell for x higher than 0.377. The oxygen/metal ratio is higher for iron-rich samples that show a γ-Fe_2O_3 superstructure, found by electron microscopy studies. The oxides show small size of the coherently diffracting domains (7-20 nm), shown by X-ray line broadening analysis and electron microscopy. BET surfaces range from 40 to 80 m^2g^{-1}. When the carbonates are decomposed at 600°C, those samples with lower crystallite size and higher microstrain content (x=0.5-0.8) cannot be prepared as single phase products. A cation redistribution takes place leading to Co_3O_4 and $CoFe_2O_4$.

The spinel phases in the $Fe_{1-x}Mn_x$ system occur in a narrow temperature interval (350-400°C in air atmosphere). at higher temperatures other phases are detected, structurally related with α-Fe_2O_3 and α-Mn_2O_3. The spinel oxides show crystallite sizes of ca. 10 nm and an increasing cubic a parameter.

EL 6 11.40

INFLUENCE OF THE CERAMIC MORPHOLOGY ON THE NATURE OF THE ELECTRICAL PROPERTIES OF α-Fe_2O_3

J.P. BONNET*, M. ONILLON, C.V. SANTILLI

Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351, cours de la Libération, 33405 TALENCE Cedex, France.

Fine powders of weakly Na-doped α-Fe_2O_3 were obtained from precipitation of Fe^{3+} ions in aqueous solution, drying and calcination.

The properties of these powders depend strongly on the aging of the initial precipitate in the solution.

The ceramics obtained from fresh precursors - strongly agglomerated - are characterized by the presence of extended defects, the order of which increases as the sintering goes on. The p conductivity of these ceramics is mainly due to the presence of cationic impurities.

The steady appearance of localized defects occurs during the sintering period of aged precursors, weakly agglomerated. As these defects are associated to donor states, a predominant n-type conductivity is observed in the corresponding ceramics.

ELECTRONIC CERAMICS : NON-LINEAR RESISTORS

Thursday 22nd June; 10.00 - 12.20 — **Chairman : K.H. Härdtl (FRG)** — **Room : 0.1**

EL 7 10.00

GRAINBOUNDARY EFFECTS IN SEMICONDUCTING $BaTiO_3$,
S.B. Desu, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 24061, USA

Despite the large amount of work in trying to unravel the semiconducting behaviour of $BaTiO_3$ produced by reduction as well as valence doping, there is no comprehensive model which can explain all the observed phenomena. We propose a comprehensive model to explain our experimental results on lanthanide doped $BaTiO_3$ which is based on the interrelations between the dopant segregation, dopant incorporation and redox reactions. The model will be extended to account the published data.

The present model describes the effect of lanthanide concentration on the room temperature conductivity as well as on the grain size. It also explains the dependence of the critical lanthanide concentration, at which doped $BaTiO_3$ has highest room temperature conductivity, on the size of the lanthanide ion. The effect of process parameters are accounted in the model through the redox reactions that occur at the grainboundaries. Both the grainboundary barrier layer effects and PTCR phenomena will be explained using the model.

EL 8 10.20

STUDY OF MACROSCOPIC THERMAL STRESSES IN $BaTiO_3$ BASED PTC THERMISTORS, C. Dewitte *, J.-P. Michenaud and F. Delannay, Université Catholique de Louvain, Dépt des Sciences des Matériaux et des Procédés, PCPM - Réaumur, Place Sainte Barbe 2, B-1348 Louvain-la-Neuve, Belgium.

When PTC thermistors are subjected to a high inrush power, some of them fail by fracturing in two parts along a plane parallel to the electrodes. This failure mode is due to the formation of transient temperature gradients in the sample during self-heating.
Temperature gradients induce high thermal stresses, more especially as a result of the contraction of the lattice resulting from the ferroelectric-paraelectric phase transformation at the Curie temperature. Using a model that takes into account the electrical and physical properties of a PTC thermistor, we calculated the thermomechanical stresses in a PTC thermistor subjected to a high inrush power. We first compute the transient temperature distributions in a PTC disk using the finite difference method. We then map these temperature values to a grid and obtain the stresses using a finite element computation method. This enable us to evaluate the influence of the intrinsic properties of the PTC thermistor and of geometrical and cooling parameters on the temperature distribution and on the intensity and position of the maximum tensile stresses. These maximum stresses are probably responsible for the nucleation and/or propagation of cracks in the sample. The results of this computation are thus discussed with reference to the appearance of the experimental fracture surfaces.

EL 9 10.40

EFFECT OF DOPING WITH YTTRIUM IN $BaTiO_3$ BASED C.T.P. THERMISTORS,

P.Blanchart*, J.F.Baumard and P.Abelard,
UA CNRS 320 ENSCI Limoges 87065 France.

When doped with yttrium in the concentration range [0.1-0.4 mol.%] $BaTiO_3$ becomes a n-type semiconductor. A thin film of gold was evaporated onto the surface of disk samples. Measurement of the capacitance - voltage characteristic proves that a Schottky barrier is present at the interface. The derived free electron concentration appears to be much smaller than the doping level. EDS and microprobe investigations show that part of yttrium is present at some of the grain boundaries. The evolution with the amount of yttrium will be discussed.

EL 10 11.00

THE ROLE OF MgO DOPING ON ZnO VARISTORS ELECTRICAL BEHAVIOUR, A. Smith*, Y. Boyat, P. Abélard and J.F. Baumard,
E.N.S.C.I., U.A. CNRS 320, 47-73 Av. A. Thomas, 87065 Limoges Cedex France.

The I-V characteristics of ZnO varistors are highly non linear and can be described by the relation $I=KV^{\alpha}$. The coefficient of non linearity α is a figure of merit and is measured at 1 mA/cm^2. In the present work we examine the effect of various MgO contents on a ZnO varistor composition (i.e. containing 1 mol % MnO, 0.5 mol % Co_2O_3 and 0.5 mol % Bi_2O_3). We show that (i) a small grained ceramic can be obtained and consequently the threshold voltage can be adjusted by varying the percentage of MgO, (ii) the non linearity is increased ($\alpha \simeq 10$ for a composition without MgO, α reaches 20 by increasing the MgO content) and (iii) the leakage current is decreased.

EL 11 11.20

ZnO VARISTORS DOPED WITH ALKALINE -EARTH OXIDES, P.Q. Mantas* and J.L. Baptista,
Dep. Eng. Cerâmica e do Vidro e Centro de Cerâmica e do Vidro (INIC), Universidade de Aveiro, 3800 Aveiro, Portugal

ZnO varistors were prepared with different concentrations of either MgO, CaO, or SrO. The presence of these dopants in concentrations between 0.05 and 0.20 molar % accelerate ZnO grain growth. Electrical properties of the sintered varistors were measured from room temperature up to 160°C. It was observed that the V-I characteristics varied with the type and amount of dopant used. The measured electrical properties were used to calculate physical parameters of the electrical barriers present at ZnO - ZnO grain boundaries. We tried to correlate the variations in barrier heigth, concentration of ionized donors at the depletion layers, and concentration of acceptor states at the grain boundaries with the type and concentration of the dopant present in each case.

EL 12 11.40

RELATIONSHIP BETWEEN MICRO-PARAMETERS AND NONLINEARITY OF ZINC OXIDE VARISTOR -- A COMPUTER SIMULATION STUDY
Cao Ze-Chun* and Song Run-Sheng
Shanghai Univ. of Sci. and Tech.., Shanghai, 201800, China.

In the study of ZnO varistor,all theories are based on nonlinear behavior of single grain boundary (GB),but actual macroscopic device presents the additional problem of a random network of single GBs, each with somewhat different nonlinear behavior. Little or no progress has yet been made on the macroscopic system of random network.
In this presentation, effort is paid by means of computer simulation to predict the nonlinearity of the varistor starting from the measured d.c. GB I-V data. In the simulation, a parallel circuit with 40 branches, each consists of 100 series units is designed as the equivalent circuit for the random network. Each unit represents a GB between adjacent grains. A data base is established with d.c. GB I-V characteristics measured.The data are extracted randomly from the data base and distributed to the units. The calculated results is in good agreement with measured device performance.
Furthermore, relationship between micro-

parameters and the device nonlinearity is examined. This parameters include I-V characteristics of individual GB, diversity of breakdown voltage, resistivity of grain, fraction of " active " GB.
The results enable us to have a insight into the factors which influence the performance of ZnO varistor quantitatively, or at least semi-quantitatively. It seems that this approach could be also used to increase our understanding to another GB controlled electronic ceramics.

EL 13 12.00

NTC THERMISTORS OF HIGH RELIABILITY, A. Feltz*, J. Töpfer, F. Schirrmeister and M. Steinbrück, Department of Chemistry of the Friedrich Schiller Univ.,6900 JENA, GDR

The electrical properties of samples of different charges of $NiMn_2O_4$ ceramics are shown to reproduce temperature measurements absolutely with $\Delta T \leq \pm 0.1$ K. Provided that the sintering regime allows to prepare sufficient dense ceramic samples of highly reproducible grain size structure, such a result is accessible despite of the metastable state of the spinel structure of $NiMn_2O_4$ below 720°C showing partially an inversed cation distribution. Starting from mixed oxalate crystals the formation of a cubic metastable defect spinel at 350°C in air, e.g. of the composition of $Ni_{0.92}Mn^{III}_{1.20}Mn^{IV}_{0.64}\square_{0.24}O_4$, is found to be a suitable precursor which involves high sintering activity. In the low temperature range the phase diagram is completed by the cubic defect spinel phase $Ni_xMn_{3-x}O_4$ in the limits $1.67<x<0.90$. Electrical data and fatigue of $NiMn_2O_4$ are compared with $Mg_{2-x}Ti^{III}_{2x}Ti^{IV}_{1-x}O_4$ and $Mg_{1-x}Ti^{III}_{2-2x}Ti^{IV}_{1-3x}O_3$ ceramics whose structure involves definite occupation of the cationic sites. The values of activation energy and of the pre-exponential factor are discussed in terms of the polaron theory whose approach seems to be the better the larger the average bond distance and the lower the site symmetry of the oxygen ions is.

ELECTRONIC CERAMICS : CONDUCTING CERAMICS

Thursday 22nd June; 15.00 - 17.00 — Chairman : B.H. Steele (UK) — Room : 0.1

EL 14 15.00

PREPARATION AND SINTERING OF YTTRIA DOPED CERIA POWDERS

D.D. Upadhyaya, R. Gopalakrishnan, H. Schubert and G. Petzow

Max-Planck-Institut für Metallforschung, Heisenbergstr. 5, D-7000 Stuttgart 80, FRG

Ceria based ceramics are interesting candidates for the solid state electrolyte applications. The chemical purity and homogeniety, the essential requirements for these materials, can easily be met by employing the powders prepared by wet chemical process for the fabrication. In the present work, ceria doped with yttria (upto 8 mol per cent) powders were prepared from chloride precursors by two different routes, viz. coprecipitation as (i) hydroxides and (ii) oxalates and their subsequent thermal decomposition.

The powders derived from oxalates were fine and well sinterable. Whereas, the hydroxide derived powders were composed of large and hard aggregates, their compacts exhibited an expansion effect in the course of sintering.

The deleterious expansion effect and the microstructural features are discussed.

EL 15 15.20

PROPERTIES OF Ca-DOPED $LaMnO_3$.

M.Fandel, W.Schaefer and R.Schmidberger
Dornier GmbH,
D-7990 Friedrichshafen,West Germany

Lanthanum manganite ($LaMnO_3$) is a ceramic semiconductor. Partial substitution of Lanthanum by Calcium (or Strontium) dramatically influences the electrical and mechanical properties. As the specific conductivities can reach an order of magnitude of about 100 $\Omega^{-1}cm^{-1}$, Ca doped $LaMnO_3$ is a promising electrode material, especially for high temperature applications e.g. solid oxide fuel cells or electrolyzers.
The paper presents experimental investigations in the system $La_{1-x}Ca_xMnO_3$ where x ranges from 0.1 to 0.5. Electrical conductivity and thermal expansion are discussed as a function of temperature and Ca-content. It will be shown, that these materials have a good electrical conductivity in the temperature range from 20°C to 1000°C. Mechanical properties like bend strength and Young's modulus are also presented.

EL 16 15.40

CERAMICS FOR CARBONATE FUEL CELLS
S.B. van der Molen*, R. de Rooy,
E.J. Siewers and H. den Uil
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands

The ECN molten carbonate fuel cell (MCFC) programme started in 1986. The component research has been concentrated on the development and testing of porous ceramic components of different size. This paper describes the application of ceramic fabrication techniques for production of porous cell components.

Optimum electrical cell performance can be realized using highly porous electrodes, Ni-$LiCrO_2$ as anode and NiO as cathode material with a bimodal pore size distribution, large pores (4-8 µm) for the gas transport and small pores (≤ 1 µm) to guarantee the presence of electrolyte in the electrode. The ion conduction is obtained by sandwiching porous Al_2O_3/γ-$LiAlO_2$ matrix material (pores ≤ 1.0 µm) filled with an eutectic mixture of Li_2/K_2CO_3 between the electrodes.

Ceramic fabrication techniques including suspension preparation, tape casting, drying, roll compaction, milling and sintering appeared to be suitable to meet the porous component design requirements with these materials. Cell tests showed excellent performance of 900 mV at current densities of 160 mA/cm².

EL 17 16.00

INFLUENCE OF MICROSTRUCTURE ON ELECTRICAL AND MECHANICAL BEHAVIOUR OF SELECTED COMPOSITIONS IN THE Zr-Ce-Y-O SYSTEM,
N. Kahn, C.A. Leach*, B.C.H. Steele.
Centre for Technical Ceramics, Imperial College, London, SW7 2BP.

A variety of compositions in the ZrO_2 rich region of the Zr-Ce-Y-O system have been prepared using either commercially available powders or powder prepared by co-precipitation routes at Imperial College. Compositions have included tetragonal, cubic, and the two phase tetragonal/cubic region. Complex impedance measurements have enabled the bulk and grain boundary contributions to the total conductivity to be separated thus allowing interpretations to be made of the role of Y_2O_3 concentration and the relative proportions of tetragonal and cubic phases present. The mechanical properties are very dependent upon the type of microstructure developed during the sintering procedure, and features of the microscructure such as grain size, phase distribution, morphology of second phases etc., are very dependent upon the composition within the phase diagram. Some comments will be made about factors believed to influence the development of the different microstructures observed.

EL 18 16.20

CERAMIC SENSOR FOR DETERMINING CO/CO_2 RATIO IN ALUMINIUM ELECTROLYTIC CELL,
E. Proverbio* and R. Cigna,
Dip. ICMMPM, University of Rome, Italy

Continuous monitoring of electrolytic bath is one of the main problems in aluminium production. The knowledge of CO/CO_2 ratio in exhaust gas is connected to the control of current efficiency (CE) and therefore to the production efficiency of the electrolytic cell. A bibliographic research on the use of ceramic probes for determining CO/CO_2 ratio has been carried out. There are very few references in literature concerning the use of ceramic probes in aluminium industry: besides, since stabilized zirconia is the more used and tested material in other industrial activities, it was selected as starting material for an experimental probe. The probe was tested in laboratory in different gasous environment at high temperature. The probe was also tested in a bench cell of 5 KA in order to evaluate its behaviour in industrial conditions.
This study was made within a collaboration contract between Aluminia Spa and ENEA.

EL 19 16.40

CONCENTRATION POLARIZATION EFFECTS IN ZIRCONIA BASED ELECTROCHEMICAL PUMPS,
F.M.B.Marques*, J.A.L.Baptista, J.R.Frade, D.M.Sá, A.P.Carvalho, Universidade de Aveiro, 3800, Aveiro, Portugal.

Concentration polarization related to oxygen transport in the gas phase was studied as a funtion of temperature (800-1000ºC), oxygen content in the gas phase (0.1 - 100 Pa oxygen partial pressure), and gas flow rate. Oxygen electrochemical pumps consisted of CSZ tubes with porous Pt electrodes. When oxygen is electrochemically pumped from a low oxygen content gas mixture, limiting current densities are observed; these limiting current densities are nearly independent of temperature, proportional to the oxygen content in the gas mixture, and independent of the gas flow rate, within the experimental conditions. These results indicate that electrode porosity might play a dominant role in these polarization losses.

EL 20 10.20

SYNTHESIS OF ADVANCED DIELECTRIC MATERIALS.
Detlev Hennings, Philips Forschungslaboratorium Aachen, D - 5100 AACHEN, FRG

High quality dielectric ceramic powders, used for the manufacture of temperature-stable ceramic multilayer capacitors are nowadays largely produced by applying wet chemical preparation techniques. A number these new preperation routes, e.g. coprecipitation, sol-gel methods and hydrothermal synthesis are discussed at the example of ferro-electric $BaTiO_3$.

EL 21 10.40

RELAXOR MATERIALS OWING REPRODUCIBLE VERY HITH DIELECTRIC CONSTANTS, AND THEIR BEHAVIOUR UNDER A D.C. BIAS FIELD, J.M. Haussonne*, M. Le Cun ; P. Bourdois, G. Desgardin
C.N.E.T. Centre Lannion B, 22301 Lannion, France ; ISMRa, Laboratoire CRISMAT, 14032 CAEN, France.

A review of the literature points out many different results concerning the value of the dielectric constant of relaxor materials ; either one particular material is supposed to own many different dielectric constants, or some materials are characterized by surprisingly high constants. The work we present here shows that this is due to the fact that, at the end of the sintering cycle, other phases than the perovskite one can diffuse and segregate as a thin layer on the surface, calculation showing then that the resulting capacitance decreases drastically. Every relaxor material is able to own a very high dielectric constant, until the eventually present secondary phases stay in the bulk material.

EL 22 11.00

IONIC AND ELECTRONIC PROCESSES IN TITANATE CERAMICS UNDER DC VOLTAGE POLARIZATION.
Rainer Waser, Philips GmbH Forschungslaboratorium Aachen, Electronics Ceramics Group D - 5100 AACHEN, FRG

Due to the mixed ionic-electronic conductivity as well as the Maxwell-Wagner polarization of the grain boundaries dominates. The barrier character of grain boundaries will be discussed. In the long term regime, a concentration polarization of oxygen vacancies is observed. This de-mixing process leads to a local change of the defect equilibria an to an increase of the electronic charge carrier concentrations. As a result, dielectric components such as ceramic multilayer capacitors may suffer a resistance degradation which limits their life time. The technological relevances will be discussed.

EL 23 11.20

DIELECTRICS WITH CONTROLLED TEMPERATURE COEFFICIENT OF THE DIELECTRIC CONSTANT FOR MULTILAYER CAPACITORS WITH BASE METALL ELECTRODES.
W.Noorlander,
Philips Components, Bredeweg 10, 6024GG Roermond, The Netherlands.

