Symposium

Advanced ceramic manufacturing in the Benelux

Friday 25 October 2024, Eindhoven University of Technology

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Oral presentations

Advanced Manufacturing of Near-Net shape Ceramic Products

Pablo Gonzalez, CoorsTek

The bulk of advanced ceramics processing is done through the rework of (pressed) preforms into final products. In the past years there has been increasing interest in (near) net shaping of parts in the framework of efficiency and sustainability. In this presentation we show some of the approaches taken to shape ceramics through plastic forming of ceramics (e.g. injection molding, extrusion or additive manufacturing). These techniques can be applied from high run components to high value short run parts made with newly developed compositions. Typical applications are found in the semiconductor, automotive and medical industries.

Speaker Bio:

Pablo Gonzalez is R&D Manager for EMEA in CoorsTek, a global leader in engineered ceramics manufacturing. He obtained his PhD in Nanomaterials from the University of Twente (MESA+ institute, NL) in 2016. His background is in materials science, ceramic engineering, additive manufacturing and laboratory technology.

Solution for long bone non-unions:
Looking for structural support for our active ingredient

Nienke de Roode, Access2bone

One of the most challenging defects in bone repair are Long Bone Non-Unions, since there is no direct bone apposition. The bone graft that would be suitable for this needs to be able to actively repair the bone defect and also provide structural support. One of the products developed by Access2Bone has active osteoinductive potential and would be very suitable as active ingredient for this bone graft. Access2Bone is looking for cooperation for the development of the structural support.

Self-standing SiAlON doughs facilitate low-volume production through green machining

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Ceramics are the preferred matreials for applications that require long-term durability, high strength, thermal stability, and chemical resistance. These desirable features, however, present significant challenges for typical production procedures, frequently leading to compromises in material or shape. Advanced ceramics typically demand customized configurations, and they are often machined at their green state for near-net shaping. The most common methods for preparing green bodies—uniaxial and cold isostatic pressing, as well as slip casting—are dependent on costly equipment and/or specialized molds [1]. Currently, there is a lack of versatile processing methods that allow the use of existing setups for rapid prototyping and production at various scales in a cost- and energy-efficient manner.

Previously, we have developed a method to create self-standing doughs for single-component ceramic systems, specifically metal oxides [2, 3]. Using particle-specific polymeric additives, we imparted a clay-like rheology to ceramic suspensions through polymer bridging-induced homogeneous coagulation. These doughs could be shaped by hand or machined using conventional or laser machining while still in the green state. We have now expanded our methodology to include a multicomponent ceramic system consisting of nitrides. Specifically, we adapted the approach to SiAlONs, which are silicon (Si), aluminum (Al), oxygen (O), and nitrogen (N)-based ceramic alloys known for their excellent thermal and mechanical properties. We were able to evenly coagulate highly-loaded SiAlON suspensions by introducing a single additive, a poly(ethylene glycol)-grafted random copolymer of acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid. This additive, used at a minimum of 2 wt. %, generates a dough containing 72.7 wt. % SiAlON in under two minutes of mixing. We machined this semi-dried dough at room temperature and compared its mechanical and microstructural properties with a commercial-grade wear part that was fabricated from the same powder through die pressing. The green bodies of self-standing doughs had a flexural strength of ~0.5 MPa, which was low enough to prevent tool wear while maintaining the integrity of samples throughout machining. Following sintering, hardness and calculated fracture toughness of the samples that are prepared from the self-standing doughs were comparable to those of the die-pressed, 13.48±0.35 GPa, 6.22±0.28 MPa·$m^{1/2}$ and 14.40±0.39 GPa, 6.40±0.40 MPa·m $^{1/2}$ respectively. These doughs produced ceramic objects with a post-sintering density of 3.24 g·cm^{-3} (~99.99% theoretical density), allowing for the fabrication and prototyping of intricate designs using traditional machining methods.