Amongst the dielectrics for class 1 capacitors the zirconates were expected to be the most stable with respect to the influence of the firing atmosphere on the dielectric properties. $SrZrO_3$-$SrTiO_3$ forms a continuous series of solid solutions with a gradual change in structure from orthorhombic for $SrZrO_3$ to cubic for $SrTiO_3$. With increasing $SrTiO_3$ content the dielectric constant increases from 35 to 300 and the temperature coefficient of the dielectric constant decreases from +150 to -3000 ppm/°C.
MnO proves to work very well as a flux for alkaline earth zirconates. The powder morphology, the amount of flux and the sintering range are interrelated. The influence of the MnO content up to 6.5 mol % on the dielectric properties has been investigated. Except for the insulation resistance there is little difference between the dielectric properties.
The influence of firing in an oxidizing and a reducing atmosphere on the dielectric properties has been investigated. Multilayer capacitors with Pd and Ni electrodes were compared. With Pd the temperature coefficient proved to be more negative and in the case of Ni there is a more pronounced increase of the equivalent series resistance as a function of the frequency. A possible explanation of the latter is found in the magnetic properties of Ni.

EL 24 11.40

MICROSTRUCTURAL DEVELOPMENT AND MICROWAVE DIELECTRIC PROPERTIES OF SOME ZIRCONIUM TITANATE CERAMICS, F. Azough and R. Freer*, Materials Science Centre, University of Manchester/UMIST, Grosvenor Street, Manchester, M1 7HS, U.K.

Zirconium titanate is a temperature stable dielectric suitable for ceramic capacitors, and its solid solutions are of technological interest as dielectric resonators for microwave devices.

At a temperature near 1200°C $ZrTiO_4$ undergoes a phase transition characterised by a change of cation ordering and a change in length of the longest cell parameter. In order to clarify the structural differences between the 'high temperature' and 'low temperature' forms we have performed TEM studies of specimens sintered at a single temperature and cooled at different rates. The paper will discuss the development of cation ordering, modulated structures and precipitates in $ZrTiO_4$. An attempt will be made to relate changes in microwave dielectric properties to microstructural modifications.

EL 25 12.00

CRYSTALLIZATION OF FINE PLZT POWDERS DERIVED FROM NITRATE SOLUTIONS AT LOW TEMPERATURE.
Yoshio Yoshikawa* and Kaoru Tsuzuki
Nihon University, Koriyama 963, Japan

Fine homogeneous PLZT powder which was prepared by hydrolysis of an aqueous nitrate solution with ammonia gas exhibited a high reactivity on calcination. Kinetics of crystallization were isothermally and thermoanalytically studied between 400°C and 600°C, using XRD and DTA, respectively. The isothermal crystallization process is best fitted to first-order equation for a random nucleation-controlled system on a large number of small particles, with an activation energy of 297kJ/mole. Characterization by X-ray diffraction line broadening and BET surface area show such a microstructure that the powder is agglomerated to 60 nm particle consisted of 20 nm subunits at the temperature range. A single nucleus generates on the subunit and grows within the subunit. The activation energy by means of non-isothermal DTA techniques is found to be in agreement with that obtained from the isothermal process.

EL 26 12.20

MICROSTRUCTURE OF MODIFIED LEAD TITANATE CERAMICS, H.K. Schmid, Materials Science and Technology Division, CSIR, Pretoria 0001, RSA

The structure of ferroelectric domain boundaries and grain boundaries in modified lead titanate ceramics was studied by means of conventional and analytical transmission electron microscopy (TEM). Transformation strains brought about by the cubic → tetragonal phase transformation at the transition from the paraelectric to the ferroelectric state are relieved by twinning on {110} planes, where each twin variant is a single ferroelectric domain. The domain width ratio at equilibrium as observed by TEM is in accordance with theoretical considerations of a martensite-type transformation. Switching of 90^0-type {110} twin-related domain walls during poling of the ferroelectric ceramics in an external electric field was confirmed by the TEM studies.

Evidence was found for the existence of vitreous intergranular phases situated in small pockets at triple grain junctions and in films at grain boundaries approximately 1 nm thick. The chemical compositions of the various phases were determined by means of EDS analysis with high spatial resolution. Implications of the segregation behaviour of modifiers and impurities present in the starting materials on mechanical and electrical properties are discussed.

EL 27 author present: 09.30 - 11.00

SOL-GEL PREPARATION OF COMPLEX PEROVSKITE CERAMICS, F.Chaput and J.P.Boilot,Groupe de Chimie du Solide, Laboratoire de Physiquede la Matière Condensée, Ecole Polytechnique, 91128 Palaiseau Cédex (FRANCE)

The chemical processing of alkaline earth perovskite powders $Ba_xSr_{1-x}(Ti_uZr_vHf_w)O_3$ (with $0 \leq x \leq 1$ and $u+v+w=1$) by an alkoxide-hydroxide route makes possible:

-The synthesis of the perovskite structure at very low temperature (60-150°C).

-The preparing of dense bodies with fine grained uniform microstructure by sintering at low temperature without prior calcination.

Concerning the pure barium titanate, powders compact to near theoretical density (1-1.5µm grain size at 1150°C) exhibit a high dielectric constant (≈5500) and a low dissipation factor (<3%) at 20°C.

EL 28 author present: 09.30 - 11.00

BARIUM TITANATE MONOLITHIC GELS, F.Chaput and J.P.Boilot,Groupe de Chimie du Solide, Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, 91128 Palaiseau Cédex (FRANCE).

Pure and doped barium titanate monolithic gels have been prepared by hydrolysis of a mixture of titanium alkoxide and acetic acid with an aqueous solution of barium acetate. As previously observed by S.Doeuff, I.R. experiments show that the titanium alkoxide is chemically modified by the bridging acetate ligands which partially substitute the OR groups and increase the coordination number of titanium atoms. This allows to stabilize the titanium precursor and consequently to avoid the precipitation of titanium oxide. By using the monomeric $Ti(O^iPr)_4$ precursor, barium titanate films have been prepared by the dip-coating technique and the optically clear gel turns in the perovskite phase at 800°C.

EL 29 author present: 09.30 - 11.00

BARIUM TITANATE PROCESSING: EFFECT OF RAW MATERIAL NATURE ON THEIR SYNTHESIS AND SINTERING BEHAVIOUR. J.F.Fernandez*, P.Durán, C.Moure. Instituto de Cerámica y Vidrio (CSIC), Electroceramic Department, Arganda del Rey, 28500 Madrid, Spain.

The solid state formation of barium titanate have been studied with respect to the physical and chemical characteristics of the TiO_2 and $BaCO_3$ starting materials. Special attention has been paid to the impurity levels and particle morphology. The effect of processing parameters such as milling media, calcining temperature and time, and sintering schedule have been also determined.

In a general mode, small particle sizes of starting materials lead to lower synthesis temperatures and times, but a strong difference in the sizes of TiO_2 and $BaCO_3$ causes an inhomogeneous reaction, with formation of agglomerates and other phases as Ba_2TiO_4, which only disappears at higher temperatures. As the purity of $BaCO_3$ increases, the synthesis temperature decreases, which leads to lower particle sizes of the obtained $BaTiO_3$.

EL 30 author present: 09.30 - 11.00

SYNTHESIS OF n-DOPED TITANATES BY PRECIPITATION OF COMPLEXES. P.H. Duvigneaud*, M. Gilbert, M. Promel. Service de Chimie Industrielle et Analytique, Université Libre de Bruxelles, 1050 Bruxelles, Belgium.

A powder suitable for PTC applications has been synthesized by precipitating a Ba(Pb, Ca, La) TiO_3 precursor in aqueous solution. The organic salts of the relevant cations were dissolved and complexed in alkaline medium. The precipitation arises from the reaction between H_2O_2 and the complexes when the solution is heated. The solid and solution were carefully analysed as a function of time and temperature. The particulate size distribution was studied at different stages of the thermal treatment by laser granulometry. Pellets were sintered and electrically tested.

EL 31 author present: 09.30 - 11.00

THE SYNTHESIS AND PROPERTIES OF $Cd_4Sb_2O_{11}$ ELECTRONIC CERAMICS,

J. L. Zhang* and B. R. Li
Huazhong Univ. of Sci. and Tech., Wuhan, P.R.C.

A new cadmium antimony oxide electronic ceramics $Cd_4Sb_2O_{11}$ which possesses unusual electrical conductivity and oxygen sensitivity performances is obtained using CdO and Sb_2O_5 as raw materials. The thermal analysis(DTA and TG), chemical analysis and high temperature X-ray diffraction analysis on $Cd_4Sb_2O_{11}$ semiconductive ceramics are carried out. The synthesis and phase transformation of $Cd_4Sb_2O_{11}$ are discussed. The results indicate that the synthetic reaction between CdO and Sb_2O_5 begins at 1000℃ and finishs at 1200℃. A reversible structural phase transformation takes place in $Cd_4Sb_2O_{11}$ at about 240℃ and the high temperature phase belongs to a higher symmetry. The phase transformation temperature of heating and cooling processes are 246℃ and 228℃ respectively. The mechanism of electrical conductivity in different temperature regions and associated defect structure are analyzed. The activation energy and mobility of carriers are calculated.

EL 32 author present: 09.30 - 11.00

STRUCTURAL STUDIES OF PMN CERAMICS, P. Bonneau, E. Husson; A. Morell

Laboratoire de Chimie Physique du Solide, URA CNRS D0969, Ecole Centrale de Paris, 92295 Chatenay-Malabry Cedex, France; THOMSON-CSF, Laboratoire Central de Recherches, Domaine de Corbeville, 91401 Orsay Cedex, France.

Lead magnesium niobate $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) is one of the most interesting relaxor. At room temperature it has the ABO_3 cubic perovskite structure ($a \simeq 4$ Å). Its Curie temperature is about -7°C; the low-temperature phase is rhombohedral and the ferroelectric transition, which is diffuse occurs in a temperature range of several tens of degrees. A very precise X-ray study between 297 and 1023 K shows Pb and Nb atom shifts from their crystallographic sites. For T> 600 K the Nb atoms are no more located at any local disordered positions and for T > 900 K the Pb atoms are also on the special positions of the ideal cubic structure. At low temperature, the powder patterns show the presence of the cubic phase at temperatures much lower than the Curie point. PMN exhibits a polar glass behaviour. These results are confirmed and completed by a neutron diffraction study. On the other hand, the electron diffraction patterns reveal (i) the existence of superstructure spots corresponding to a fcc cell of ≃ 8 Å parameter and attributed to a local 1-1 cation ordering on the B site of the perovskite, (ii) the existence of diffuse streaks due to atomic shifts in the (110) planes of the structure.

EL 33 author present: 09.30 - 11.00

FERROELECTRIC CRYSTALS BY GLASS CRYSTALLIZATION, M.Todorović , L.Radonjić

Faculty of Techonoloy, 11000 Belgrade, Faculty of Technology, 21000 Novi Sad, Yugoslavia

Lithium niobate is of interest because of its increasing application in electrooptic and surface-acoustic devices. Several methods of preparing lithium niobate films have been reported: 1) epitaxial growth from melt, 2) liquid-phase epitaxial de eping process and, 3) rf-sputtering.
In this paper was examined the crystallization of $LiNbO_3$ and its solid solutions with $LiTaO_3$, from glassy matrix. This method of preparing ferroelectric crystals has many advanteges over the mentioned one. Transparent glass ceramics containing $LiNbO_3$ and its solid solutions ferroelectric crystals have been obtained from different glass compositions. In the heat treatment process intensive phase separation occurred in all systems, followed by nucleation of LiNbO and Li $(Nb,Ta)O_3$ solid solutions, in the glassy matrix. Transparent glassy sample after quen ching the melts could be prepared only for specific B/N ratio. It was found that transparent $LiNbO_3$ glassy sample could be obtain for this molar ratio higher than one, and for solid solutions, about one. Optimal heat treatment temperature for the crystal nucleation was determined for all samples. The optimal temperature is that temperature of crystal nucleation in glassy matrix when the sample is still transparent.

EL 34 author present: 09.30 - 11.00

SYNTHESIS, SINTERING AND DIELECTRIC MEASUREMENTS OF PMN - PT CERAMIC MATERIALS,

Antoinette MORELL, THOMSON-CSF / LCR, B.P. 10, 91401 ORSAY Cedex, FRANCE

Solid-solutions between lead magnesium niobate $Pb\ Mg_{1/3}\ Nb_{2/3}\ O_3$ (PMN) and lead titanate $Pb\ Ti\ O_3$ (PT) are synthesized according to the columbite route. Sintering parameters (temperature, time, atmosphere) are studied. The dielectric characteristics of the sintered pellets are measured as a function of temperature (between 50 and + 150°C) and frequency (between 1 KHz and 10 MHz). Among all the prepared compositions, many are Z5U ceramic materials. As an example, at 20°C and 1 KHz, one composition has a dielectric constant of 21000 and a loss tangent factor of $2.1\ 10^{-2}$, the sintering taking place at 925°C for 4 hours in air atmosphere. Micrographs of the sintered materials are presented.

EL 35 author present: 09.30 - 11.00

HUMIDITY MEASUREMENT AND CONTROLLING IN DRYING PROCESSING

Robert Spichiger

rotronic ag, P.O.Box, 8040 Zurich, Switzerland

Capacitive sensors with polymere dielectric material

Humidity sensors based on plastic polymers have a much better longterm stability than sensors that use non organic dielectric materials such as aluminum oxide, titanum oxide or tantalum oxide.
Polymer sensors can be used in the range of -60°C to +30°C Dew Point, at temperatures up to +100°C, or in the range of 0 to 100%RH, at temperatures from -80°C to +200°C.
The polymers used in the sensors have a high resistance to contaminants, including organic solvents. Selection of appropriate materials for the electrodes further contributes to sensor resistance.Typically, the sensors are not destroyed by condensation and do not require a new calibration after drying.

EL 36 author present: 09.30 - 11.00

BOROPHOSPHOSILICATE GLASS AS AN INTERLEVEL DIELECTRIC,

S.B. Desu, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 24061, USA

Due to their low temperature flow properties, borophosphosilicate glasses (BPSG) are extensively used as an interlevel dielectric, isolating the gate electrode from source/drain electrodes, in VLSI devices. To process reliable devices, it is very important to understand the effect of process parameters on the properties of BPSG. Electron microprobe, TEM and AES analyses are used to study the structural and compositional changes in the BPSG during the fabrication of 1 Mb dynamic random access memory devices. The BPSG films are deposited around 450°C, by low pressure chemical vapor deposition using the oxidation of silane, phosphine and diborane mixtures.

As-deposited films are highly moisture sensitive and the boron and phosphorus can be leached out by water. High temperature densification stabilized the properties. During the gettering process of the devices, significant compositional and structural changes in BPSG were observed. The phosphrous concentration was enriched and the boron concentration was depleted near the surface region of the glass. The thickness of this surface depends on the temperature and time of the gettering process and also on the original boron concentration of the BPSG. In some cases crystallites of the composition BPO_4 were formed.

EL 37 author present: 09.30 - 11.00

SINTERING AND DIELECTRIC PROPERTIES IN THE SYSTEM $BaTiO_3$ - $CaZrO_3$,

D. Suvorov, D. Makovec, D. Kolar, "Jožef Stefan" Institute, Ljubljana, Yugoslavia

Reaction sintering in the title system leads to formation of (Ba, Ca)(Ti,Zr)O_3 solid solution and $CaTiO_3$ intergranular phase. Characteristics of non-equilibrium structure depend on preparation conditions. Solid solution formation shifts the Curie temperature whereas intergranular phase controls the grain growth during sintering. By optimisation of compositions and by proper choice of preparation methods, good quality ceramic dielectric materials can be made.

EL 38 author present: 09.30 - 11.00

OPTIMIZATION OF PZT POWDERS. QUANTIFICATION BY PHYSICAL METHODS OF GRINDING POLLUTION. EFFECTS ON SINTERING AND CERAMIC PROPERTIES, R. Makala*, M. Descamps, B. Thierry ; C.R.I.T.T. Céramiques Fines Techniques, 59600 MAUBEUGE, FRANCE.
G. Palavit, P. Vast ;
Laboratoire Chimie Appliquée, U.S.T.L., 59655 VILLENEUVE D'ASCQ, FRANCE.

After calcination, PZT powders have low physical properties which decrease electrical performance. So, to improve them, attrition grinding has been studied through various parameters as grinding time, rotation speed, dry material rates. The evolution was measured by different analytical methods : grain size distribution, specific surface, S.E.M. and X-Rays. The pollution has a great influence on powder quality. We tried to control this phenomenon by qualitative and quantitative analysis : an original method was developed by using density measurement with gas auto-pycnometer. Optimized powders obtained by this way allowed us to study sintering.
Various time and temperature cycles were made to define best conditions to obtain ceramics without open porosity to be densified by H.I.P. So, we get ceramic densities upper to 99% with physical and electrical properties improved.

EL 39 author present: 09.30 - 11.00

EFFECTS OF MICROSTRUCTURE ON THE MECHANICAL AND ELECTRICAL PROPERTIES OF Yb-TZP CERAMICS.

M.González*, C.Moure, J.R.Jurado, and P.Durán.
Instituto de Cerámica y Vidrio (CSIC), Electroceramics Department, Arganda del Rey, 28500 Madrid, Spain.

Phase relationships in the ZrO_2-rich region of the ZrO_2-Yb_2O_3 system was studied. Fine-grained sintered samples Yb_2O_3-containing approximately 100% tetragonal zirconia (2-3 mol% Yb_2O_3) exhibited good mechanical properties (K_{IC} 8-10 $MPam^{1/2}$). However those samples obtained by a sintering-precipitation process (3 mol% Yb_2O_3) showed a mechanical behaviour strongly affected by the microestructural development. In order to know its applicability as a high temperature solid electrolyte the electrical properties of both kind of samples were studied. Finally, the low temperature degradation of Yb-TZP ceramics was also studied.

EL 40 author present: 09.30 - 11.00

MICROSTRUCTURE AND DYNAMIC BEHAVIOUR OF PZT OBSERVED IN A HIGH RESOLUTION ELECTRON MICROSCOPE,

L.A.Bursill[1], Peng Ju Lin[1] and J.R. Sellar

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[2] Research Group, ICI Australia Operations P/L., Newsom Street, Ascot Vale, 3052, Victoria Australia

High resolution electron microscopy has been undertaken to obtain images of PZT (lead zirconate titanate) made from Z-TECH EF-SUPER grade zirconia powder, with varying amounts of nickel niobate additive. Under favourable conditions, the 400kV accelerating voltage of the JEOL 4000EX electronmicroscope permits ultrahigh resolution of fragments of this material, allowing a wide variety of microstructure and behaviour to be observed. These include the gross morphology, domain structure and twinning of small grains, and phase analysis of very small crystals. As the 400kV electron beam current is raised, however, dynamic domain switching becomes apparent and real-time surface modification may be observed if the electron microscope is operated in profile-analysis mode.