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Teaser video: Process flow of malleable, self-standing doughs of SiAlONs: https://vimeo.com/983029726

Keywords: ceramic machining, SiAlONs, computer numerical control, rapid prototyping, green machining

Template-free and Size-controlled Synthesis of Rod-like Zirconia via Co-solvent Systems

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Synthesis of anisotropic, monodispersed and well-crystallized zirconia without using templates or surfactants remains a challenge. In this study, inspired by the solvent shell surrounding ions or particles, we developed a approach using co-solvent system to induce steric hindrance around initial crystallites, thereby promoting anisotropic crystals growth. The effects of temperature and reaction time were systematically investigated to elucidate the formation mechanism. Notably, large-scale production potential was demonstrated, achieving a high yield of 98.8% for rod-like zirconia powders. This approach offers a promising route for size-controlled synthesis and scalable production of rod-like, phase-pure m-ZrO_2 without the need for surfactants or additives.

Additive manufacturing of multi-material ATZ and 3Y-TZP parts for implant applications

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Multi-material components provide enhanced performance by combining the beneficial properties of their constituent materials. In the case of implants with an alumina-toughened zirconia (ATZ) surface and a 3Y-TZP core, the combination of ATZ's low-temperature degradation (LTD) resistance and 3Y-TZP's toughness has the potential to offer better mechanical properties compared to single-material implants. Additionally, the mismatch in thermal expansion coefficients and elastic moduli between the two materials induces residual stresses during cooling, with beneficial compressive surface stresses that enhance both strength and wear resistance.

Direct Ink Writing (DIW) is an extrusion-based additive manufacturing (AM) technique where objects are built layer-by-layer by depositing a paste with controlled rheology through a narrow nozzle. This cost-effective and versatile approach allows for the fabrication of multi-material parts with compositional variation in both the xy and z directions, which is difficult to achieve through conventional processing methods.

This study demonstrates that ATZ and 3Y-TZP components produced via DIW exhibit mechanical properties comparable to those of conventionally manufactured parts. Process parameters were further refined to produce multi-material structures with an ATZ surface and a 3Y-TZP core. Residual stress magnitudes, arising from varying layer thickness ratios of the constituent materials, were measured using X-ray diffraction (XRD) and µRaman spectroscopy. These measurements informed the selection of an optimized design, achieving the highest compressive surface stresses for improved performance.

Grafting ceramic supports for creating hydrophobic surfaces

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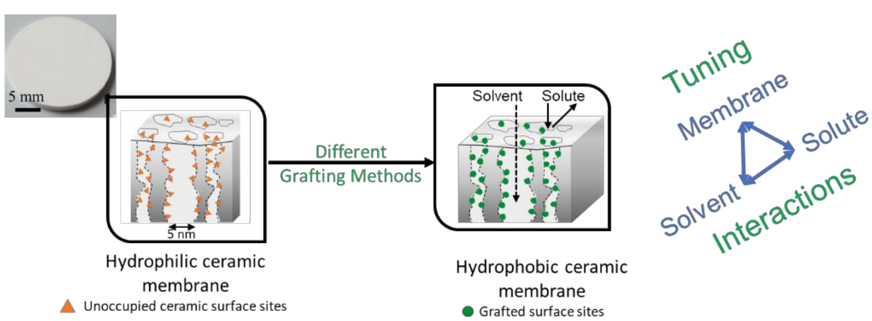
Keywords: grafting-to, alkyl-based phosphonic acid, nanofiltration ceramic membranes

Abstract

Hydrophobic organo-functionalized ceramic membranes represent a remarkable advancement in membrane technology, offering a versatile solution for a wide range of separation and purification processes. One intriguing utilization of hydrophobic ceramic membranes is nanofiltration (NF) membranes, applied for the recovery of apolar solvents, and/or valuable molecules contained therein, require not only high chemical, thermal, and mechanical stabilities to withstand the operating conditions but also require favorable interactions between solvent, and solute. The desired stability can be achieved by using ceramic NF membranes. However, due to the hydrophilic nature of ceramic membranes a decrease in apolar solvent flux is observed compared to water flux [1]. To tackle this issue, the surface modification of mesoporous ceramic membrane with alkyl-based phosphonic acid molecules is a promising solution to tune the hydrophilic surface into hydrophobic/oleophilic one. Simultaneously it reduces the pore size of the membrane from the ultrafiltration to the nanofiltration range [1,2]. In this work, the possibility to functionalize ultrafiltration ceramic membranes with alkyl-based phosphonic acid molecules were presented. Relevant analysis methods have been used to show the successful grafting and resulting pore reduction to the NF range as well as the change in surface property of the ceramic membranes.



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Molecular layer deposition modified pore size and hydrophobicity of ceramic membranes for nanofiltration

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Membranes are used at large scale to purify surface or wastewater and are increasingly applied in nanofiltration (pore size range 1-10 nm) of organic solvents. However, mass organic solvent streams containing small molecules are still treated with traditional energy-intensive technologies like distillation. Here, polymeric membranes suffer from swelling [1], which can change pore sizes significantly due to solvent-membrane interaction. In contrast, ceramic membranes are hydrophilic and thus more robust, yet more challenging to reproduce commercially [2].

The modification of membranes by ALD has recently been reviewed by Weber et al. [3]. In this study we have used Molecular Layer Deposition (MLD) to modify high-porosity Al_2O_3-based ceramic membranes with average pore size of 20 nm, by coating their internal surface with titanicone-type hybrid layers grown by MLD. Objectives were to 1) narrow the membranes' pore size and pore size distribution, and 2) to investigate the hydrophilicity of hybrid layers grown by MLD from $TiCl_4$ and three different organic co-reactants, being heptanol, 3-aminopropyltriethoxysilane (APTES), and n-propyltrimethoxy-silane (n-PTMS). Depositions were carried out at temperatures ranging from 100 to 200 °C, at pulse times ranging from 0.1 to 0.4 sec for $TiCl_4$ and from 1 to 20 sec for the co-reactants, and from 60 to 120 for N_2 purging.

The respective hybrid layers were tested on their ability to reduce pore size. Typically, by using MLD, the average pore size of the bare ceramic support (~20 nm) could be reduced down to 2 nm as determined by permporometry [2].

The three hybrid layer types were also grown with identical process recipes on planar silicon substrates. This way they could be tested on their surface hydrophilicity and chemical stability in different solvents

- Surface hydrophilicity was measured by way of measuring the respective Water Contact Angle (WCA). These WCA values were 78° (EG), 114° (n-PTMS), 109° (heptanol) and 106° (APTES).
- Chemical stability was measured by immersing the samples in solvents with decreasing polarity: water > ethyl acetate > acetone > hexane. The n-PTMS-based hybrid layer showed the most promising results: while the heptanol- and APTES-based layers reacting with solvents lost hydrophobicity (WCA reducing to < 90°), the n-PTMS based hybrid layer exhibited excellent stability against hexane (non-polar), without layer degradation or change in its wetting performance (WCA constant at 114° after 24 hrs and seven days).

The results obtained so far provide new insights into the effect of using different organic co-reactants in MLD to optimize pore size and surface hydrophilicity in order to improve the performance of ceramic membranes in organic solvent nanofiltration.

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Additive manufacturing of ceramics by Binder Jetting and PAM: towards a hybrid approach

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Pellet Additive Manufacturing (PAM) is a material extrusion process using pellets feedstock from injection molding. These pellets are shaped by a micro-extruder with nozzles down to 200 µm diameter. In this study, we assess the relevance of this technology for producing dense ceramic parts from commercial zirconia feedstock. The parts were manufactured on a PAM-MC printer (Pollen AM). A parametric study determined the optimal printing conditions. Based on a qualitative examination of the samples (no over/under-extrusion and/or macroscopic defects) as well as the absence of detectable porosities, test specimens were debinded and sintered. Mechanical properties comparable to those of injected zirconia parts were achieved: maximum relative densities of up to 99.8%, a hardness about 1379 HV1, and flexural strength up to 1256 MPa. Such performances, along with the ease of implementation of PAM technology, make it a credible option for the production of technical ceramics. However, an inherent limitation of PAM shaping process is surface finishing. Sintered parts retain a "staircase" surface defect resulting from the overlap of the filaments.

Binder Jetting (BJ) is recognized as the most productive additive manufacturing technique, enabling high production rates. However, the fabricated parts typically exhibit significant porosity, which can limit their mechanical properties. In this work, we achieved ceramic parts with a relative density of up to 80%, improving their structural integrity. Another challenge inherent to this process is the surface roughness of the parts, which remains a limiting factor for certain applications.