EL 41 author present: 09.30 - 11.00

EFFECT OF MICROSTRUCTURE ON THE DIELECTRIC PROPERTIES OF LEAD MAGNESIUM NIOBATE CERAMICS

Dong Heon Kang and Ki Hyun Yoon*

Department of Ceramic Engineering,
Yonsei University, Seoul, Korea

(Abstract)

The effects of microstructure on the dielectric properties, such as dielectric constant, dissipation factor and dielectric hysteresis characteristics, of lead magnesium niobate (PMN) ceramics have been studied as a function of the amount of excess MgO. The dielectric constant and remnant polarization increased with increase in grain size, and then decreased with the addition of grain growth inhibitator. The diffuseness coefficient showed a tendency nearly reverse to that for the dielectric constant and remnant polarization change.

EL 42 author present: 09.30 - 11.00

A TEM STUDY OF Sb-DOPED PZT CERAMICS,

M.Pristavec, M.Kosec and V.Kraševec, "J.Stefan" Institute, University of Ljubljana, Ljubljana, Yugoslavia

Transmission electron microscopy of Sb-doped $Pb(Zr_{0.52},Ti_{0.48})O_3$ ceramics revealed extended defects within grains and several secondary phases such as an Sb containg pyrochlore, PbO and higher Sb-oxides along the grain boundaries. Using BF-DF imaging criterion the extended defects were identified as antiphase boundaries (APB´S). It was supposed that these APB´S are formed in the early stage of PZT-grain formation by incorporation of the Sb^{5+} $\boxed{Pb}$ Sb^{5+} complex into the perovskite lattice.

EL 43 author present: 09.30 - 11.00

HIGH SENSITIVE PZT CERAMICS AND ITS APPLICATIONS

Jia qi Shen, Xiao quang Wang, Zheng he Shen

The principle of multiple substitutions in the A-site defined by L.Eyaud etal. was developed. The authors simultaneously added BaO,SrO and the third substituting oxides of La2O3 or Bi2O3 etc. to a PZT composition to obtain higher sensitive piezoceramics (Kp=0.68, d33= 700.10^{-12}C/N, g33= 40.10^{-3} Vm/N, and E33=2000) than the materials with only BaO,SrO substituted. This kind of high sensitive PZT ceramics has been used for making pick-up elements, ultrasound air transducers, sound generators, telephone microphone and ultra sonic Doppler diagnostic transducer etc. satisfactory results.

EL 44 author present: 09.30 - 11.00

THE BAND STRUCTURE MODEL OF $Pb(Zr,Ti)O_3$,

T. Kala, Research Institute of Electrotechnical Ceramics, Hradec Králové 500 64, Czechoslovakia.

The band structure model of $Pb(Zr,Ti)O_3$ polycrystalline solid solutions modified by MnO_2 and La_2O_3 oxides is proposed on the basis of diffuse reflectance and EPR spectra measurements.

The model is discussed in the face with some physical properties of $Pb(Zr,Ti)O_3$, namely electrical conductivity, pyroelectric effects, time and temperature coefficients of piezoelectric rezonators frequencies and other.

EL 46 author present: 09.30 - 11.00

PYROELECTRIC PZT-CERAMICS,

J.P.Hahn*, P.Bohac, R.Deyeler; G.Kostorz; M.Forster, S.Strässler; A.Martin, B.Barbisch; AFIF,ETH-Hönggerberg, CH-8093 Zürich; IAP,ETH-Hönggerberg, CH-8093 Zürich; Cerberus AG, CH-8708 Männedorf; Schaffner AG, CH-4708 Luterbach; Switzerland

An improved ceramic process was developed for the preparation of doped PZT ceramics suitable for pyroelectric applications. The effects of the different process parameters - mixing, calcining, grinding, spray drying, pressing, sintering, poling - on the physical properties of PZT ceramic containing MnO_2 were investigated. It was found that the figure of merit of pyroelectric detector material is sensitively affected by the stoichiometry, Zr/Ti-ratio and doping of the specimens. The variations of the pyroelectric properties within the system lead zirconate - lead titanate and the effects of additives and stoichiometry are reported and discussed.

EL 47 author present: 09.30 - 11.00

EFFECT OF SrO ADDITION ON THE ELECTRICAL AND THERMAL PROPERTIES OF $LaMnO_3$

J.Palma, P.Durán, J.R.Jurado, C.Pascual*.
Instituto de Cerámica y Vidrio (CSIC), Electroceramics Department, Arganda del Rey, 28500 Madrid, Spain.

Strontium-doped lanthanum manganite is a good electronic conductor and an excellent candidate to be used as electrode in SOFCs. Compositions of strontium-doped manganite, $La_{1-x}Sr_xMnO_3$ ($0 \leq x \leq 0.5$) were prepared by using MnO, La_2O_3, and $SrCO_3$ as starting materials and by the citrate method. Phase evolution, thermal expansion coefficient, and electrical conductivities were characterized as a function of density, Sr/La ratio and temperature.

EL 48 author present: 09.30 - 11.00

EFFECT OF CeO_2 and Al_2O_3 PARTICLES ADDITIONS ON THE ELECTRICAL PROPERTIES OF PSZ CERAMICS

M. T. Hernández, P. Recio, J. R. Jurado and P. Durán
Electroceramics Departament
Instituto de Cerámica y Vidrio
Arganda del Rey, MADRID (Spain)

ABSTRACT

AC impedance complex plane spectroscopy have been used to characterize electrically Y_2O_3-PSZ-CeO_2/Al_2O_3 composites. Small amount of Al_2O_3 (10% wt) particles are incorporated to the PSZ powder which contains concentrations of 0-2 mol% of CeO_2. A wet-chemical route to coprecipitate all the components heve been used to achieve good alumina particles disperssion.

Al_2O_3 dispersed particles reduce considerably the T-M transformation of PSZ and also increase its electrical conductivity. When small quantities of CeO_2 are added the electrical and ageing behaviour favourably change.

EL 49 author present: 09.30 - 11.00

ELECTRICAL AND MECHANICAL PROPERTIES OF Y_2O_3-TZP-CeO_2-Al_2O_3 COMPOSITES

M. T. Hernández, J. R. Jurado F. Capel, P. Durán
Electroceramics Departament
Instituto de Cerámica y Vidrio
Arganda del Rey, MADRID (Spain)

Yttria-doped tetragonal zirconia solid solution (TZP) with appropiate amount of CeO_2 prevent the typical transformation T-M and consequently its mechanical degradation at temperatures ranged 200º at 300ºC. On the other hand Al_2O_3 dispersed particles trends to improve the mechanical and ageing properties of TZP. In this work compositions in the ZrO_2-rich region of the ZrO_2-Y_2O_3-CeO_2 system have been studied, and composites materials of Y_2O_3-TZP-CeO_2/(Al_2O_3) have been also prepared. AC impedance spectroscopy, ionic domain, mechanical properties, ageing, and microestructure are the parameters used to characterize sintered bodies.

High electrical conductivity, grain boundary electrical resistance reduction, excellent ageing behaviour and promising mechanical properties as a function of temperature, are the results wich allowing to consider those composites as a good solid electrolyte candidate for fuel cell reactors and structural applications.

EL 50 author present: 09.30 - 11.00

CONDUCTIVE $LiFe(Mg)O_2$ CERAMICS FOR MOLTEN CARBONATE FUEL CELLS

J.P.P. Huijsmans* and S.B. van der Molen
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands.

$LiFe_{.97}Mg_{.03}O_2$ is used as an alternative cathode material in molten carbonate fuel cells (MCFC) at ECN. The powder is obtained from a mixture of appropriate amounts of Fe_2O_3, Mg-acetate and excess Li_2CO_3 (Li/Fe = 1.03) which is heated at 650°C for 17 hours under MCFC cathode gas conditions (30% CO_2 in air).

To obtain the required microstructure for MCFC cathode electrodes, i.e. 70-80% porosity, mean pore size (mps): 9 µm and 80% pore range of 5-18 µm, various amounts of activated charcoal together with a binding medium are mixed with $LiFe_{.97}Mg_{.03}O_2$ powder. Pressed disks are sintered for 4 hours at 850°C and 1 hour at 950°C in cathode gas. Depending on the amount of activated charcoal used, the sintered material shows an open porosity of 30-86% and a mps of 0.5-24.6 µm. Conductivity of dense $LiFe_{.95}Mg_{.03}O_2$, measured in cathode gas at 650°C, is relatively low: .01-.02 $S \cdot cm^{-1}$, whereas .05 $S \cdot cm^{-1}$ is a minimum requirement. However, preliminary results from small cell (3 cm^2) experiments indicate that the presence of molten carbonate positively influences conductivity.

EL 51 author present: 09.30 - 11.00

MEMBRANE-BASED THIN-LAYER SOFC COMPONENTS
J.P.P. Huijsmans* and S.B. van der Molen
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands.

Membrane-based thin-layer technology is developed with the aim to improve efficiency and to reduce ohmic and polarisation losses of SOFC reactors. The main objective for the first phase of our research program on membrane-based thin-layer solid oxide fuel cell (SOFC) technology was the development of a supported air-electrode as a conductive substrate for thin electrolyte structures.

Integration of support material (CSZ or TSZ) and air-electrode ($La(Sr)MnO_3$) is achieved by a film-coating technique. This technology is based upon procedures for making gas separation ceramic membranes by ECN. For application of a thin, dense electrolyte structure (YSZ) on top of the film-coated porous air-electrode, the pore size distribution of the latter may, eventually, further be modified by slip casting a ceramic layer on top of the air-electrode.

The techniques applied strongly depend on the properties of the suspenions used. Powder morphology of $La(Sr)MnO_3$, an important input parameter for suspension technology, was studied in relation to synthesis conditions, anion reactant composition and Sr concentration. Firing experiments were carried out to investigate sintering behaviour of individual components and composites.

EL 52 author present: 09.30 - 11.00

SINTERING AND DIELECTRIC PROPERTIES OF SiO_2-DOPED $BaTiO_3$ CERAMICS.
J.F.Fernandez*, P.Durán and C.Moure.
Instituto de Cerámica y Vidrio (CSIC), Electroceramic Department, Aranda del Rey, 28500 Madrid, Spain.

Barium titanate powders doped up to 1.0 weigth of SiO_2 were sintering between 1150ºC and 1250ºC for times ranging from 1 to 10 h. The sintering process was followed by a dilatometric method. The microstructute was studied by means of SEM. Dielectric parameters, such as the dielectric constant and losses were also determined.
For low amount of SiO_2, the maximum density temperature decreases from 1225ºC to 1175ºC. The end-point sintering temperature lowers to 1200ºC for 0.4% doping. The dielectric constant increases for 0.1% and lowers for higher contents for doping above 0.4% weight, a two-step sintering process was appreciated. The maximum density values lower significatively, and the end-point temperature raises. A second phase, barium titanium silicate, appears. Liquid phase sintering seems to be the dominant mechanism for those doping levels.

EL 53 author present: 09.30 - 11.00

THE ELECTRICAL DURABILITY OF THE FERRO-ELECTRIC CERAMICS (THE SYSTEM ANALYSIS),
Y.G.Sindeyev*, V.E.Yurkevich**
* Rostov on Don State Pedagogical Institute, 344717, Rostov on Don, USSR
**The Youth Initiative Company, 344717, Rostov on Don, USSR

The electical durability of ferro-electic ceramics depends on many factors: temperature and shape of the sample and electrodes, tension change frequency, tension amplitude growth rate etc. The influence on the ceramics electrics durability most of above-mentioned factors does not yield to the certain quantitative value because of the present theories' defects and non-complect experimental data' influences.

The attempt to carry out the system analysis of the problem "The ferroelectric ceramics electrical durability" was made in the present parer. The main part of this article is devoted to the research of the idea formation about the ferroelectrical ceramics electrical durability.

In this part of the article various factors, influencing the ferroelectrical ceramics electrical durability in the different technological stages of its structure)monocrystal, powder, ceramics) have been discovered by the authors on the base of the large amount of the experimental and theoretical papers' analyses.

Based on these factors, the authors have formulated the influesce descriptions' system on the electrical durability size of the ferrielectrical ceramics element, which permit to obtain the diserable electrical durability, while changigng the necessary parameters on the different stages of the sample making.

To a certain extent, the obtained results one can consider as a base for the phenomenological forecasting and control of such important physico-technical characteristics of ferroelectrical ceramics as electrical durability. Besides, it is essentially, that the obtained complex of results could be summarized (taking into account the internal structure peculiariries of the specific material) on the whole set of ferroelectrical materials.

EL 54 author present: 09.30 - 11.00

FREQUENT DEPENDED CAPACITY CERAMICS CONDENCERS,

Y.I.Goltzov*, L.A.Shpak*, V.E.Yurkevich*,**
* Rostov on Don State Pedagogical Institute, 344717, Rostov on Don, USSR,
**The Youth Initiative Compamy, 344717, Rostov on Don, USSR

New ceramics condencers, which can find rather wide application in the technology are differed from the present time known condencers by the fact, that their electric capacity essentially depends on the frequency of the current, passing through it. As dielectrics for such condencers were used non-homogeneous (compositional) materials, based on the semiconductoral modificatioos of some different ferroelectrical oxides, in which the phenomenon of dispersion of their dielectric constant with ε' -as a real part of the complex dielectric constant $\varepsilon^*=\varepsilon'-j\varepsilon''$ in the area of sound ($10^1...10^4$ Hz) frequencies has been discovered. The above mentioned dielectrics were obtained by means of glass ceramics technology. They are matrix' system made of conductor crystal grains, with size L_g dielectric constant ε_g and specific resistance ρ_g "placed" into the continuous dielectrical surrounding with ε_l, ρ_l parameters and forming the interlayers with thickness L_l.

It is necessary to take into account, that $\varepsilon_l \ll \varepsilon_g$ and $\rho_l \gg \rho_g$. If the well-known equivalent scheme for bilayer dielectrics is applied to the electrical properties description of such systems it is possible to obtain that at $L_l \ll L_g$ the dispersion area centre ε' will be presented on the $\nu_m = L_l/2\pi\varepsilon_l\rho_g L_g$ frequency.

The necessary ρ_g values (at $\rho_g \ll \rho_l$) and ε_l (at $\varepsilon_l \ll \varepsilon_g$) for the dispersion observing in the $10^1...10^4$ Hz area are presented by $PbTiO_3$ alloyed with Lu^{3+} and Sc^{3+} iones and $BaSnO_3$ alloyed with Sb_2O_5 oxide and glass of $PbO(BaO)-B_2O_3(GeO_2)-Al_2O_3(Ga_2O_3)$-system.

The dielectrics were obtained by means of liquid phase sintering. For this purpose the mixture of glass powders and crystal substance in form of disks (i.e. diameter 15 mm, hight 2 mm) were pressed and then placed into special ceramics kiln. The dependences ν_m from the alloying additive and glass matrix composition have been established also. The dielectrical spectra of composites at the various temperatures have been tested too.

EL 55 author present: 09.30 - 11.00

ACOUSTIC-MECHANICAL EFFECTS IN THE GLASS CONTAINING FERROELECTRICAL CERAMICS,

E.A.Dulkin*, V.P.Zotzarinnyi*,
V.A.Yurkevich**, Yu.I.Goltzov*
* Rostov on Don State Pedagogical Institute, 344717, Rostov on Don, USSR.
**The Youth Initiative Company, 344717 Rostov on Don, USSR

The acoustic emission modified method for the experimental research of acoustical, solid and differmational characteristics of the ferroactive ceramics material with different glass contain has been given, elaborated and tested by the authors. The results of the experimental research of the $Pb(Zr_xTi_{1-x})O_3$ ferroelectrical ceramics in the form of disks with diameter 10mm and thickness 2mm are presented in the given paper.

As it was exepted, the experimental data have shown that the glass introduction into ceramics leads to the filling of pores with the glass, to the interlayer physical properties' change and to the considerable compactness position immediately of the grains themselves, that can not but influence the whole set of the physico-technical characteristics of the system and first of all on the internal mechanical tentions' field in the ceramics.

The correlational dependences between ceramics composition (in particular the glass contain), its elastic, acoustic, solid electrophysical and deformational characteristics are presented by the authors on the base of obtained exprinental data analysis. Special attention was paid to the phase transition area where the internal structure of the presented system is changed.

The consideration of the glass content influence not only on the phase transition temperature of the ceramic material and its properties, but also on the phase transition character itself i.e. the diffusion degree has been carried out.

Besides, the phenomenological theory of the acoustic mechanical effects in the glass contain ferroactive crramics has been suggested by the authors in the framework of the self-consistend field modified theory.

The obtained theoretical results are presented in qualitative (and ofted in quantitative) accordance with the experimental data.

EL 56 author present: 09.30 - 11.00

PHENOMENOLOGICAL THEORY OF FERROACTIVE CERAMICS,

V.E.Yurkevich
Rostov on Don Pedagogical State Institute, Rostov on Don, 334717, USSR

The ferropiezoactive ceramics phenomenological model was suggested and worked out in the framework of self-coordinated field modified theory. Ceramics is presented as some matrix, where are disposed grains and pores. It is supposed that in general case the structure (and the whole set of physico-technical characteristics) of the matrix and grains can be essentially differed one from other. While analysing the energetical balance of the system, its thermodynamical potential is considered to be superposition of reciprocally competing of volumic and surfacial constituents. Each ofthe constituents is built, based on the Landau-Ginsburg-Devonshire model.

The suggested model permits as a result to make analytical description of the whole set of behaviour peculiarities of the ceramics macroscopic properties (polarization, dielectrical penetration, piezomodul etc.) in the phase transition (PZ) area, taking into account the whole set both of the immediate thermodynamical parameters of the system itself (composition, temperature, size add density of pores, size and shape of grains etc.) and of the external influences of different types (electrical, mechanical and magnet fields).

Special attention was paid to the elaboration of the general PT formalism in the real system, when their internal structure rebuilding takes place in one constant chose point of the current thermodynamical variable (i.e. temperature, pressure or composition), but is extended in some final interval.

The developed formalism permits to give consequential analytical description of the ceramics physical properties based on so called function (characterizing new phase part as regarsd to the system as a whole). All the received theoretical results have been carefully and repeately tested on the wide experimental material their qualitative (and often quantitative) accordance has been also shown.

The elaborated phenomenological theory of the ferropiezoceramics can be regarded as some base for the phenomenological material studies, which permit not only to obtain the ferropiezoceramics with the concret (previously given) physico-technical properties, but also to control its characteristics at the expence of external influences.

EL 57 author present: 09.30 - 11.00

SHORT-RANGE ORDER IN PMN CERAMICS, E. Husson, N. de Mathan, P. Bonneau; A. Morell

Laboratoire de Chimie Physique du Solide, URA CNRS D0969, Ecole Centrale de Paris, 92295 Chatenay-Malabry Cedex, France; THOMSON-CSF, Laboratoire Central de Recherches, Domaine de Corbeville, 91401 Orsay Cedex, France.

$PbMg_{1/3}Nb_{2/3}O_3$ (PMN) is a relaxor ferroelectric material which has at 20°C the cubic $A(B'_{1-x}B''_x)O_3$ perovskite structure ($\varepsilon > 15000$, tg $\delta \simeq 0.006$ at 1 KHz and 20°C). The dielectric properties and the diffuse character of the ferroelectric phase transition of PMN are closely related to the structure, the microstructure and the short-range order in the compound.

According to the X-ray diffraction patterns, B' and B'' cations are statistically located on the B site of the perovskite and the cell parameter is $\simeq 4$ Å. However, an electron diffraction study reveals the existence of a superstructure corresponding to a fcc cell of $\simeq 8$ Å parameter which can be attributed to a local 1-1 cation ordering on the B site. This hypothesis is confirmed by HRTEM images where we observe nanodomains with superstructure. STEM analysis shows fluctutions in the Mg/Nb ratio.

The modification of the short-range order has been studied by (i) thermal annealing of ceramics and (ii) substitution on the B site by W^{6+} cations and on the A site by La^{3+} cations. The obtained compounds have been studied by electric measurements, diffraction techniques and Raman spectroscopy.

EL 58 author present: 09.30 - 11.00

THE FLUORITE-STRUCTURE DOMAIN IN THE Bi_2O_3-Y_2O_3 SYSTEM,

F.J.Sanz, J.R.Jurado, C.Moure, J.Palma, P.Recio, P.Durán, C. Pascual*.
Instituto de Cerámica y Vidrio (CSIC), Electroceramics Department, Arganda del Rey, 28500 Madrid, Spain.

The fluorite-structure cubic phase in the Bi_2O_3-Y_2O_3 system transforms at low temperature into a stable hexagonal phase which shows a smaller cell volume and a lower electrical conductivity. Compositions with the hexagonal structure were prepared at low temperature by the oxalate method in the Bi_2O_3 rich region to stablish the fluorite domain in the Bi_2O_3 - Y_2O_3 system. Transformation temperature and electrical conductivities of the hexagonal and cubic phase were determined.

EL 59 author present: 09.30 - 11.00

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY: AN EXCELLENT TOOL FOR THE TOTAL CHEMICAL ANALYSIS OF TITANATE-BASED ELECTROCERAMICS. J.C. Fariñas, Mª F. Barba.
Instituto de Cerámica y Vidrio (CSIC), Chemical Analysis Department, 28500 Arganda del Rey, Madrid, Spain.

The synthesis of the new electroceramic materials requires an exhaustive analytical control of all the fabrication process. It is necessary to determine the final product stoichiometry, as well as its impurities contents.
Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) permits a total chemical analysis of all the interested elements in such kind of materials.
The application of this technique have been studied with respect to the analysis of barium or lead titanate based ceramics ($BaTiO_3$, Ca-PT, La-PT, Gd-PT, PZT, PLZT) doped with various metal oxides and rare earth elements (REE). The results obtained for the major elements, dopants and impurities (Al, Ca, Co, Cr, Cu, Fe, Hf, Mn, Nb, Ni, P, Si, Sr, W, Zn, alkali metals and REE) are showed.

EL 60 author present: 09.30 - 11.00

STRUCTURE AND PTCR STUDIES IN BARIUM LEAD TITANATE PREPARED BY THE MOLTEN SALT SYNTHESIS METHOD

Ki Hyun Yoon*, Man Hwa Lee and Sang Ok Yoon

Department of Ceramic Engineering,
Yonsei University, Seoul, Korea

(Abstract)

The variation in lattice constant and PTCR effect in the barium lead titanate system prepared by the Molten Salt Synthesis (MSS) method have been investigated. The c/a ratio of $(Ba_{1-x}Pb_x)TiO_3$ $(0<X<0.5)$ prepared by the MSS method are greater than those of the Conventional Mixed Oxide (CMO) method due to a decrease in PbO loss. In Nb doped $(Ba_{0.8}Pb_{0.2})TiO_3$ ceramics, the density and the grain size decrease above 0.4 mol% Nb ion, and the room temperature resistivity increases above 0.6 mol%, and with increasing the KCl weight ratio the room temperature resistivity decreases. These results can be explained by the solubility limit of the Nb ion and the charge compensation effect between electrons due to the Nb ion and holes due to the K ion.

EL 61 author present: 09.30 - 11.00

DIELECTRIC PROPERTIES OF HIGH-PURITY $BaTiO_3$ CERAMICS, D.A. Hall* and A.J. Moulson
Ceramics Division, School of Materials, The University of Leeds, Leeds LS2 9JT, U.K.

The microstructural dependence of the dielectric properties of $BaTiO_3$ ceramics is well-documented. To date most publications have been confined to the effect of grain size on the real part of permittivity, ε'.

The present paper describes the ceramic processing necessary to produce fine- and coarse-grained materials, and reports the effect of grain size on the temperature- and frequency-dependence of the complex permittivity (both ε' and ε''). The results are discussed in terms of the existing models.

EL 62 author present: 09.30 - 11.00

PIEZOELECTRIC AND PYROELECTRIC PROPERTIES OF 0-3 COMPOSITES CONTAINING $PbTiO_3$, C.E. Millar* and A.J. Moulson
Ceramics Division, School of Materials, The University of Leeds, Leeds LS2 9JT, U.K.

Piezoceramic-polymer composites offer improved properties over those of single phase materials for applications such as sonar and pressure-sensitive devices.

The present study concerns 0-3 composites comprising $PbTiO_3$ powder dispersed in a low density polymer matrix. Details of the corona poling technique are presented and data for composites polarized by this method are compared with those obtained by conventional poling.

Simple experimental techniques that have been developed to measure the piezoelectric coefficient (d_{31} and d_h) and the pyroelectric coefficient (λ) are described. Data are presented covering a range of ceramic loadings and special attention is given to the effect of the elastic compliance of the polymer phase on the piezoelectric and pyroelectric properties of the composite.

EL 63 author present: 09.30 - 11.00

ADVANCED CERAMIC MATERIALS FOR PACKAGING SOPHISTICATED ELECTRONIC COMPONENTS: a brief review of current developments. You Song Kim, AT & T Bell Laboratories, 555 Union Boulevard, ALLENTOWN PA 18103.

Today's sophisticated electronic components have created an ever increasing demand for new packaging technology, including the development of materials that can accommodate high circuit wiring density and high data-processing capability. New materials that can meet the needs have recently been developed. A Low-Temperature-Co-Fired ceramic tape is the prime example of this material. The salient features of the tape are its potential use in multilayer form, low dielectric constant (k=4) and low cost. Characteristics of the new materials (tapes) and the processing techniques of tapes to be fabricated into multilayer structures of sophisticated ceramic packages will be reviewed.

EL 64 author present: 09.30 - 11.00

DEVELOPMENT OF CRYSTAL PHASES AND NONLINEAR PROPERTIES IN VARISTOR CERAMICS PREPARED BY METHODS OF COPRECIPITATION AND EVAPORATION OF SUSPENSIONS AND SOLUTIONS, O.Milošević*, D.Vasović, D.Poleci, Lj.Karanović, V.Petrović and D.Uskoković, Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Belgrade, Yugoslavia

Advanced ceramic processing techniques were used to fabricate ZnO based varistor ceramics having the nonlinearity coefficient from 35 to 45, the breakdown field in the range from 400 to 1000 V/mm and the leakage current below 1 $\mu A/cm^2$. Processing steps included chemical synthesis of powders with complex initial composition, mechanical activation of calcinated powders and sintering in the temperature range from 1000-1300^{o}C. Two methods for powder preparation were used: 1) coprecipitation and 2) evaporation of ZnO suspensions with additive solution. In both cases their composition corresponds to final seven component varistor system with 92,7 mol% ZnO and 7,3 mol% additives from the group of soluble salts of Bi, Sb, Co, Mn, Ni and Cr. Various analytical methods, such as are lighting and scanning microscopy, DTA, TGA, X-ray, EDAX and EPR were used for the characterisation of powders and resulting nonlinear ceramics. The process of the formation of the main phases: ZnO, spinel and intergranular layer was investigated as well as their influence on the resulting nonohmic properties.

TRADITIONAL : NEW TRENDS

Monday 19th June; 11.30 - 12.30 — Chairman : W. Krönert (FRG) — Room : 0.1

TR 1 11.30

NEW WAYS IN THE FIRING TECHNOLOGY FOR WHITE WARE CERAMICS (Porcelain)

Dipl.-Chem.R.Sladek, Riedhammer GmbH & Co.KG, Klingenhofstraße 72, 8500 Nürnberg

The general development of technology - in some fields one can even talk of a "speedy" development - also influenced the process of modernization in the ceramic industry, though only gradually.
Reflections on how to obtain a better flexibility for the firing process resulted in corresponding new developments which guarantee a faster firing, a lower energy consumption and an optimum quality due to a more precise sintering process control. Parallelly to these achievements, endeavours are made to provide for an ecological relief and to bind and/or to dispose of the "classical" harmful substances released in the production of ceramics (fluorides and hydrocarbons) accordingly.
The realization of the ceramist's "dream" to develop a technology for a continuous production line even for whiteware seems to be quite near. The preservation and improvement of competitiveness can no longer be guaranteed without keeping up with the technical progress.
The use of a modern firing technology may create the necessary prerequisites such as a new technology for the production of hotel porcelain.
The firing units can be operated both continuously and periodically, whereas the latter operation type concerns mainly small-size production units.
The above-mentioned details will be explained.

TR 2 12.10

NEW TRENDS AND DEVELOPMENTS OF PRODUCTION PROCESSES IN THE CERAMIC FLOOR AND WALL TILE SECTOR, G.Nassetti* and M. Poppi,

Centro Ceramico, Bologna, Italy; Studio Poppi S.p.A., Sassuolo, Italy.

A review is made of the more important innovations relative to fabrication technology (in particular as regards the phases of raw materials preparation, drying and firing) recently introduced by the ceramic floor and wall tile industry. The description of the innovative solutions regarding machinery and equipment is accompanied by a discussion of the requirements leaded to such innovations and characterization of the advantages resulting from their introduction with regard to quality of the semi-worked pieces and final products as well as the optimization of energy consumption and management of the processes as compared with traditional technology. The picture that emerges provides a precise detailed outline of the evolutional trends in a sector, that of ceramic floor and wall tile, in which Italy holds an important and stable position of leadership, not only as regards production capacity but also in relation to progress in fabrication technology and the attainment of higher levels of quality.

TRADITIONAL : WHITE WARE

Monday 19th June; 15.20 - 17.00 — Chairman : A.A.M. van Mierlo (The Netherlands) — Room : 0.1

TR 3 15.00 withdrawn

TR 4 15.20

PORE STRUCTURE IN PLASTER MOULDS, Sven Karlsson*, Roger Carlsson, Swedish Institute for Silicate Research, Box 5403, S-402 29 Göteborg, Sweden.

Test pieces of plaster moulds used in production of wash basins were investigated. Test pieces were taken from one and the same mould after 10, 20, 30,.....100 (for one type of plaster mould up to 150) castings. The open porosity, pore size distribution (Mercury) and microstructure (SEM) of mould surface layer as well as interior layers were examined.

The pore size distributions show that the amount of large pores ($1.7<\phi<3.3$ my) increase with increased number of castings but also with the distance from the casting surface into the mould. On the other hand, the content of finer pores ($0.7<\phi<1.7$ my) decreases at the same time.

The microstructure in a plaster mould used for appr 100 castings is coarser compared to a not used one. The gypsum crystals change in shape and the "fibre-type" structure seen earlier has disappeared.

TR 5 15.40

COLOUR DEVELOPMENT IN UNGLAZED FLOOR TILES, Sven Karlsson*, Roger Carlsson, Swedish Institute for Silicate Research, Box 5403, S-402 29 Göteborg, Sweden.

The colour development and crystalline phases in 13 unglazed floor tiles have been studied. Glass compositions of the glass phase in the tiles were prepared by mixing raw materials and melting. The colour behaviour and crystallization of the glasses were studied during heat-treatment in a gradient furnace.

The surface colour of tiles fired in a reducing atmosphere becomes darker with increased temperature. The change in colour is from light red to black. Phase analysis of the surface shows quartz, mullite, cristobalite, and glass as main phases. The dark tiles also show a fairly high content of iron-cordierite (ss), which probably causes the surface colour. The analyse also indicates phases which are not so easiliy identified.

Crystallization of a glass composition which is close to the real one in the tiles shows a yellow-brown surface colour and needle-like $Fe_2O_3.TiO_2$ crystals. Crystallization of a glass composition without TiO_2 results in a dark-brown surface colour and hematite crystals. This development together with the clay can cause a reddish-brown colour of the fired tiles.

TR 6 16.00

RELATION BETWEEN MANUFACTURING PARAMETERS AND RESIDUAL STRESSES IN POROUS SINGLE FIRED PRODUCTS, G. Garcia, Ferro Espanola S.A., Spain.

Porous single fastfired walltiles have to meet relevant European product standards (EN 88) like crazing resistance, dimensions, porosity and curvature (residual stress).
In order to achieve a specific porous one side coated solid material with an optimal curvature (connected with crazing resistance and moisture expansion) the ceramic engineer is composing a chemically determined clayish composition.
The curvature of the fired tile has been affected than first by the tilepressing of the semidry factory standardized spraydrier-granulate. Here is the regularly controlled and corrected apparent density an important process parameter.

A study, involving a lot of superior and inferior firing curves in rollerkilns, is showing the relations between the temperature related expansion-contraction movements of the ceramic body and the resulting curvature after firing.

There is a special contribution to the residual stress (thus curvature) of fired walltiles by the glaze-coating only or by the engobe-glaze coating.

TR 7 16.20

POSSIBLE EVALUATION OF ADHESION BETWEEN GLAZE AND SUBSTRATE IN TRADITIONAL CERAMICS. R. Dal Maschio*; G. De Portu and B. Fabbri.
Engineering Department of the University, Trento, 38050, Italy.
Research Institute for Ceramic Technology C.N.R., Faenza, 48018, Italy.

A test of adhesion of the glaze with the substrate may be carried out by the classic tensile methods. A different approach can be tried using the indentation technique and measuring the resistance to propagation of the crack along the interface. In this work, tensile test results are compared with some data of interface fracture resistance by the introduction of a mechanically stable crack with usual indentation procedure. These tests have been performed in two ways by changing the direction of the applied load: perpendicular to the glazed surface of the tile, using the lateral crack system, or parallel to the interface, after sectioning normal to the glazed surface, such that one radial crack propagates along the interface.

TR 8 16.40

WEAR PROPERTIES OF CERAMIC WHITEWARE GLAZES,
K. Linde*, S. Karlsson and R. Carlsson,
Swedish Institute for Silicate Research,
box 5403, 402 29 Göteborg, Sweden

Wear studies of a number of ceramic whiteware glazes have been conducted, principally by measurement of the frictional force of steel balls in contact with the glaze surface. Plates, cut out of ceramic whiteware, were exposed to steel balls sliding at low speeds under loads from 15 to 120 N. Friction measurements were also performed with glazed vs. glazed and glazed vs. unglazed alumina whiteware couples.

Friction coefficients for the sliding couples were determined and glaze damage arising during the test was studied. Characteristics of wear tracks on different glazes could be distinguished and related to the friction coefficients. The causes for the different wear properties are also discussed.

TR 9 09.00

TECHCON® DRYER

H.J. Timmers
Technisch Centrum voor de Keramische Industrie,
De Steeg, P.O. Box 40, 6994 ZG, The Netherlands.

The paper deals in particular with the drying process of products formed out of a plastic mass of clay, such as roofing tiles and bricks. The main drying problems are discussed, with special consideration of the significance of the specific surface and the "overall" diffusion figure.
Then the Techcon® dryer is dealt with.
This type of dryer is a cross between a chamber-dryer and a tunnel-dryer. Shaping and drying are separated, as is also the case with tunnel dryers. Transportation is fully-automatic and computer-controlled. Each time of the day or the night a chamber can be unloaded and refilled.
The "wet" and "dry" products are stored in conditioning chambers. If a chamber dryer is chosen, for instance because of poor drying properties of the raw materials or a large amount of different products to be dried, the Techcon® dryer gives the following advantages:
- optimum drying times can be chosen,
- a practically equal heat load, both during working days and weekends,
- a continuous drying process without shiftwork,
- fewer drying rooms and yet the required output,
- production problems during holidays can more or less be overcome.

The paper ends with the presentation of a model to determine the energy costs (gas, electricity) and keep them as low as possible.

TR 10 09.20

INVENTORY OF RAW MATERIALS IN THE NETHERLANDS FOR HEAVY CLAY PRODUCTS

J.H. van Wijck*,
H.J.Timmers, M. van Meerten
Technisch Centrum voor de Keramische Industrie,
De Steeg, P.O Box 40, 6994 ZG, The Netherlands.

Against the background of a reduced availability of clay in the Netherlands, caused by more stringent environmental requirements, an inventory was made of about 12 clay deposits.
The paper gives a summary of clay deposits in the Netherlands which are or may, in the future, be used for the manufacture of heavy clay products (building bricks, paving bricks, roofing tiles).
The geological aspects of clay, i.e. its formation, are discussed as well as several properties of the clay sediments. The various clay properties have been collected per deposit in so-called "raw material sheets".
The physical, chemical and thermal properties and the mineralogical composition typical of Dutch clays are considered and illustrated by an example.
Furthermore, an explanation is given of a method to calculate the mineralogical composition of a clay on the basis of a quantitative chemical analysis, XRD analysis and optical analysis.

TR 11 09.40

THE INFLUENCE OF PROCESSING CONDITIONS ON THE PORE SIZE DISTRIBUTION AND DURABILITY OF CLAY BRICKS, R.W. Ford.

British Ceramic Research Limited, Queens Road, Penkhull, Stoke-on-Trent, ST4 7LQ, England.

The relation between pore size distribution and the resistance to freeze/thaw conditions has been examined for a range of bricks made from Mercian Mudstone [Keuper Marl]. Results show how raw material processing, and the moisture content and method used to form the bricks affect these characteristics.

TR 12 10.00

INFORMATISATION AND AUTOMATION IN THE CERAMIC INDUSTRY

J.C. Marks
Technisch Centrum voor de Keramische Industrie.
De Steeg, P.O. Box 40, 6994 ZG, The Netherlands.

To prevent a chaos in the ceramic industry, in the field of informatisation and automation, each company will have to work out an information infrastructure and set up a configuration plan.

Recent research in the ceramic sector carried out by the Technisch Centrum in cooperation with the "Instituut Informatietechnologie voor produktieautomatisering TUE-TNO" gives an insight into the state of affairs with regard to automation and information requirements among producers of ceramic building materials.
A model has been set up for an information infrastructure and a production and energy Management Information System (MIS). This may have positive effects on the control of processes and the availability of machines, and brings about the integration of new production means into existing structures.