In an attempt to address, the issue of surface finish, we demonstrate the possibility of hybridizing PAM and BJ printing by adding a green state milling using cutting tool (PAM) or laser (BJ). This manufacturing approach significantly improves surface quality and allows us to envision other perspectives.

Keywords: Zirconia-CIM feedstock, Pellet Additive Manufacturing (PAM), Binder jetting, Hybridized process

Abstract

AM Ceramic CATs

Empowering Sustainable Housing on Earth and beyond with AM Technology and Ceramic-type Geopolymers

This presentation introduces **Circular Architectural Techniques (CATs)** as a crucial solution to global challenges such as the **ABC Crisis**—Affordable Housing Shortage, Biodiversity Loss, and the Climate Crisis—while improving construction efficiency. Our first **Minimum Viable Product (MVP)**, the **LunarNomad Yurts**, and the Circular BlueMoon Village project, offer scalable, affordable, and sustainable housing solutions for Earth and beyond.

CATs is composed of three core components:

1. **AI-powered design software**
2. **Portable Production Units**
3. **DIY construction system**

The focus will be on the **Portable Production Units**, which enable the on-site manufacturing of **Circular Bricks and Blocks** using **Ceramic-type geopolymers**. These blocks can be produced using **Additive Manufacturing (AM) technologies**, specifically **Selective Laser Sintering (SLS)** and **Binder Jetting**, which provide flexibility and efficiency in construction. We are exploring how these methods can contribute to affordable, sustainable housing solutions.

With the global market for sustainable and affordable housing projected to grow to **trillions of euros**, the **AM ceramic community** is invited to join this journey, contributing to **MVP development**, **licensing partnerships**, and future R&D collaborations.

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Poster presentations

Experimental and numerical analysis of the sintering behavior of multi-layer membranes

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Multi-layered membranes are becoming increasingly important for separation techniques required in energy applications such as fuel cells. By reducing the thickness of the membrane to improve its transport properties, a porous supporting layer is required to improve mechanical stability. The addition of this layer introduces fabrication issues such as anisotropic shrinkage and bending effects. By substituting the conventional flat interface between the layers with a wavy contact surface, studies have found that the densification can be optimized to minimize distortion. These rough interfaces generate a desirable stress distribution, reducing the bending of the membrane during sintering. Realization of such interfacial designs is hindered by its demanding manufacturability in size and shape, although recent advancements in additive manufacturing technologies such as 3D printing can provide solutions. To optimize the design for minimal bending, numerical models are designed to overcome the costly trial-and-error methods. In this project, we are aiming to manufacture membranes with increased surface contact and reconstruct a numerical model to evaluate the evolution of the membrane during sintering.

Additive manufacturing of polymer-derived ceramics with multiscale architectures

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Most of ceramics are difficult to process due to their high melting points and the lack of ductility. How to prepare bulk ceramics with high damage tolerance and complex shapes has become the focus of extensive research. Herein, we propose a strategy to develop and strengthen structural ceramics by multiscale architectures. Using additive manufacturing technologies, the preceramic polymers will first be processed to form three dimensional polymer frameworks that can have a honeycomb structure or various other bioinspired shapes. Through a route based on polymer-derived ceramics, the preceramic polymers will be first chemically modified with metal precursors (e.g., Cu, Ni), and subsequently pyrolyzed to obtain ceramic matrix composites containing metal nanoparticles. The combinations on the macro and micro levels are expected to produce advanced ceramic parts. These cellular architectures will allow the implementation of these ceramics to a wide range of applications, such as electrocatalyst for producing hydrogen.

Mechanical characterization of ceramic-organic supercrystalline nanocomposites by nanoindentation

Cong Yan, Eindhoven University of Technology

Supercrystalline nanocomposites (SCNCs) are a new category of materials, consisting of inorganic building blocks that are surface-functionalized with organic ligands. They are architected into the periodic arrangements, reminiscent of classic crystalline materials. SCNCs feature multifunctional properties (opto-electrical, magnetic, catalytic etc) and are promising building blocks for hierarchical materials. Understanding the mechanical behavior of SCNCs is an essential requirement for a future implementation into functional devices. Here, the creep and flow behavior of SCNCs are explored by using nanoindentation. The underlying creep mechanism in SCNCs is identified as the rearrangement of organic ligands and a free volume-based model is proposed to predict their creep behavior. As for the flow behavior, a new approach based on the expanding cavity model is proposed to extract stress-strain curves from the nanoindentation data. The elastic-plastic with strain hardening deformation behavior is observed in SCNCs.