Based upon this model a list of requirements has been submitted to European suppliers of measuring and control systems as well as computersystems for machines used in the ceramic industry.
In order to make possible an exchange of data between man and machine in this field, international cooperation will be required for the realization of a Ceramics Exchange Communication Standard (CECS).

TR 13 10.20

FUNDAMENTAL APPROACH TO DETERMINATION OF DRAYING TECHNOLOGY CRITERIA, Lj.Pavlović and M.Stamatović

Institute for Nuclear Technology and Other Mineral Raw Materials, Belgrade, Yugoslavia

Drying by means of heating, as a most common way of drying, besides removal of moisture often has other goals (e.g.change of structure, mechanical, thermal of technological features, etc).
Achievement of these goals in a drying process in influenced greatly by the parameters of the process which determine the drying technology. These parameters define the material temperature, strentgh, deformations, cracks, transfer of water etc.
Present approaches determine the criteria for critical values of the technology (drying parameters) which can predict occuring or not occuring of the desired phenomena. These criteria are usually not a function of the drying kinetics and dyinamics and this are very unereliable and defficult to determine and demand large number of experiments.

The best way of defining a drying technology is through non dimensional balacne equations of the drying process. These balances are called the "Basic equations of the drying kinetics" and technology of the drying process.

The goal of this paper is to prove that using of the "Basic equations" is the correct way for determination of a drying technology. It also shows the problems and the best manner of defining the non-dimensional criteria for the drying process.

TR 14 10.40

ENVIRONMENTAL ACCOUNTANCY IN BRICK INDUSTRY

Dr Ing. Lau S. de Jonge
Royal Association of Dutch Brickmakers,
De Steeg 6994 ZH The Netherlands

The life cycle of structural ceramic products can be thought to consist of the stages clay (digging and preparation), manufacture, application and rubbish. Though the environmental behaviour of building ceramic materials during that life cycle must be valued positively, small negative effects cannot be denied. In the Netherlands the common opinion grows that authorities haven't hands enough to register and control all negative effects on environment caused by traffic, industry and people. Under the flag of self-responsibility procedures of environmental control, analogue to quality control are created. In cooperation with dutch authorities a system was developed that enables management to control the environmental effects of building ceramic materials before, during and after manufacture.

TRADITIONAL : REFRACTORIES

Tuesday 20th June; 15.00 - 17.00 — Chairman : C. Korevaar (The Netherlands) — Room : 0.1

TR 15 15.00

INFILTRATION MECHANISMS IN STEEL REFRACTORIES

J.E. Davies*, P.M. Marquis, School of Metallurgy and Materials, University of Birmingham, Birmingham B15 2TT, UK;
M. Hankin, Foseco (FS), Tamworth, West Midlands, UK.

The erosion of steel refractories by slags can be reduced if infiltration and interactions are minimised. In this paper it will be shown how back-scattered electron microscopy and light element X-ray analysis have been used to study the microstructure of both Zr/graphite, Zr/silica and fused silica refractories after their use during metal casting. Results will be presented showing how the molten slag can infiltrate even through sub micron pore structures accelerating internal erosion through the decomposition of filler phases. It will be discussed how the control of pore structure in zirconia/silica systems can produce an erosion performance comparable to the more expensive zirconia/graphite refractories whilst retaining good thermal shock characteristics.

TR 16 15.40

REFRACTORY ZIRCONYL PHOSPHATE CERAMICS WITH HIGH THERMAL SHOCK RESISTANCE

C. Zografou, N. Kalthoener, W. Krönert
Technical University of Aachen

D. v.Mallinckrodt
Hüls Troisdorf AG, 5216 Niederkassel,FRG

Refractory Zirconyl Phosphates are a new generation of compounds with determinable thermal properties. Such materials are predictable for high temperature applications for materials with adjustable thermal property demands. The aim of the presented results is to demonstrate the applicability of the possibility to change every property of the material to produce thermal shock resistant materials and furthermore materials for low temperature ionic conduction.

TR 17 16.00

PREPARATIONS AND PROPERTIES OF ALUMINA-CHROMIA (CORUNDUM) REFRACTORIES CONTAINING MULLITE,

A. Harabi(*) and T.J. Davies
Manchester Materials Science Centre, University of Manchester and UMIST, Grosvenor Street Manchester M1 7HS ENGLAND (U.K.).

The objective of this study is to obtain correlations between properties and microstructures in corundum-mullite refractories. Corundum $(Al,Cr)_2O_3$ compositions have been studied as potential matrices in which mullite($3Al_2O_3.2SiO_2$) is dispersed as a second phase.
For the matrices, the effect of chromia addition on densification, volume change, porosity, shape of grains, average grain size, lattice parameters and tensile strength has been examined.
The effect of firing temperature and holding time at temperature was also studied.
In particular, the effects of additions of fused mullite on densification, microstructure, porosity and mechanical properties in corundum refractories is reported.

(*) Solid State Physics Laboratory, Institute of Physics University of Constantine 25000, ALGERIA. (After January 15, 1990.)

TR 18 16.20

SOL GEL PROCESS OF PHOSPHATE ALUMINA SYSTEM,

G. Palavit *, P. Vast, R. Chi ; B. Thierry, M Descamps
Laboratoire de Chimie Appliquée Université des Sciences et Techniques de Lille Flandres Artois 59 655 Villeneuve d'Ascq Cedex ; Centre Régional d'Innovation et de Transfert Technologique "Céramiques fines" ZI la petite Savate59600 Maubeuge.

Phosphate bonding as been utilized in the refractories field for many year, particulary with alumina. Hardening between alumina and phosphoric acid is caused by the formation of monoaluminium phosphate. We develop a new way which leads to systems phosphate- oxide by sol gel process approach, particulary those contening Al_2O_3, Na_2O, P_2O_5, H_2O.
In this paper we discuss about the various parameters necessary to obtain the stability of gel. The importance of the solvent acidity medium (aqueous or hydroalcoholic) is discussed.
Thermal treatment of gel are characterized by thermal analysis method and ^{31}P NMR.

TR 19 16.40 withdrawn

TR 20 author present: 15.00 - 16.30

SYNTHESIS OF WOLLASTONITE FROM SPANISH LOW COST RAW MATERIALS. A. Ibañez*; F. Sandoval*; J.Mª Gonzalez-Peña*;+V. Beltrán and J.L. Amorós+. * Instituto de Cerámica y Vidrio, C.S.I.C., Arganda del Rey, Madrid (Spain); + Instituto de Tecnología Cerámica, A.I.C.E. Castellón (Spain)

In a line of investigation in which low cost raw materials are tried to use in the manufacturing of ceramics by fast firing, β-wollastonite was synthesized from two diatomites, by solid state reaction and via hidrosilicates. Compositions formed by diatomite and chalk and another one formed by chalk and quartz which is taken as a standard were formulated. The silica/calcium carbonate ratio was the corresponding to wollastonite. The results of the two synthesis methods and also those obtained from the different compositions (mass % wollastonite) are compared

TR 21 author present: 15.00 - 16.30

INFLUENCE OF PREPARATION AND FORMING OPERATIONS ON RAW CERAMIC TILE QUALITY,
Lj. Petrašinović-Stojkanović*and B. Živanović,Material Testing Institute, 11000 Belgrade, Yugoslavia;
S. Despotović
"ZORKA" - Institute, 15000 Šabac, Yugoslavija;
O. Gajić,
"ZORKA"-Ceramic Tile Plant, 15000 Šabac, Yugoslavia;
M. Penić-Mandić and R. Vrhovac,
"ZORKA"- Development Dept.,15000 Šabac, Yugoslavia.

The paper considers the influence of certain parameters from preparation and pressing operations on the quality (mechanical properties) of raw ceramic tiles. A statistical processing of monthly ceramic tile production data has been made, establishing that uneven mould filling as well as variations in thickness and density for central and peripheral mouldes cause considerable dispersion of bending strength results for raw tiles. Elimination of these imperfections results in quality improvement and waste reduction.

TR 22 author present: 15.00 - 16.30

THE INFLUENCE OF THE MOISTURE CONTENT ON THE COMPACTION BEHAVIOUR AND PRODUCT PROPERTIES OF A WALL TILE GRANULATE,
J. van der Zwan.
TNO Institute of Applied Physics,
Ceramics Department, P.O. Box 513,
5600 MB EINDHOVEN, The Netherlands.

Results are given of a long term project on the compaction behaviour of wall tile granulates with various moisture contents. The relationships between compaction pressure, density and porosity of the compact and mechanical properties of the product are presented. The water content of the pressing powder has a large effect on the compaction mechanisms of the spray dried granulate. However, a limiting maximum moisture content exists. Above 8-9 w% water the compact density will not increase with increasing pressure. Thus, compact density depends on compression technology and water content. The known compaction formulae can be extended with a moisture content depending factor.

TR 23 author present: 15.00 - 16.30

FLOC STRUCTURE IN KAOLINITE SUSPENSIONS,
Margarida Almeida*, M.M.M. Diz, C.S.F. Gomes, Universidade de Aveiro, 3800 AVEIRO, Portugal.

The application of the van Olphen-Schofield-Samson heteropolar model for the particle charge distribution in kaolinite particles results in the possibility of three basic types of particle interaction in suspension. These lead to floc structures which differ by their size and density. On the other hand, temperature variation affects particle interaction and modifies their state of aggregation. In the present work, the electrophoretical, rheological and sedimentation behaviour of kaolinite aqueous suspensions was studied in the temperature range of 20-60ºC. Floc sizes and densities were determined. The results were interpreted in terms of the heteropolar model. Variations with temperature were attributed to quantitative differences in the total energy involved in particle interactions within the floc structure, an assumption which was supported by the application of the elastic floc model to this system.

TR 24 author present: 15.00 - 16.30

OPTIMIZING COMPOSITION OF RAW MATERIAL MIXTURE FOR THE PRODUCTION OF SINTERED CERAMIC TILES BY LINEAR PROGRAMMING METHOD, Lj. Petrašinović-Stojkanović* and B. Živanović, Material Testing Institute, 11000 Belgrade, Yugoslavia;
S. Despotović,
"ZORKA"- Institute, 15000 Šabac Yugoslavia;
O. Gajić
"ZORKA"- Ceramic Tile Plant, 15000 Šabac Yugoslavia.

Based on the mathematical model comprising total material balance in the mixture as well as particular oxide balances, calculation of optimum composition of starting mixture (share of particular raw material components) for the production of sintered ceramic tiles has been made. The calculation also includes minimizing raw material mixture costs by using linear programming method. Based on calculation results, the possibility of reducing the share of raw materials that are not readily available on the market or those incurring higher costa without affecting the desired quality of sintered ceramic tiles has been studied.

TR 25 author present: 15.00 - 16.30

WALL TILE BODIES FROM SYNTHETIC WOLLASTONITE OBTAINED BY POROUS FAST SINGLE FIRING. A. Ibañez*;F. Sandoval*;J.L. Amorós+ V. Beltrán+and J.Mª Gonzalez-Peña*
* Instituto de Cerámica y Vidrio, C.S.I.C Arganda del Rey, Madrid (Spain). + Instituto de Tecnología Cerámica, A.I.C.E. Castellón (Spain).

Wall tile bodies based on, 1)natural wollastonite, 2)synthetic wollastonite and 3) $CaCO_3$ were formulated according to the $CaO-Al_2O_3-SiO_2$ system. The wollastonite was synthesized from a Spanish low cost raw material by solid state reaction and the final bodies were obtained by porous fast single firing. On the fired bodies quantitative X-ray analysis and scanning electron microscopy were performed, and physical properties, such a, dry and firing bending strength, thermal expansion coefficient, moisture expansion, etc, were measured and compared in order to check if synthetic wollastonite improve the properties of this kind of ceramics. From the results it can be concluded that the obtained materials have good performance.

TR 26 author present: 15.00 - 16.30

ANALYTICAL INVESTIGATION ON VAPOUR CONDENSATIONS FROM SINGLE LAYER - ROLLER KILNS FAST FIRING
G.Tosi and P.Zannini *
University of Modena, Chemistry Dept.
I 41100 Modena , Italy

Analytical characterization of solid condensations inside fast firing kilns was made by means of XRF, XRD, AAS, SEM-EDS, TGA, DTA and classic wet analysis on 48 samples, collected from very different production technologies. Aim of the work was to localize critical zones and temperatures, and to assess the average chemical and mineralogical composition, then to relate got results with possible pollution starting materials. It was found that :
a) high temperature condensations (500-800°C.) are mainly composed by $PbSO_4$ in Anglesite or glassy form, while
b) low temperature condensations (100-300°C.) are as NH_4Cl, NH_4BF_4, $(NH_4)_2SO_4$ etc. .

TR 27 author present: 15.00 - 16.30

THE USE OF SPECIAL T.G. APPARATUS TO STUDY REACTION MECHANISMS IN FAST FIRING,
H.J. WESTERBEEK, FERRO (HOLLAND) B.V., ROTTERDAM, the Netherlands.

The study of decomposing reactions in a greentile due to heating action provides information, which is almost indispensable in optimizing the glaze-bodyfiring system, especially in fastfiring.

Standard TGA and DTA techniques are useful, but have not enough correlation with the industrial practice.

The special developed T.G. device is able to fire glazed tiles with the appropriate fastfiring curve and with continuous recording of the weightlosses together with visual inspection possibilities.

The information derived has proven itself very useful to select glaze frits, optimizing firing curves and check upon various production parameters.

TR 28 author present: 15.00 - 16.30

EFFECT OF TEMPERATURE AND EXCHANGEABLE CATION ON WATER DIFFUSION IN KAOLINITE, M.Stamatović, Lj.Pavlović

Institute for Nuclear Technology and Other Mineral Raw Materials, Belgrade, Yugoslavia

Water transfer phenomena in the interlayer space of kaolinite structure is a complex and not yet completely solved scientific problem.

The main objective of this paper was to determine the coeficients of water molecular diffusion dependence on the exchangeable cation of kaolinite and the temperature of the system.

By using the diffusion couple metod in isothermic conditions, at five different temperatures, viz.: 303, 308, 313, 318 and 323 K, the coefficients of molecular diffusion of water were determined. The water transfer was studied in the diffusion couple with saturated boundary between two samples of different water content, ranging from 34 to 50 percent.

To calculate the molecular diffusion coefficient of water, the simplified Wagner`s equation for the incompressible system was used. The results are interpreted in terms of standard difusion theery based or. Hlick`s laws.

TR 29 author present: 15.00 - 16.30

PRELIMINARY REPORT ON THE MIGRATION OF LEAD AND CADMIUM FROM CERAMIC ARTICLES SOLD IN ITALY AND INTENDED TO COME INTO CONTACT WITH FOODSTUFFS, B. Fabbri* and G. Ercolani.

Research Institute for Ceramic Technology C.N.R., Faenza, 48018, Italy.

Four equal specimens for about 150 different ceramic articles have been collected to determine the eventual migration of lead and cadmium by acid attack (according to a council directive of the European Community). Part of the articles were purchased directly from the producers, and the remaining ones from normal shops. The migration data revealed that only a very small number of pieces released a high level of lead, while no abnormal migration of cadmium was ever noted. The lead releasing articles were artistic models, often not conceived to come into contact with foodstuffs, also when their shape allows they can be used for that purpose. In most cases, the lead release is correlated with the production or decoration technique.

TR 30 author present: 15.00 - 16.30

CERAMIC APPLICATIONS OF AN ANGOLAN CHINA CLAY, A. de Pretis*; A. Pinto de Ceita,

Università di Udine, Udine, Italy.
Universidade A.Neto, Luanda, Angola.

A raw kaolin from a primary deposit of Quihita district (Angola) was tested for its processability and quality of the thereby attainable products. The kaolin products were intended to have ceramic and paper filler qualities. Through refining methods it has been possible up to now to meet the increasing quality demand of the silicate-ceramic raw materials as the results of ceramic tests have shown.

TR 31 author present: 15.00 - 16.30

COMPARISON OF TECHNOLOGICAL PROPERTIES OF BODIES FOR "MAIOLICA" AND "TERRAGLIA" WARES,

V. Venturi ; C. Fiori
Geoceramic Researches, M.S. Pietro, Italy

Two typical bodies supplied to the italian producers of "maiolica" and "terraglia" wares have been characterized as regards their technological properties. The following analyses have been carried out: chemical, mineralogical through x-ray diffraction (qualitative) and via rational calculation (quantitative), DTA and TG; then the following tests have been performed: plastic index, dilatometry, shrinkage and mechanical strength of shaped green specimens; and shrinkage, water absorption, thermal expansion coefficient, mechanical strength of fired specimens. The "terraglia" body shows a higher plasticity and a lower shrinkage after drying, but the mechanical strength of both the dried and fired pieces is less good if compared with the same paramaters of the "maiolica" body. These results are discussed on the base of the grain size distribution and the mineralogical composition.

TR 32 author present: 15.00 - 16.30

MARKET PROSPECTS FOR CERAMIC TABLEWARES IN NIGERIA, E. P. Oaikhinan,
Bendel State University, Ekpoma, Nigeria.

Abstract

The Nigerian consumption of ceramic tablewares remains extremely high despite strong and continous import restrictions enacted by government over the last few years. This has made the Nigerian market increasingly attractive to foreign producers who have problems of over capacity and static markets in their domestic sectors. About 53 million tonnes of various types of ceramic tableware are currently being imported into Nigeria from Britain, Germany, Korea, China and Japan.

Local production first approximates to 5.8 million tonnes per annum despite the availability of manpower and essential natural resources that are of major interest to the tableware industry. The market, structure and problems of ceramic tablewares production in Nigeria are discussed.

TRADITIONAL POSTERS : HEAVY CLAY PRODUCTS
Tuesday 20th June; 09.00 - 19.00

TR 33 author present: 15.00 - 16.30

THE CLAY-WATER RELATIONSHIP - A DIFFERENT APPROACH: MOISTURE RETENTION, M.B.G. Ketelaars*; J. van der Zwan.
* TNO Institute for Building Materials and Structure, 2600 AA DELFT, The Netherlands,
TNO Institute of Applied Physics, Ceramics Department, P.O. Box 513, 5600 MB EINDHOVEN, The Netherlands.

In basic science on ceramic materials the drying process is in most cases described from a physical technological point of view. We present a new approach for the description and interpretation of the drying behaviour of ceramic masses and green products. This approach exists already 50 years in soil science and deals with the energy relationship between the solid and its water. The clay moisture retention (pF-)curves can be obtained by a measuring device. From these curves the pore size distribution can be calculated. The obtained curves show the moisture retention or suction as function of the equilibrium moisture content of the clay mass. The curves characterize uniquely each clay, sand or mixture. Variations in deflocculation result in different structures and equilibrium moisture contents in the green products.

TR 34 author present: 15.00 - 16.30

THE SPECIFIC SURFACE EXPOSED, J. van der Velden
Ceramics Department of TPD-TNO Eindhoven.

With regard to the shaping and drying behaviour, the particle size distribution of a clay body is considered one of the main parameters, although its value turns out to be confined to clay bodies of similar mineralogical association and geological evolution.
The intention of the paper is, to point out the great significance of the total specific surface in this respect and to promote the use of this still underestimated parameter for evaluating the shaping and drying behaviour of clay bodies.
Data of a large number of properties of Dutch and other European clays, gathered by the Ceramics Department of the Netherlands Organisation for Applied Scientific Research, TNO, in the past years, are plotted versus the total specific surface of the samples.
The investigation leads to several useful rules of thumb, which demonstrate the great importance of the parameter in question.

TR 35 author present: 15.00 - 16.30

THE RHEOLOGICAL AND FILTRATION PROPERTIES OF CLAY, J. van der Zwan*, M.B.G. Ketelaars.
* TNO Institute of Applied Physics, Ceramics Department, P.O. Box 513, 5600 MB EINDHOVEN, The Netherlands.
TNO Institute for Building Materials and Structures, 2600 AA DELFT, The Netherlands.

The filtering properties of a clay slip and its rheological behaviour are quantitatively related. Casting rate, filtering rate and rheological parameters conform to the classical description of the deflocculation mechanism.
A high filter cake resistance and a very low hydraulic conductivity of the cakes and casts can be explained with the high tortuosity ratio and compressibility of the (partly) flocculated cast and cake.
In general, several properties of the clay slips and casts were influenced by the degree of flocculation, such that minimum c.q. maximum values of the properties were found at roughly the same state of flocculation. There are indications that this behaviour is influenced by the occurrence of orientated clay particles in the cast or cake and most probably, in the clay slips.

TR 36 author present: 15.00 - 16.30

A PRACTICAL APPROACH OF THE USE OF DRY STEAM INJECTION IN CLAY PROCESSING FOR THE BRICK AND TILE INDUSTRY, W. Somers, Clayton of Belgium N.V., Bornem, Belgium

The advantages of hot shaping of clay through steam treatment are common knowledge in the trade.

These advantages, which result in a finished product of a higher and more uniform quality, produced in less time and at less energy cost, are achieved under the sole condition of consistency in STEAM QUALITY.

WET STEAM, injected as a mixture of water and steam, will upset the mixing behaviour and, consequently, plasticity and homogenization.

Varying amounts of boiler water, carried along with WET STEAM, will make monitoring of plasticity by temperature regulation unreliable or, more often, completely impossible.

DRY STEAM (less than 0.5% moisture) is an absolute must.

TR 37 author present: 15.00 - 16.30

CURRENT RESEARCH INTO THE DRYING PROCESS OF DUTCH BRICKS, J. de Jong, A.H. de Vries,
TNO Institute of Applied Physics, University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

A special laboratory air-conditioned drying apparatus was developed by the TNO working group "structural ceramics". The specifications of this device under full climatization conditions are: temp. 5-90°C, relative humidity 10-95%, heating/cooling 0.3°C/min.; without humidity trajectories are controlled by computer. Output consists of: air flow, temperature and rel. humidity in testing room and linear shrinkage and weight change of the object. Data are imported by a microcomputer, calculated, and printed as colour plots. The possibilities and limitations of this experimental device will be discussed as well as drying characteristics of some Dutch bricks.

TR 38 author present: 15.00 - 16.30

HARBOUR SLUDGE FOR STRUCTURAL CLAY PRODUCTS
Dr Ing. Lau S. de Jonge
Royal Association of Dutch Brickmakers, De Steeg 6994 ZH The Netherlands

New dutch legislation surely will cause problems with respect to the continuous supply of suitable clay compositions. Following the considerations of dutch government, the use of (bulk) waste materials like harbour sludge, coal fly ash and ground rubbish would be the solution.
In the harbours of Rotterdam an enormous quantity of sludge is deposited by the outgoing rivers Rhine and Maas, and by the incoming North Sea.
That sludge has to be removed in the interest of trade, industry and shipping.
Research was made to make clear what technological and environmental problems would be met during fabrication, using more or less contaminated sludge.
After that studies were made to find profitable markets for new products.

TR 39 author present: 15.00 - 16.30

DEVELOPMENT OF AN USER-FRIENDLY COMPUTER MODEL OF THE TUNNEL KILN PROCESS IN THE CERAMIC INDUSTRY

Author: J.B. de Wit
TNO/MT Department of Heat and Refrigeration,
P.O. Box 342, 7300 AH Apeldoorn

ABSTRACT

An optimal design and operation of industrial processes requires insight in all the relevant factors influencing the process. Modelling and simulation techniques can give this insight. The Heat and Refrigeration Department of the Dutch organisation for Applied Physics (TNO) has developed two computer models:

- Q-KILN: For calculating the steady-state energy- and mass transport process in a tunnel kiln.
- Q-CAR: For calculating the dynamic thermal behaviour of the tunnel kiln cars.

In the model Q-KILN, the process is divided in a preheating zone, a firing zone and a cooling zone. Each of this zones is subdivided in sections. These sections are the basic elements of the model Q-KILN. The user can interactively change parameters and variables up to the level of a section. The output of the model is graphically and/or alphanumerically presented.

The model Q-KILN has its applications in energy conservation and in the design of tunnel kilns in the ceramic industry.Moreover, it seems very appropriate for operator training and for calculating the optimal process conditions. The model Q-CAR calculates the thermal accumulation and the heat transport in the tunnel kiln cars. It can be used as a separate model or as a module of Q-KILN.

TR 40 author present: 15.00 - 16.30

RHEOLOGY OF REFRACTORY CONCRETE,

H. Gorter*, J. v.d. Zwan
TNO Institute of Applied Physics,
Ceramics Department, P.O. Box 513,
5600 MB Eindhoven, The Netherlands

The rheological properties of two low cement castables have been studied. One of these concretes contained a deflocculant. We studied the influence of the water content on the viscosity, the apparent bulk density before and after vibration, consistency, cold crushing strength and modulus of rupture. The viscosity was measured with a rotational viscometer and the consistency with a funnel. The results show a distinct relationship between the water content of the mortar and the different material properties as cold crushing strength, modulus of rupture, viscosity, etc. By comparing the two concretes the influence of the added deflocculant becomes evident. Water content of the mortar is critical with respect to strength, consistency and the densification process. Doubt exists about the reliability of the consistency test. The results that should lead to an optimal water content close to standard PRE/R26, in fact yield a too high water content.

TR 41 author present: 15.00 - 16.30 withdrawn

TR 42 author present: 15.00 - 16.30

REFRACTORY BRICKS IN HIGHEST QUALITY PRODUCED WITH SGP-HYDRAULIC PRESSES,

Gerhard Zottl
Simmering-Graz-Pauker AG (SGP)
Brehmstraße 16, A-1110 Vienna
Phone: (0222) 7469/ext 412
Telex: 135436, Telefax: (0222) 7469/601

The press is the key for perfect refractory bricks
The production programme of SGP for the refractories industry ranges from simple presses with manual mould filling to computer-assisted, freely programmable and fully automatic production lines with setting and unloading devices.

SGP has two different press-designs in its programme:
The HSP oil-hydraulic floating table press is especially suitable for the manufacture of products withtop and bottom surfaces of equal area, such as feather-edged bricks, slide gates, etc.

The HSDP oil-hydraulic double-plunger press as our latest development is in particular suitable for pressing parts which have unequally sized surfaces or which are of considerable height, such as spouts or chimney linings.

For the highest quality of refractory bricks there is also very smooth handling necessary. The setting equipment produced by SGP cover all demands on such device

BI 1 10.00

BIOLOGICAL STUDY OF POWDERED CALCIUMPHOSPHATE CERAMICS IN SMALL RODENTS

C.A. van Blitterswijk[1], K. de Groot[1], G.J.J. Beckers[2], M.J.A.A. Goris[2], R.A. Terpstra[2]

[1] Biomaterials Research Group, University of Leiden, School of Medicine, the Netherlands
[2] Netherlands Energy Research Foundation, ECN, Petten, the Netherlands

We have started the study of new calciumphosphate materials for application as bioceramic. Many authors have shown that hydroxyapatite itself (HA) is very compatible with living bone and that thin (50 microns) coatings of this material onto metallic implants may be a good solution to circumvent the poor mechanical properties of bulk ceramics.
However, thin coatings of HA may dissolve after several years due to its - albeit limited - solubility.
$Ca_{10}(PO_4)_6(OH)F$ (= HFA = hydroxyfluorapatite) is less soluble, and, therefore, in theory more suitable for obtaining durable coatings.
However, its biocompatibility has not been demonstrated yet. Therefore, we studied the reaction of powdered HFA in small rodents in order to obtain information about its solubility in vitro and its biocompatibility.

BI 2 10.20

APATITE CERAMICS WITH TAILORED MICROSTRUCTURES FROM HYDROTHERMALLY-PREPARED ULTRAFINE HYDROXYAPATITE CRYSTALS, M. YOSHIMURA*, K. IOKU and S. SŌMIYA, Tokyo Inst. Tech., Nagatsuta, Midori, Yokohama, 227 Japan.

We have fabricated various apatite ceramics :Porous,Fully dense,Integrated microstructure from porous to dense, and zirconia-toughened. First,ultrafine HAp single crystals with homogeneous size,90nm×25nm,were prepared under hydrothermal conditions of 200°C and 2 MPa for 10 h. These powders start to sinter above 800°C to yield porous ceramics with 40% porosity of 0.5μm in diameter pores and grains at 900°C for 3 h, or to yield >99% dense ceramics with homogeneous grain size of 0.7μm at 1100°C for 3 h, by a pressureless sintering in air. Transparent specimen could be obtained from this ceramics by HIPing without capsule at 1000 °C under 200 MPa Ar for 1 h. By similar sintering and HIPing technique, ceramics with integrated microstructures from fully dense to porous could be prepared from layered compacts of fine powders and coarse grains. Starting from hydrothermally prepared 3Y-ZrO_2 fine crystalline powders dispersed in the apatite powders,toughened apatite ceramics with K_{1c}≈2 could be obtained.

BI 3 10.40 withdrawn

BI 4 11.00

THE IMPACT OF THE CLINICAL ENVIRONMENT ON THE SERVICE LIFE OF DENTAL CERAMICS

P.M. Marquis, School of Metallurgy and Materials, University of Birmingham, P.O. Box 363, Birmingham B15 2TT, UK

Relative physical properties of dental ceramics have been the subject of significant research for many years. The majority of studies have been undertaken in air and compared relative strengths. In contrast in clinical service the environment is saliva and cements and patients and clinicians are concerned about the incidence of failure. Results of an extensive set of strength measurements undertaken in a variety of environments, including a series of cements and saliva at different pH will be presented. It will be shown how variable strain rate tests can give the probability of failure at different biting loads and reductions in the load carrying capacity in time in the oral environment predicted. It will be discussed how the results explain the unexpected high survival rate of dental veneers and the implications to the use of other medical ceramics will be discussed.

BI 5 11.20

STABILITY OF HYDROXYLAPATITE IN A BIOACTIVE GLASS MATRIX AT SINTERING TEMPERATURES,

I. Kangasniemi* and K. de Groot,
Biomaterials Research Group, Dept. of Biomaterials, School of Medicine, Leiden University, The Netherlands.

The properties of hydroxylapatite (HA), bioactive glasses and glass ceramics have been well documented.
It has been shown that the rate of bone growth depends on the rate of ion release from the surface and on its chemical composition. It has been suggested that although both HA and bioactive glasses and glass ceramics are able to bond to bone, there seems to be a difference between the bone bonding mechanisms of HA and the two other materials. Hench suggested that the missing link between the two types of mechanisms might be the different concentration of Si at the interface of the biomaterial and the bone.
In this study we report on a biomaterial containing HA particles in an optimized bioactive glass matrix. It is shown that the HA particles are sufficiently stable in the glass matrix up to temperatures around 870°C and that it is possible to produce dense material for in vitro and in vivo studies.

BI 6 11.40

MODIFIED HYDROXY-APATITE COATINGS FOR BIOMEDICAL APPLICATION

J.A. Helsen*, I. Paulus
Dept. MTM, Katholieke Universiteit Leuven, Belgium

Hydroxyapatite (HA) coatings were applied by electrophoresis. The aim of the study was: 1) to improve the (rather poor) mechanical properties of the HA-coating; 2) to lower the sintertemperature in order to decrease the adverse effects of the post heat-treatment on the substrate; 3) to improve the adherence of the coating to the substrate.
Codeposition of fibres during electrophoresis, preliminary coating of the HA-particles with surface active components and modification of the Co-Cr-alloy surface resulted in an improved over-all behaviour of the coating. The interface between substrate and coating was studied by micro-Raman spectrometry.

BI 7 12.00

THE BONDING OF ALUMINOUS DENTAL PORCELAIN TO PLATINUM FOILS

Huaxia Ji and P.M. Marquis
School of Metallurgy and Materials, University of Birmingham, P.O. Box 363, Birmingham B15 2TT, UK

The fabrication of dental jacket crowns by bonding aluminous dental porcelain to a platinum foil base is a well established clinical system, although there is controversy as to whether a significant improvement in strength results. Results of a transmission electron microscopy study, including energy dispersive X-ray analysis, of the dental porcelain platinum interface will be presented showing that a tin oxide layer induces the formation of a rough surface giving a mechanical key. In contrast bonding to clean platinum involves a chemical bond. In both cases significant interdiffusion between the porcelain and metal occurs. It will be discussed how strength depends on the different types of bond and correct processing. The implications to the clinical performance will be reviewed.

BI 8 author present: 09.30 - 11.00

PREPARATION ROUTES OF $Ca_{10}(PO_4)_6(OH)F$ FOR BIOCERAMIC APPLICATIONS

G.J.J. Beckers*, M.J.A.A. Goris, R.A. Terpstra, K. Zeilstra
Netherlands Energy Research Foundation, ECN Petten, the Netherlands
J.G.C. Wolke, K. de Groot
Dept. of Biomaterials, Univ. of Leiden, the Netherlands

Recently we have started a new project on bioceramics in which some calciumphosphates will be prepared and studied which have up to now received little attention as implant material, but which are expected to have interesting properties as bioceramic implants.
In this paper we will discuss different preparation routes for one of these calciumphosphates, i.e. calciumfluorhydroxyapatite, $Ca_{10}(PO_4)_6(OH)F$ (FHA).
The following preparation routes have been studied, all based on mixtures of β-$Ca_3(PO_4)_2$, $CaCO_3$ and CaF_2:
Dry-mixing, pressing into pellets, reacting.
Wet mixing, milling, slip casting, reacting.
Wet mixing, milling, spray drying, reacting.
Wet mixing, spray roasting.
Purity of the FHA-phase is determined with X-ray diffraction.
In addition, we used FHA-powder for plasma spraying. Using a nitrogen/hydrogen mixture as plasmagas, we were able to produce coatings of about 50 micron onto metallic susbstrates.

BI 9 author present: 09.30 - 11.00

POROUS BIOCERAMIC OBTAINED WITH GLASS POWDER OF aO, MgO, P_2O_5 SYSTEM SEALED BY DIAMIDOPHOSPHATE.

H.Boutigny*, E.Delcourt-Debruyne*, G,Palavit**, P.Vast**, Y.Parent**, M.Héritier*.
*Lab. de Biologie Buccale,Fac.de Ch.dentaire,Pl. de Verdun,59045 Lille,France
**Lab. de Chimie Appliquée,Université des Sc. et Tech. Lille-Flandres-Artois, 59655 Villeneuve d'Ascq,France.

One of the metaphosphate glasses used in the field of bioceramics concerns the system Na_2O,CaO,P_2O_5. Obtained by sol-gel or sol-coacervate glass process,this glass is easily corroded in vivo.
By an exchange ion reaction with the initial coacervate,we can obtain the system Na_2O,CaO,MgO,P_2O_5 glass. Mg-Na ratio variations permit the modulation of glass corrosion in vivo. By heating at 770°C. a mixing of glass powders and sodium diamidoorthophosphate,we obtain a porous ceramic due to the loss of the main part of the nitrogen in ammonia form from diamidophosphate. It's possible to control the porosity of the ceramic so obtained.
We are testing in vivo the possible biocompatibility of this kind of porous

BI 10 author present: 09.30 - 11.00

A NEW Ca-BIPHOSPHATE BIOIMPLANT CERAMICS

T.S. Chin, Dept. of Materials Sci.& Eng. National Tsing Hua Univ. Hsinchu, Taiwan
D.C. Wu*, M.P. Hung*, S.S. Chou*, Dept. of Materials. Eng., National Cheng Kung University, Tainan, Taiwan, R.O.C.

A new Ca-biphosphate glass ceramic(Ca-2P for short) was successfully developed with properties superior to the conventional Ca-triphosphate glass ceramic (Ca-3P) glass ceramic for bioimplants.
The crystalline phases are b-$Ca_2P_2O_7$ and CaP_2O_6 for the Ca-2P glasses. Porous implants were sintered with loose powder technique at 610 C. Pore volume decreases steadily with sintering time and a pore size distribution remians in the range of 70-100 um, which is a function of starting frit size. The strength of Ca-2P is comparabale to the Ca-3P.
No apatite phase formed after boiling the Ca-2P in water for 3 hours depicting better stability than the Ca-3P which usually does. In vivo test in rabbits shows that the implanted tooth roots cause no inflammation and are nearly com pletely absorbed, with new vessels and osteoid ingrowing into the pores after a 90-day testing, while for the Ca-3P the absorption is reported to be just begun.

BI 11 author present: 09.30 - 11.00

SINTERING OF HYDROXYLAPATITE - GLASS COMPOSITE MATERIALS, E.Tkalčec*, N.Vrbos; and D.Navala, Faculty of Technology and Faculty of Metallurgy, University of Zagreb, 41 000 Zagreb, Yugoslavia.

Sintering of hydroxylapatite - glass composite powder compacts was studied. Hydroxylapatite was prepared by hydrothermal synthesis from shells OSTREA EDULIS. Optimal conditions of hydrothermal synthesis have been determined.
Homogenized mixture of glassy frits of various compositions but with constant CaO/P_2O_5 = 1.1 ratio and hydroxylapatite powder were dry pressed at 100 MPa and sintered at 900-1200°C for 2h. Phase analysis and microstructure of sintered compacts were determined by XRD and SEM, respectively. Apparent density and compression strenght of sintered compacts depend on hydrothermal synthesis conditions and on the glassy phase composition.

BI 12 author present: 09.30 - 11.00

BONE SEGMENTS OF DIFFERENT DIMENSIONS BASED ON HIDROXYLAPATITE AND ALUMINA, C.Galassi, A.Krajewski, A.Ravaglioli, E.Roncari Research Institute For Ceramics Technology - CNR, Faenza, Italy.