Manufacturing the next generation of fiber reinforced ceramic materials

Joost Guiking
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A material with a zero coefficient of thermal expansion (CTE) will have many benefits in precision engineering. This can be achieved with ceramic matrix composite (CMC) materials, specifically a carbon fiber reinforced silicon carbide (C/SiC) material. An in-house setup will be developed to manufacture CMC specimens, to be able to analyse how the production process influences the material properties.

Low-Temperature Breakthrough: Progressing the consolidation of Hydroxyapatite and polymer Composites through Cold Sintering

<u>Muthusundar Kumar</u>[1,2], Mohamed Aymen Ben Achour[2], Marie Lasgorceix[2], Rosica Mincheva[1], Jean-Marie Raquez[1] and Anne Leriche[2]

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Abstract

The Cold Sintering Process (CSP) offers a rapid and energy-efficient method for consolidating ceramics in the presence of transient liquids at low temperatures (≤300°C) and pressures (≤500 MPa). This technique also provides a novel approach for integrating ceramics and polymers into a single system, which is not possible with conventional sintering methods. This study explores the consolidation behavior of hydroxyapatite (HA) ceramics at the nanoscale, as well as HA/polylactic acid (PLA) composites, for bone regeneration applications. Our results show successful consolidation of HA and HA/PLA composites at 200°C under 360MPa. For HA, the liquid phase chemistry significantly influences densification, with 2M H_3PO_4 facilitating 90% densification. In the composites, the fluidity of PLA governs the consolidation behavior. Notably, the effective incorporation of PLA into the HA matrix improves flexibility and reduces brittleness, creating new possibilities for customizable, patient-specific biomedical implants. This approach not only lowers the energy demands of ceramic manufacturing but also enables the integration of temperature-sensitive polymers and active drugs, leading to multifunctional composites with wide-ranging applications in the medical field. The findings represent a significant advancement in sustainable ceramic processing and open new pathways for the development of advanced bio-composites for bone regeneration.

Dominique Hautcoeur, Geoffroy Bister, Laurent Boilet, Nonna Nurmi, Erkki Levänen, Erkka J. Frankberg

Ceramic parts printed by stereolithography: process through optimised post printing and debinding steps.

Stereolithography is a proven additive manufacturing technique that is used for printing ceramic part in 3 dimensions. However, it requires the use of organic compounds for the formulation of feedstocks that need to be removed before sintering in order to obtain dense ceramic parts. When the parts are small or porous (scaffold for instance) this debinding process is generally carried out in a thermal way, at a slow heating rate, to allow time for the gases resulting from the decomposition of the organic material to escape. However, despite relatively long debinding times, obtaining big defect-free parts remains a challenge. To solve this problem, pre-debinding cycles or specific treatments could be done before the thermal cycle.

Previous work suggested that using supercritical extraction with CO_2 (SC) as a pre-debinding step could be interesting compared to a conventional water debinding on SLA-printed parts. The influence of both soaking time and specimen size have been evaluated by measuring the mass loss and performing TGA analysis. Considering soaking time and extraction time (limited at 6 hours due to our equipment) no preferential pre-debinding treatment has been clearly identified expected on surface defects. A combined cycle (SC + water debinding) has been studied and evaluated for improving processing time, part integrity and mechanical properties (3pts bending).

The Belgian Ceramic Research Centre (CRIBC) and Tampere University (TAU) have started a collaboration project on that topic. The project will focus on the improvement of post processing and characteristics of 3D printed ceramic oxide samples. The possibility to decrease debinding time and to enhance the mechanical strength of the sintered parts will be assessed by modifying the post-printing treatments (cleaning and debinding) Two levers have been selected to reach the goals: a proper selection of the good monomers for paste preparation and an improved chemical debinding process involving supercritical extraction with CO_2.