Aim of the work is the optimization of the processing parameters for the production of bone segments of different shape and made of alumina (as inert material) and hidroxylapatite (as a bioactive material). Slip casting on plaster moulds is the shaping method used for the preliminary production of several prototypes. Solid phase content, pH effects, deflocculant type and concentration, rheological characteristics in considering also the complexity and the dimensions of the chosen shape were optimized in order to obtain high density and defect free green bodies. Microstructure, green density, pore size distribution were evaluated on green bodies, final density, microstructure and microhardness were evaluated on the fired bodies in order to meet the requirements in view of biomedical applications of these materials.

BI 13 author present: 09.30 - 11.00

PHASE TRANSFORMATION IN DENTAL PORCELAINS FOR PORCELAIN-FUSED-TO-METAL-RESTORATIONS, M.M. Barreiro and E.E. Vicente, CNEA, Depto. Materiales, Av. del Libertador 8250, 1429 Buenos Aires, República Argentina.

Most commercial dental porcelains for porcelain fused-to-metal restorations are partially crystallyzed feldespathic glasses that consist of low (tetragonal) leucite ($K_2O.Al_2O_3.4\ SiO_2$) crystals embedded in a glassy matrix. Dental porcelains have a tendency to devitrify during certain heat treatments and may change their thermal expansion coefficients and their optical properties. In this work we have studied a dental porcelain body with a typical composition with different heat treatments (between 700-1200 °C and 10 min to 7 days). The techniques used were X-Ray diffraction, reflection optical microscopy, scanning electron microscopy, microprobe analysis and differential thermal analysis. Besides glass, we have found either low leucite or potash feldspar ($K_2O.Al_2O_3.6\ SiO_2$) or both, depending on the firing cycle. Many leucite crystals showed a substructure of lenticular plates internally twinned. Ceramography confirmed the nature of the transformation from high (cubic) to low (tetragonal) leucite upon cooling. We have explained the crystallization behavior of typical body compositions in the ternary phase diagram $K_2O-Al_2O_3-SiO_2$.

BI 14 author present: 09.30 - 11.00

THE STRUCTURE AND MECHANICAL PROPERTIES OF CORUNDUM BIOMATERIALS OF DIFFERENT POROSITY, C. Miksiewicz*, G. Rosiek, Institute of Civil Engineering, Technical University, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

At the Institute of Civil Engineering of Wroclaw Technical University methods were develcped of preparing a corundum biomaterial of porosity ranging from several to several tens percent (up to ca. 80%) and a sandwich-type corundum biomaterial consisting of dense and porous layers. The porosity of the material containing not less than 96% of Al_2O_3 was adjusted by changing the content of CaO and MgO added in a small amount.
In this work, the mechanical characteristics, pore sizes, and pore interconnecting chanels are presented as functions of the total porosity of these materials.
The method of joining a porous layer to a dense one allows to prepare materials of any number of strongly interconnected layers, thickness ranging from 400 µm up to several centimeters, and makes it possible to produce surgical elements of different shapes.
Long lasting experiments on animals and recently carried out clinical studies on application of the porous and dense-porous materials revealed its biocompatibility and good adaptability in living organisms.

BI 15 author present: 09.30 - 11.00

IS THE SOLUBILITY PRODUCT OF SYNTHETIC CALCIUM PHOSPHATES A GOOD PREDICTOR FOR THEIR BIODEGRADABILITY? F.C.M. Driessens, Dept. of oral Function and dental Prosthetics, Catholic University, 6500 HB Nijmegen, the Netherlands.

The following calcium phosphates were synthesized according to the usual methods of ceramic technology and their solubility product was determined by equilibrations in buffers at room temperature: hydroxyapatite, oxyhydroxyapatite, octocalcium phosphate, brushite, β-tertiary calcium phosphate and magnesium whitlockite. The solubility studies indicate that the resorbabilities for implants of these materials should be in the following order: magnesium whitlockite < hydroxyapatite < oxyhydroxyapatite < β-tertiary calcium phosphate. Comparison with biological studies in which these materials were implanted and studies for loss of material, indicate that under in vivo conditions the loss of material is determined not only by a physicochemical process like dissolution but also by biological processes like the scavenging of mineral particles by macrophages, as has also been found with metallic implants.

BI 16 author present: 09.30 - 11.00

ORTOPEDIC AND CLINICAL APPLICATION OF PIEZOFERROACTIVE CERAMICS,
V.E.Yurkevich, L.P.Belov, V.M.Mergold, B.S.Farber
Rostov on Don State Pedagogical Institute, 344717, Rostov on Don, USSR

T The system of the multifunctional microminiaturized medical devices, based on the piezoferroactive ceramics, used as informational transmitter as well as control systems and energy sources device (more exactly, transfers of the mechanical energy into electric one) have been given, elaborated and tested by the authors. Having no analogies in world practice and being original, these devices are characterized by compactness, little weight, engineering technical design sipmlicity, enegetical autonomy (i.e. absence of extermal power supply: electrical grid, accumulator, battery etc.) and the usage of piezoelectrical transformers of mechanical energy) as well as convinience and long-term exploitation. It is necessary to stress, that the practical use of the elaborated devices don't need special training (i.e. they are accessable for people). The simplicity and small size of the mentioned devices influence their designs, which are of great importance while dealing with children.

A number of apparatus such as devices for the biologically active zone influence, for the cordial activity stimulation (defibrilator) for bone growth control and also single working units for the artificial limb functioning control have been worked out by the authors, on the base of piezoferroactive ceramics, Positive results have been received by means of the long-tetmed clinical tests of the above-mentionrd devices: these have shown the absence of any negative side effects.

As an example it is necessary to mentioned the devices elaborated by the authors for the stimulation of special skin points, associated with such illness as diabetes at children.

Clinical tests have shown, that the application of these devices leads to the high clinical effect and to reduction of medicine required. Of considerable importance is also the fact, that the devices elaborated by the authors use the elements of microprocessor technology elements, which permit not only to batch the degree of influence, but also to chose the optimal paramerers of such influence.

BI 17 author present: 09.30 - 11.00

EVALUATION OF TISSUE INGROWTH INTO CORUNDUM BIOMATERIALS OF DIFFERENT POROSITY, G.Rosiek*, C. Miksiewicz, Institute of Civil Engineering, Technical University, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

Rod-shaped porous corundum implants with:
- global porosity 70-75%, pore size up to 1800 µm, pore-interconnecting canals up to 600 µm,
- global porosity 50-55%, pore size up to 800 um, pore-interconnecting canals up to 260 µm,
- global porosity 30-35%, pore size up to 450 µm and pore-interconnecting canals of up to 115 µm

were surgically implanted in drill holes in both femurs of the sheeps. The implants were retrieved after implantation times of 5 months.
The push-out test was used to evaluate the bond strength porous ceramic implant-bone joint.
The depth of bone growth and tissue mineralization in relation to global porosity was estimated using optical and scanning microscope.

BI 18 author present: 09.30 - 11.00

DISSOLUTION OF DENSE HYDROXYAPATITE FOLLOWED BY SURFACE ROUGHNESS DETERMINATION, **P. Gohar C.E.A. Fontenay aux Roses, France F. Bisson and D. Bernache-Assollant* Laboratoire de Céramiques Nouvelles, Limoges, France.**

Due to their good biocompatibility, calcium phosphates (H.A.P. and T.C.P.) are used as cement for filling cavities or dense implants for the replacement of bone in unloaded parts. Consequently a perfect knowledge of their reactivity in vivo and in vitro, particularly the mechanisms of their degradation and the relationships with microstructure are needed. Two kinds of dense H.A.P. were prepared. Powder of H.A.P. was spray-dried in water, calcined at 900°C and hot-pressed at 1200°C in the first case, only calcined at 900°C and hot-pressed at 1200°C in the second case. Dissolution of different samples was studied in buffered water at pH = 3.4. The evolution of the surface roughness was then followed with the aid of a rugosimeter apparatus. The experimental results confirm that dissolution always occurs through grain boundary corrosion, resulting in the decohesion of particles from the sample surface. The surface roughness increases at the beginning but become stable after several hours. The particles pulled out are large agglomerates for the spray-dryied samples (50 µm) and small grains (2 µm) in the second case. This reveals that relationships exist between batch prepa-ration and properties of the sintered materials.

SU 1 10.00

PHASE RELATIONSHIPS IN AIR IN THE SYSTEM $BaO-CuO-Cu_2O$, RELEVANT IN THE DEVELOPMENT OF CERAMIC SUPERCONDUCTORS, A.J. Lau and A.M. Segadães*

Depº Engª Cerâmica e do Vidro, Univ. de Aveiro, 3800 AVEIRO, PORTUGAL

Ceramic materials based on $YBa_2Cu_3O_7$ are the best superconductors known so far. Their development depends on the control of processing variables so that the materials produced do not contain the so called *green phase* (Y_2BaCuO_x), which is not superconductor. The knowledge of phase compatibility relationships in the system $Y_2O_3-BaO-CuO-Cu_2O$ is, therefore, of utmost importance.

It is known that the oxygen stoichiometry plays a fundamental role in the superconducting properties of these oxides and thus it must be considered in the determination of phase equilibria within the overall non-condensed system.

The present work was aimed at determining the relevant part of the isobaric phase diagram in air of the sub-system $BaO-CuO-Cu_2O$, up to 1200°C, using mainly thermogravimetric analysis, as a first approach to the system $Y_2O_3-BaO-CuO-Cu_2O$ into which this work will progress.

SU 2 10.20

SYNTHESIS AND SINTERING OF FOUR DIFFERENT $YBa_2Cu_3O_{7-\delta}$ COMPOUNDS, Jie Wang, G. Desgardin* ; F. Boterel, J.M.Haussonne, J. Lostec

ISMRa, Laboratoire CRISMAT, 14032 CAEN, France ; CNET, Centre Lannion B, 22301 Lannion, France.

When synthesizing $YBa_2Cu_3O_{7-\delta}$ by mixing and calcining powders, we can control the formation of a pure quadratic phase, so called P, previously to the formation of the classical orthorhombic (two different cells) and quadratic phases. The sintering of these different materials points out different behaviours characterised for example by dilatometric analysis.

The obtained ceramics own quite different microstructures and superconducting characteristics (particularely Ic).

SU 3 10.40

A VERSATILE SOL-GEL METHOD FOR SYNTHESIS OF CERAMIC SUPERCONDUCTORS

T. Eggermont, J. Fransaer, O. Arkens, O. Van Der Biest*

Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, Belgium

A sol-gel method will be described which is based on the use of ethylene-diamine-tetra-acetic acid (EDTA) as a complexing agent in the base solution.
An important advantage of the method is its versatility due to the fact that EDTA forms stable complexes for a wide range of elements. YBaCuO superconductors as well as a range of composition in the Bi-Pb-Sr-Cu-O system have been prepared using this method. Precise control of cation stoichiometry is possible. Powders prepared via this technique are in the micron size range and allow the use of reduced firing times and temperatures for densification, compared with powders produced via the solid state. The properties of superconducting thick films prepared via this technique will be presented and discussed.

SU 4 11.00

DENSIFICATION OF $Y_1Ba_2Cu_3O_x$ SUPERCONDUCTING CERAMICS. C.Moure, J.F.Fernández, P.Recio and P.Durán.

Instituto de Cerámica y Vidrio (CSIC), Electroceramic Department, Arganda del Rey, 28500 Madrid, Spain.

The sintering and densification of $Y_1Ba_2Cu_3O_x$ powders, obtained from several synthesis processes were studied. Density, microstructure and electrical properties were measured. The crystalline structures were determined by means of XRD. The coordination type and valence state were followed by XPS. The solid state reaction between the oxides and barium carbonate leads to a no well synthesized powders, which densified at high temperatures, with liquid-phase formation. Better results were obtained using a chemical process of oxalate coprecipitation. A solid state reaction between intermediate barium copper and barium yttrium compounds, given to a good sinterability powders, without second phases. Apparent densities higher than 95% D_{th} were attained. A correlation between density and tetragonal-orthorhombic transition was exposed.

SU 5 11.20 withdrawn

SU 6 11.40

PREPARATION AND CHARACTERISATION OF HIGHLY ORIENTED CERAMICS AND LARGE CRYSTALS OF Y-Ba-Cu-O SUPERCONDUCTOR,
P.Murugaraj, J.Maier* and A.Rabenau,
Max-Planck Institute für Festkörper-forschung und Metallforschung (PML)*,
7000 Stuttgart 80, F.R.G.

We successfully prepared BaO-deficient YBaCuO- ceramics with high degree of orientation[1] and extended the same technique to produce larger crystals (typically 3*3*1.5 mm). The critical temperature, (T_c) for these materials lie between 90 and 94K. The metal content is determined by ICP-technique and detailed oxygen non-stoichiometry by two different analytical techniques described earlier[2]. X-ray,magnetic and electrochemical measurements on these samples are discussed and electron microscopic investigations at various stages during the growth of the crystals are presented.

References: 1. P.Murugaraj, J.Maier and A.Rabenau, Solid State Commun. (1988) 735.
2. J.Maier, P.Murugaraj, C.Lange and A.Rabenau, Angew.Chemie 27(1988) 980.

CERAMIC SUPERCONDUCTORS : CHARACTERIZATION

Friday 23rd June; 10.20 - 12.40 **Chairman : P.H. Duvigneaud (Belgium)** **Room : 0.6/0.7**

SU 7 10.20

Characterization of High Temperature Superconductors by Thermal Analysis
W.-D. Emmerich, E. Kaisersberger * (1)
C. Politis, W. Krauss (2)
(1) Netzsch Gerätebau GmbH, 8672 Selb/FRG
(2) Kernforschungszentrum Karlsruhe GmbH, 7500 Karlsruhe/FRG

The preparation of high temperature superconductors from various precursors is mainly achieved by grinding and sintering of powders at appropriate temperatures. This is basically a ceramic technology which traditionally allows an extensive application of thermal analysis methods for its characterization. But also the further treatment of ceramic superconductors during tempering, oxidation, reduction, melting or decomposition offers a wide application field.

Yttrium-, bismuth- and thallium-based oxidic superconductors were prepared showing critical temperatures at 93, 108 and 125 K respectively.

Dilatometry, thermogravimetry and differential scanning calorimetry were applied to show phase transitions, structural changes, oxygen stoichiometry and decomposition. Kinetic evaluations were made to work out optimal process parameters.

SU 8 10.40

MICROSTRUCTURE AND PROPERTIES OF CITRATE-GEL PROCESSED Bi-CONTAINING Cu-OXIDE SUPERCONDUCTORS.

M. Rajabi and F.R. Sale*
Manchester Materials Science Centre,
University of Manchester, Manchester M1 7HS, UK.

Differential thermal analysis has been used to determine the temperatures of significant thermal events associated with the production of Bi-containing Cu-oxide superconductors from citrate-nitrate gel precursors. Powders have been prepared by thermal decomposition, characterised by scanning electron microscopy and X-ray diffraction analysis, pressed and sintered at the critical temperatures determined by DTA.

Microstructural studies of the pressed and sintered pellets, using optical and electron metallography, have been carried out and related to the temperature and time of sintering, atmosphere and cooling rate. The temperature and width of the superconducting transition have been determined using ac magnetic susceptibility measurements and have been related to microstructure and X-ray identification of phases.

SU 9 11.00

DEVELOPMENT OF Bi-Sr-Ca-Cu-O CERAMIC MATERIALS,

M.Peuckert*, J.Bock, B.Hettich, M.Schwarz
Hoechst AG, D-6230 Frankfurt/M. 80, F.R.G.

Basically, Bi-superconductors can be prepared in related structures with single, double and triple CuO_2-layers, and corresponding T_c-values of 60-75K, 80-90K and 95-110K. A detailed analysis of the structure of the BiO_2-layers by neutron diffraction revealed the possibility of doping these materials in order to increases T_c. The effect of various kinds of heat treatment and chemical doping on the formation of the different Bi-superconductors, as well as the consequences for the preparation of single phase powders and bulk ceramics will be discussed.

SU 10 11.20

Bi-CONTAINING SUPERCONDUCTORS PREPARED FROM RAPIDLY-QUENCHED AMORPHOUS FILMS, Masahiro YOSHIMURA*, Tae-Hyun SUNG, Nobuo ISHIZAWA, Zenbe-e NAKAGAWA, Tokyo Inst. Tech., Nagatsuta, Midori, Yokohama, 227 Japan.

Amorphous films in Bi-Sr-Ca-M(=Cd, Pb)-Cu-O system were prepared by rapid quenching after rapid melting technique without any containers using a twin roller. The $Bi_2Sr_2CaCu_2O_x$ amorphous films absorbed oxygen above 300°C, crystallized in c_o=2.5 nm phase above 500°C, and then yieled c_o=3.0 nm phase above 800°C in air. $Bi_2Sr_2Ca_2Cu_3O_x$ film anealed at 880°C for 1 hour, showed two-step superconducting transitions at Tc(onset-1)=111 K and Tc(onset-2)=90 K. In the samples $Bi_2Sr_2Ca_{2-x}Cd_xCu_3O_x$, substitution of Cd for Ca increased in Tc, vanished tailing of transition and well-oriented in c_o=3.0 nm phase. The sample with x=0.4 showed the highest Tc(end)=87 K and the best-oriented thick film. Futher substitution of Cd for Ca brought about lowering in Tc and finally showed no superconducting phase with c_o=2.5 nm which formed instead of c_o=3.0 nm phase. Effect of Pb substitution for Bi has also been studied.

SU 11 11.40

MASS TRANSPORT BEHAVIOUR AND DEFECT CHEMISTRY OF $YBa_2Cu_3O_{7-x}$ AND $Y(Ba_{1-y}K_y)_2Cu_3O_{7-x}$ CERAMIC SUPERCONDUCTORS,
I. Kontoulis, X. Turrillas, J.A. Kilner
B.C.H. Steele*
Centre for Technical Ceramics, Imperial College, London, SW7 2BP.

The oxygen stoichiometry and electrical resistivity of $YBa_2Cu_3O_{7-x}$ and $Y(Ba_{1-y}K_y)_2Cu_3O_{7-x}$ has been measured as a function of oxygen partial pressure in the temperature range 450-850°C in miniature sealed oxygen pump-gauge devices incorporating ceramic electrolytes. These data have been combined with results obtained by other workers using TGA equipment to provide a model for the defect chemistry of these materials. This model has been used to interpret oxygen self diffusion coefficient values obtained by $^{18}O/^{16}O$ exchange with dynamic SIMS depth profiling measurements and AC/DC solid state electrochemical techniques. The role of oxygen transport in optimising the composition of $YBa_2Cu_3O_{7-x}$ and other high T_c oxide superconductors for engineering applications will also be discussed.