Keywords: Stereolithography, debinding, supercritical extraction CO_2

The European Regional Development Fund (ERDF) and Wallonia, are gratefully acknowledged for their financial support to these research projects CERAMTOP and CERAMPLUS “Iawatha” in the frame of the “Transition programme.” In addition, we acknowledge financial support from Business Finland within the project cerAM.

Optimizing UV-assisted Direct Ink Writing for Ceria-Stabilized Zirconia Ceramics in Dental Restorations

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Ceria-stabilized zirconia ceramics are highly suitable for dental restorations due to their strength, fracture toughness, biocompatibility, and resistance to low-temperature degradation. Additive manufacturing (AM) techniques, such as direct ink writing (DIW) combined with UV curing, provide a precise approach for fabricating these ceramics. This research focuses on optimizing key parameters in the DIW process, including paste composition, filament spacing, and UV light exposure to enhance the printability of the ink.

The paste, containing 12 mol% ceria-stabilized zirconia nanopowder, was prepared through speedmixing, with rheological measurements guiding the balance of ceramic powder, dispersant, monomers, diluents, and photo-initiator. The DIW and UV-curing parameters were fine-tuned to produce disc-shaped samples, which were subsequently thermally debinded and sintered. Results indicate that layer thickness plays a crucial role in ensuring proper inter-filament gap filling and paste curing, while the optimal UV-light focal point is essential for achieving uniform layer curing. By optimizing these parameters, this study aims to enhance the mechanical strength of the final dental restorations.

Studying the effect of temporal energy deposition of fs laser pulse for crack-free machining of ceramics

Mathieu Chabanel[1], Sooraj Shiby[1], Balasubramanian Nagarajan[1], Sylvie Castagne[1]

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The very properties that make ceramics desirable to many industries - such as their hardness and brittleness - also present significant challenges in machining and surface modification. Yet, creating microfeatures in these materials is often crucial for several applications. For biomedical applications, surface functionalization of alumina-toughened zirconia (ATZ) enhances osseointegration in dental implants while improving the friction resistance of hip replacement components.

Conventional contact-based machining methods like turning, milling, and grinding are prone to causing cracks and require expensive diamond-toughened tools, while limiting feature size. These drawbacks, along with high tool wear rates and costs, have led to the exploration of non-contact, laser-based techniques for machining ceramics. Ultrashort pulse (USP) laser machining is one such novel process. By delivering high energy in pulses of femtosecond (fs) range, it minimizes heat-affected zones, mechanical and thermal stresses.

However, challenges remain with fs laser processing of ceramics. The attainable energy density, and thus the material removal rate (MRR) is limited by the generation of micro-cracks (Fig. 1) and laser-induced phase transformation (LIPT) at high energy densities. Machining pre-sintered ceramics followed by sintering is, to some extent, the only proposed mitigation approach. Unfortunately, thermal post-processing brings its own restriction affecting the manufactured geometries negatively.

Our research aims to deepen the understanding of light-matter interaction in hard and brittle dielectrics, by investigating the defect formation process in ATZ. Our primary objective is to identify the impact of temporal energy deposition on thermal crack propagation. Laser-induced defects (LID) were characterized by type, size, and direction using a combination of surface topography analysis through SEM and confocal microscopy. This experimental investigation suggests trends in defect formation based on USP process parameters, especially, the temporal energy distribution. and highlight the potential of novel temporal shaping techniques.

Developing a deeper understanding and to be able to model these trends is key to achieving defect-free, high-speed machining of microfeatures in ceramics.

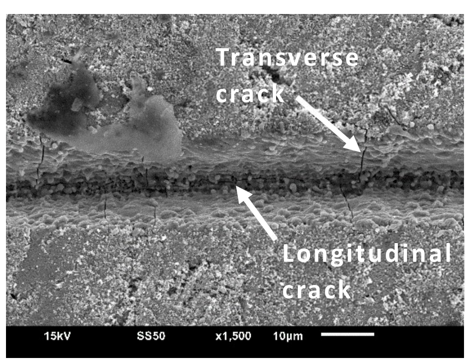

Figure 1 - Scanning Electron Microscopy (SEM) image of a USP machined channel on pre-sintered ATZ ceramics. Micro-cracks are formed longitudinal and tranverse to the channel/machining direction

Design of macroporous hydrophobic ceramic membranes for water desalination applications

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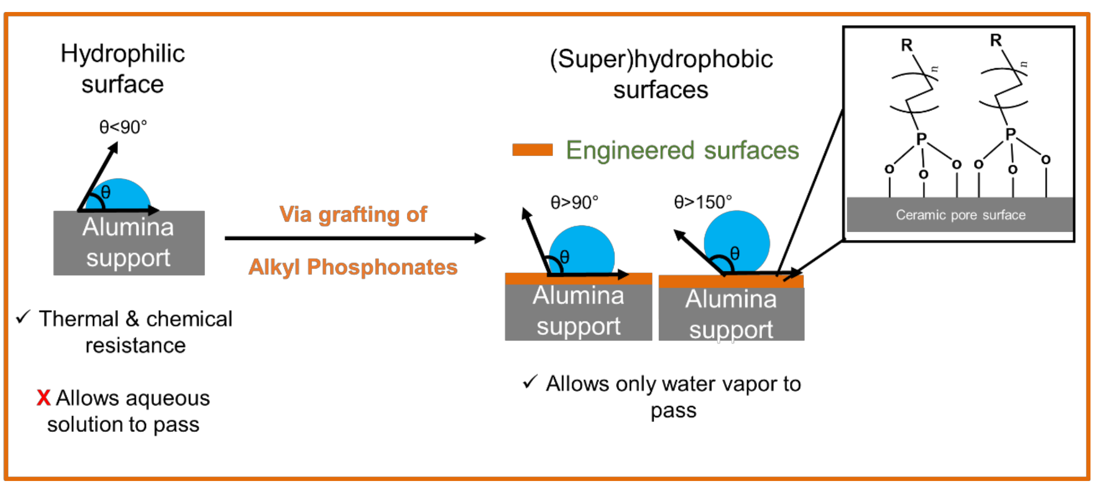
Keywords: grafting, alkyl-based phosphonic acid, ceramic membranes, membrane crystallization

Abstract

Hydrophobic organo-functionalized ceramic membranes represent a remarkable advancement in membrane technology, offering a versatile solution for a wide range of separation and purification processes. While their applications are diverse, one intriguing utilization of hydrophobic ceramic membranes is membrane distillation (MD) and membrane crystallization (MCr). This study presents the development of hydrophobic macroporous ceramic membranes functionalized with alkyl-based phosphonic acids. Traditionally, hydrophobizing agents like perfluoroalkylsilanes (PFAS) have been used, but they pose environmental risks and stability issues, particularly in aqueous applications. In contrast, the alkyl-based phosphonic acid grafts offer a more sustainable and water-stable alternative [1]. Ceramic membranes with pore diameters greater than 80 nm were modified to achieve water contact angles exceeding 130°, ensuring strong hydrophobicity. Stability tests under desalination conditions confirmed their durability, demonstrating the potential for these membranes in efficient, long-term membrane distillation and crystallization applications.



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High-Densification ZrC_x Ultra-High Temperature Ceramic (UHTC) Synthesis and Oxidation Response under Low Oxygen Partial Pressure

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Abstract:

ZrC Ultra-High Temperature Ceramic (UHTC) has desirable thermal and mechanical properties such as its high melting point (3700 K), good thermal shock resistance, high creep resistance, high phase stability at elevated temperatures, etc. These properties render ZrC UHTC a promising material for extreme environmental applications including nuclear fission, nuclear fusion, rocket engines, hypersonic vehicles, TPS, etc. Despite the favorable properties of ZrC UHTC for extreme environments, its fabrication and susceptibility to oxidation at elevated temperatures remain major issues. In this study, high-densification ZrC_x with low contamination was fabricated with two-step spark plasma sintering (SPS) and the oxidation responses at different temperatures and environment were investigated. The stability of ZrO_2 scale on the ZrC substrate under different conditions was also studied. The research could potentially lead to future optimization and design of oxidation-resistant refractory ceramics for extreme environmental applications.