SU 12 12.00

EFFECT OF GRAIN, TWIN GRAIN AND GRAIN BOUNDARY OF YBCO SUPERCONDUCTOR, B.R. Li,* A.Chen, Solidstate Electronic Department, Huazhong Univ.of Sci.& Tech. Wuhan, China

The microstructure (including grain, twin grain, grainboundary and so on) of YBCO ceramic superconductor was discussed. Large portion of twin-grains was observed in the pure YBCO of good superconductivity whose Tc=93K and T 1K. The ratio of the twin-grain is nearly 95%. Some researchers regard that it is the twin-grains that do favor to the current density. The microstructure of the doped YBCO system was also studied by the polarizing microscope. The fine grain structure with few twin grains has been observed. The current density was raised obviously comparing with that in pure YBCO material. The microstructure analyses and properties show that the fine grain structure is more important than the twin grain structure to raise Tc.

SU 13 12.20

MICROSTRUCTURE EFFECTS ON TRANSPORT PROPERTIES OF SUPERCONDUCTING CERAMICS,

R. Kormann*, J.P. Ganne,
Thomson-CSF, Laboratoire Central de Recherches, BP 10, 91401 Orsay, France.

The electrical properties of $YBa_2Cu_3O_7$ ceramics are highly dependent on its microstructure. In order to understand this relation, we have measured the electrical resistivity and critical current of materials which are different only in their milling technique and sintering temperature. The results are discussed in relation with material density, microstructure, grain morphology, presence of liquid phase in the grain boundaries and possible microcracks.

SU 14 author present: 16.30 - 18.00

VARIANTS OF SYNTHESIS AND DISTINCTIVE PROPERTIES OF THALLIUM CUPRATES SUPERCONDUCTORS,
L.Shustov*, V.Ozhogin, A.Myasoyedov, N.Tolmacheva, A.Inyushkin, A.Taldenkov, N.Babushkina, E.Krasnoperov, Yu. Teterin, Kurchatov Institute of Atomic Energy, 123182 Moscow, USSR.

We report a various methods of synthesis of tallium HTSC ceramics. Samples with Tc = 103 and 117 K were prepared by solid state reaction starting from Tl, Ca, Cu oxides and Ba nitrate. We have investigated the influence of the ceramic preparative conditions on superconducting properties. The samples were characterized by x-ray diffraction, electrical resistivity and ac magnetic susceptibility.
From XPS data Cu ions are found to be in Cu(I) and Cu(II) valence states, and Tl ions - in state close to Tl(I). There are two Ca and Ba valence states in the oxides, one of which is essentially lower then 2+. The fine structure of XPS spectra in the energy range of 10-40 eV is assumed to result from the interaction of Tl5d, Ca3p, Ba5p, Ba5s and O2s orbitals. This structure is an evidence of appreciable influence of inner valency orbitals on the outermost one. A structural scheme of the tallium HTSC is proposed.

SU 15 author present: 16.30 - 18.00

EFFECT OF Sc ON SUPERCONDUCTIVE PROPERTIES OF Y-Ba-Cu OXIDES,
Shatalov V.V.,* Buchikhin E.P., Kosynkin V.D., Kuzj V.E., Sycheva V.Y., Chernoplekov S.E., Kucheiko S.I., Ionov R.A., Bashun V.I., Sinchenko A.A., Evstignejev V.V., Rudnev I.A., All-Union Research Institute of Chemical Technology, Moscow, 115409, USSR

Using the method of solid phase synthesis we have succeeded in creating Sc-containing volumetrical superconductive ceramics with composition approching "1-2-3". The structure and phase composition of the products with various Y:Sc ratio have been studied. The values of T_c and critical current densities, obtained at various sintering temperatures, have been measured.

SU 16 author present: 16.30 - 18.00

DOPANT EFFECTS ON THE SUPERCONDUCTIVITY OF Bi-Sr-Ca-Cu-O SYSTEM,
T. Kanai*, T. Kamo and S. Matsuda, Hitachi Research Laboratory, Hitachi Ltd., Hitachi, Ibaraki, 317 Japan.

The effects of 36 different dopants on the $BiSrCaCu_2Ox$ ceramics were investigated. The dopants can be classified into four categories depending on their solubilities and substitution to the Bi-Sr-Ca-Cu-O structure. Dopants in the first category, e.g., Fe and Co, substitute in the copper sites and significantly reduce the transition temperatures(Tc's) of higher and lower Tc phase. The second category dopants, e.g., Y, substitute in the Ca sites and cause the disappearance of the higher Tc phase and the rise of Tc's of the lower Tc phase. While the dopants, e.g., alkalinc metals, in the third category have a limited solubility and a strong tendency to decompose the superconducting phase. This causes the disappearance of the higher Tc phase. Since the dopants in the fourth category, e.g., B, have a limited solubility and reactivity with the Bi ceramics, superconductivity of the higher Tc phase remains uneffected.

SU 17 author present: 16.30 - 18.00

CERAMIC STRUCTURE AND SUPERCONDUCTING PROPERTIES OF Bi-Pb-Sr-Ca-Cu-O,
B. Seebacher*, B. Jobst, G. Zorn, Siemens AG, Research Laboratories, P.O.Box 830953, D-8000 Munich 83, FRG

Ceramic specimens of Bi-Pb-Sr-Ca-Cu-O show superconductivity with zero resistance temperatures of 30 K to 90 K dependent on sintering procedure and chemical composition. For nominal composition $Bi_{1,7}Pb_{0,4}Sr_{1,7}Cu_3O_x$ almost single phase material with a structure corresponding to $Bi_2Sr_2CaCu_2O_{8+y}$ is obtained at low reaction temperature as shown by x-ray diffractometry. Zero resistance temperature is 62 K. With increasing sintering temp. phases corresponding to $Bi_2Sr_2Ca_2Cu_3O_{10+y}$ and $Bi_2Sr_2CuO_{6+y}$ are formed additionally. Diffractometry, resistance and a.c. inductance data demonstrate that a significant portion of a phase with transition temperature 108 K is formed, although zero resistance temperature is 90 K. Microphotographs show that the occurrence of this phase is associated with a plate-like porous structure without shrinkage. A more dense structure is obtained at higher reaction temperatures. However, extensive decomposition of the superconducting phases is then occuring.

SU 18 author present: 16.30 - 18.00

A NEW LIQUID SOLUTION BASED PROCEDURE FOR SYNTHESZING POWDERS OF THE BISCCO HIGH Tc SUPERCONDUCTORS,

Anne K. B. JAHRE* and Stein JULSRUD
Institute of Inorganic Chemistry
Norwegian Institute of Technology
N-7034 Trondheim

The polysaccharide "Xanthan" was added to stoichiometric solutions of the relevant oxides in nitric acid. After slow dehydration, a solid precursor material was formed, which on decomposition gave the multicomponent oxide compound. Several compounds in the system Bi_2O_3-SrO-CaO-CuO-PbO were synthesized, and the powders were characterized by X-ray diffraction and magnetic susceptibility measurements.

SU 19 author present: 16.30 - 18.00

EFFECT OF pH ON THE PREPARATION OF HIGH Tc SUPERCONDUCTING Y-Ba-Cu-O COMPOUNDS, Esa Immonen, Microelectronics Laboratory, University of Oulu, Oulu, Finland.

When producing 123 materials by chemical routes it is important to know the influence of the pH of the solutions from which the precursors are precipitated on the superconducting properties. There has been work on the influence of low pH on the formation of the precursors. There has been a suggestion that high pH leads to the enhancement of the precipitation of Y^{3+} and Ba^{2+} ions. In this study the effect of use of pH higher than 10 on the formation of precursors by the oxalate route was investigated using sodium hydroxide and tetramethylammonium hydroxide as the base. The use of ammonium hydroxide was not successful. It was not possible to precipitate the precursor at a reasonable rate. The solutions were studied using DC plasma emission spectrometry. The precursors were studied using TG analysis and X-ray diffraction after firing at different temperatures between 700 °C and 900 °C. SEMs were prepared to study the particle size of the dried precursors. The main phases present were identified using compo techniques. The materials were sintered as pellets and the superconducting behaviour investigated by measuring the resistivity. It is concluded that pH values much higher than 10 results in rapid precipitation of the precursor of very fine particle size. It is possible to sinter these homogeneous materials at temperatures around 870 °C to produce uniform single phase materials with zero resistance around 90 K.

SU 20 author present: 16.30 - 18.00

PROPERTIES OF Ag_2O DOPPED HIGH-T_c Y-Ba-Cu-O SUPERCONDUCTORS PREPARED BY HOT-PRESSING TECHNIQUE, K. Hrnčíř, T. Kala, V. Skácel, M. Janda, L. Čižinský, J. Fiedlerová, A. Koller, Research Institute of Electrotechnical Ceramics, Hradec Králové 500 64, Czechoslovakia

The Hot-Pressing technique was used for the sintering of bulk Y-Ba-Cu-O samples with different amounts of silver oxide.

X-ray diffraction, scanning electron microscopy and electrical measurements were used for investigation of the influence of sintering conditions as well as the silver oxide dopping levels on the structural and transport of these samples. The results are compared with those obtained on Y-Ba-Cu-O ceramics without any dopants.

SU 21 author present: 16.30 - 18.00

PRODUCTION OF A $YBa_2Cu_3O_7$ CYLINDER FOR MAGNETIC FIELD SHIELDING

L.P.L.M. Rabou*; Z. Tarnawski[+] and H.P. van der Meulen
Netherlands Energy Research Foundation, ECN
P.O. Box 1, 1755 ZG PETTEN, the Netherlands;
University of Amsterdam, the Netherlands

A ø19x50 mm cylinder has been produced from a high-quality $YBa_2Cu_3O_7$ powder prepared by a citrate synthesis route [1]. The cylinder is to be used as a shield against the magnetic field ripple of a high-field magnet [2]. Data on the shielding capacity of cylinders produced by various ceramic shaping techniques are presented. The effect of different sintering procedures and variations in the chemical composition are discussed.

[1] D.H.A. Blank et al., J. Phys. D 21 (1988) 226.
[2] Z. Tarnawski et al., Cryogenics 28 (1988) 614.

[+] on leave from Academy of Mining and Metallurgy, 30-059 Krakow, Poland.

SU 22 author present: 16.30 - 18.00

DEPOSITION THICK FILM PATTERNS OF THE HIGH-T_c SUPERCONDUCTOR $YBa_2Cu_3O_7$ ON CERAMIC SUBSTRATES.

K.Przybylski*, J.Obłąkowski, J.Koprowski, M.Wierzbicka

Institute of Materials Science, Academy of Mining and Metallurgy, Kraków, al.Mickiewicza 30 Poland.

Superconductor thick films of Y-Ba-Cu-O on Al_2O_3 and $SrTiO_3$ substrates were obtained by means of screen printing and direct painting. The high-T_c superconducting oxide $YBa_2Cu_3O_{7-x}$ has been prepared by precipitation of amorphous oxalates and by reaction of Y_2O_3, CuO and $BaCO_3$ powders of appropriate ratio. Precipitates of oxalates were decomposed at around 400°C to yield a solid precursor material. The precursor was fired to high temperature to form the desired compound. The decomposition mechanism was studied with thermogravimetric analysis and X-ray diffraction. The influence of PbO addition on the formation and sintering of the superconducting compound was also investigated. The microstructure of the films was characterised using SEM and TEM. The resistivity measurements indicated that the films deposited on strontium titanate and sintered at 960°C for about 1,5 h gave the best superconducting properties /$T_c \sim$ 90 K/.

SU 23 author present: 16.30 - 18.00

SUPERCONDUCTIVE LAYERS ON COPPER RIBBONS

V.Hajko jr.*, S.Molokac, M.Timko, A.Zentko, O.Hudak ; Yu.N.Ivashchenko, Yu.V.Milman, S.V.Pan, V.V.Kovylyaev,
Inst. of Experimental Phys. Slovak Acad. of Sci. 043 53 Kosice, Czechoslovakia ; Inst. for Probl. of Mat. Sci. Ukrainian Acad. of Sci. 252180 Kiev, USSR.

Copper ribbons doped with Y and Ba were prepared by using the melt spinning method. Structure, magnetic susceptibility and electrical resistance of thermally oxidized ribbons were studied. Surface oxide layers of the ribbons have a granular microcrystalline structure with a multiphase nature. The experimental results on magnetic susceptibility and resistance revealed the anomalous behaviour of these ribbons at room temperature. The critical fields H_{c1} and H_{c2} were estimated to be equal to zero for $T_c \sim 330K$. A variety of the data reveals that for currents of $\sim 10^{-4}$A and at room temperature the samples display the presence of regions with abnormally low resistance that form a fairly unstable " Josephson medium". The above mentioned anomalous behaviour in the measured samples has been observed for four weeks.

SU 24 author present: 16.30 - 18.00

MICROSTRUCTURAL STUDIES OF SCREEN PRINTED SUPERCONDUCTORS,

J.S. Abell*, F. Wellhofer; D. Holland, E.A. Logan.
School of Metallurgy and Materials, University of Birmingham, U.K.; Department of Physics, University of Warwick, U.K.

The development of superconducting tracks on various substrate materials by screen printing depends on processing variables such as sinter regime, thickness and particle size. The resultant microstructures of both the tracks and the track/substrate interfacial layer have been studied by a variety of methods and their significance in determining the superconducting properties has been assessed. Experiments on both YBCO and BSCCO will be reported and the potential for employing barrier diffusion layers to restrict substrate interaction will be discussed.

SU 25 author present: 16.30 - 18.00

SPECTRAL, SUPERCONDUCTING AND MAGNETIC PROPERTIES OF $Ba_2YCu_{3-x}M_xO_{7-\sigma}$,

N. Brničević, Lj. Tušek-Božić, P. Planinić*, A. Turković, B. Šantić, S. Popović, Rudjer Bošković Institute, 41000 Zagreb, Yugoslavia; G. Leising, E. Schweiger, V. Wippel, Institut für Festkörperphysik, Technische Universität Graz, A-8010 Graz, Austria

The partial substitution of copper atoms in the superconducting system $Ba_2YCu_{3-x}M_xO_{7-\sigma}$, M=V, Nb, Ta was investigated. The samples were prepared by the solid state reaction of $BaCO_3$ and metal oxides using subsequent isothermal treatment at 860^o, 900^o and 950^oC. The infrared spectra indicated complete decarbonization of the samples. Superconducting transition was found at 90-93 K and higher Tc values were favored by the presence of small amount of dopands. Higher amount of transition metal elements caused the formation of a separate nonsuperconducting phase. The signal in the EPR spectra obtained for the zero values of magnetic field was of considerable higher intensity than in the nonsubstituted samples. Spectral, superconducting and magnetic properties are discussed.

SU 26 author present: 16.30 - 18.00

MICROWAVE SURFACE RESISTANCE OF SUPERCONDUCTING CERAMICS, F. Lainée*, M. Labeyrie, R. Kormann and J.P. Ganne, Thomson-CSF, Laboratoire Central de Recherches, BP 10, 91401 Orsay, France.

A coaxial resonator method has been developped to characterize the new superconducting ceramics (YBCO) in the range 1-10 GHz.

The surface resistance shows an abrupt decrease at the transition temperature (90 K). The low temperature (4 K 70 K) value compares favourably to the values for copper, which is a necessary condition for possible microwave applications.

The value of the low temperature surface resistance is compared to theoretical predictions. Its dependence on various parameters (frequency, magnetic field, sample processing) is studied, giving an insight in the anomalous microwave losses exhibited by superconducting ceramics.

SU 27 author present: 16.30 - 18.00

AMORPHOUS TO CRYSTALLINE TRANSFORMATION IN YBCO SUPERCONDUCTORS, R. Dal Maschio*; A. Maddalena.
Engineering Department of University, Trento, 38050, Italy.
Mechanical Engineering Department, Materials Section, University of Padova, Padova, 35100, Italy.

Recently YBCO superconductor ceramics have been synthetized by crystallization of amorphous samples. This route seems to permit production of samples with increased density, better fracture resistance and enhanced electrical caracteristics in comparison with samples prepared by the standard method of sintering powders. This work was undertaken to investigate the crystallization of amorphous samples prepared either by the sol-gel method or by quenching the molten mixture.
The transformation from amorphous to crystalline was studied by differential thermal analysis and poxder x-ray diffraction. The effect of different thermal treatment or atmospheres was also investigated.

ST 1 15.00

ADVANCED CERAMICS STANDARDS DEVELOPMENT,
S. Schneider
Natl. Inst. of Standards & Technology
Gaithersburg, MD 20899, United States

Advanced ceramics, because of their unique properties, are being extensively researched, developed and brought to market as rapidly as possible. Currently there are no consensus standards that allow national or international comparisons and this lack represents one of the more important technical unknowns in the commercial market equation. While the needs are diverse and product specific, foremost is a singular need for a unified classification system as it sets the basis for unanimity in information transfer and coherent standards development. Advanced ceramics standards development is gaining momentum with independent efforts now underway in several countries. However, early international collaboration is needed to harmonize standards before conflicting national systems emerge. This paper presents a perspective on advanced ceramics standards needs, current activities and necessary future directions required for equivalence in data between groups and nations.

ST 2 15.40

STANDARDIZATION OF STRUCTURAL CERAMICS.
Prof. M. Van de Voorde, European Communities,
Joint Research Centre, P.O.Box 2, 1755 ZG PETTEN

Structural ceramics are becoming important and receive more and more popularity in advanced technologies e.a. aerospace and aeronautics, automotive industry, energy sector, petrochemistry etc. For example, in gasturbine applications, superalloys operate at the limit of their capability and industries have high hopes in the breakthrough of the new ceramics technology.
The requisite for commercial introduction is the "reliability" of engineering ceramics:
I) The reproducibility in processing and
II) The reliable performance and life time prediction in service.
To assure the production of high quality ceramics necessitates control of the processing parameters : powders characterisation, sintering process etc. To master the materials degradation implies properties characterization and evaluation: mechanical, thermal, corossion, wear etc. including methods for high temperature testing and standards for design.
This paper will give an overview of the standardization initiatives in the industrial ceramics community to validate testmethodologies for ceramics processing and reliability in service
It focusses on the research and development efforts to realize standard testmethodologies.

ST 3 16.20

STANDARDIZATION IN SOFT MAGNETIC CERAMICS LEADS TO INTERCHANGEABILITY AND QUALITY ASSESSMENTS
P.N. Faase*, C. Vlas. Philips Einhoven BFI

Soft magnetic ceramics fin' their application as core-material in transformers and inductors in electronic equipments. Furthermore the evolution of different technologies and their influences on the electronic equipment, have lead to the need for international standardization.
For the standardization of the electronic components, international committees already existed. On European level CECC and World-wide level IEC. These organizations became also active in the field of soft magnetic ceramics.
This paper presents an overview of the results of these standardization efforts. The organization structure and additional benefits in the fields of quality assessments and certification will also be presented.

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