Student Speech Contest

Research in advanced ceramics

On April 30 of this year - formerly known as the Queen's Birthday - the Dutch Ceramic Society NKV organised a meeting in the city of Nijmegen in the Netherlands. Part of this meeting was 'Research in advanced ceramics', where a total of six PhD and MSc students of Dutch universities took the opportunity to present their research. At the same time, they competed with each other in the Dutch qualifying round for the Student Speech Contest. The winner of this national contest would be the Dutch representative for the European Student Speech Contest, to be held in June of this year during the European Ceramic Society conference in Toledo, Spain. Ana Pinheiro, winner of the Dutch Student Speech Contest of 2013, became runner-up in the European edition of that year. Quite an ambitious task for the current six contestants!
A broad range of ceramic subjects were passed in review during the six presentations: from ceramic fibers via bioceramics to ceramics with a metallic behaviour, and from ultrathin ceramic coatings on ceramic nanoparticles to soft ceramics as lubricant for high temperature application. This article presents the essentials of the six ceramic subjects in their practical context

Eddy Brinkman,
Nederlandse Keramische Vereniging
Foto's: Pim van der Vliet

Gerard Cadafalch Gazquez (University of Twente) kicked-of with his presentation on forming nanostructures using the combination of two techniques that are relatively inexpensive compared to cleanroom techniques: sol-gel processing and **electrospinning**. The latter technique, already known for manufacturing of polymeric structures, has now been extended to deposit ceramics. Gerard uses a precursor solution of zirconia alkoxide and polymer, and feeds this into a hollow needle in the direction of a collector plate. When applying a high voltage between the needle and the collector plate, the solution is drawn to the collector plate, dried, collected and heat-treated afterwards. This results in yttria-stabilised zirconia (YSZ) nanofibers with a diameter of approx. 300 nm. By playing with the precursor and polymer concentration, the fiber diameter can be modified, ranging between 300 and 800 nm. Moreover, coaxial electrospinning with a zirconia precursor in the outer needle and an immiscible polymer in the inner needle followed by a heat treatment results in hollow YSZ fibers. When a single collector plate is replaced by a version with two separated segments, deposition of aligned nanofibers appears to be possible - even in large areas and with fast deposition rates. Foreseen applications of these types of nanofibers are as bioinert or bioactive scaffolds in biomedics, in electronics and as catalysts with nanochannel porosity. Recently, Gerard and coworkers have established a company with the aim to further commercialise this technology.

Julia Stikkelman of Delft University of Technology, the only MSc student in the company of six, gave a presentation on the synthesis and **self-healing of MAX phase ceramics**. Self-healing materials are able to repair cracks and scratches

by themselves in a more or less autonomous way, with the aim to extend the life time of these materials and, hence, to decrease maintenance costs. Just like thermally grown oxide layers and thermal barrier coatings, MAX phase ceramics are examples of ceramic materials that are investigated or optimised for their self-healing properties. 'Metal-like' ceramic MAX phase materials are thermodynamically stable nanolaminates, with $Ta_{n+1}AlC_n$ as an example. They combine the good properties of metals and ceramics: good electrical as well as thermal conductivity, ability to deform plastically and therefore being relatively easy to machine, and sufficient mechanical strength at high temperatures.
Heating these materials for several hours in air at about 1100-1200 °C can repair small cracks that have appeared in these materials, for example during use. By thermal oxidation of the material, mainly aluminium oxide is being formed. This reaction product fills the cracks that are repaired in this way - in fact by only using oxygen from the environment and heat. For manufacturing of $Ta_{n+1}AlC_n$ ceramics, spark plasma sintering is being explored as a technique to end up with fully dense bulk materials.

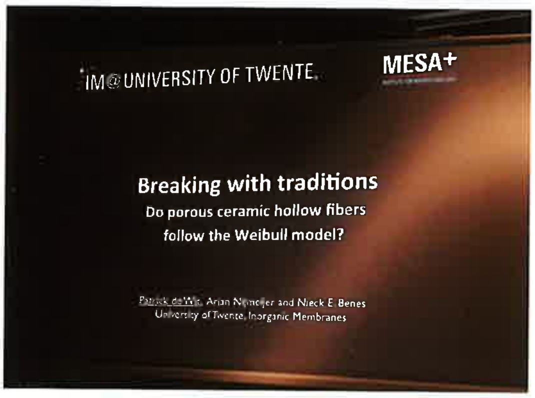
Patrick de Wit, again of University of Twente, posed an interesting question to the audience: 'do **ceramic hollow fibers** follow the Weibull model?' Often, the distribution of defects in ceramic materials is described via the Weibull model, in fact a 'weakest link theory' where a certain volume of material under a uniform tension will fail at the spot of the largest defect. The probability of finding such a defect is described by Weibull statistics.
Ceramic hollow fibers find their application as filters, membrane supports or catalyst substrates. Normally, their flexural strength is measured via

30 April meeting of the Dutch Ceramic Society

On this date, a total of almost 40 members and non-members of the society gathered together in restaurant Croy-De Goffert in Nijmegen. The day kicked-off with the annual general meeting, for members only, after which the public part started with a small symposium on 'ceramics and colour'. Laurens Peters shared some thoughts with the audience on fundamental aspects of colour and light, and especially on the interaction of light as a form of electromagnetic radiation with materials such as ceramics. After that, Leen Baaij, author of the book 'Het uitdagende rood', discussed ways it would be possible to manufacture ceramic components coloured with several kinds of 'exciting red'.

After lunch, the participants left to visit the High Field Magnet Laboratory on the premises of Radboud University in Nijmegen. As materials behave different in a strong magnetic field compared to a 'normal situation', extremely high magnetic fields (currently around 37.5 Tesla) are used here to reveal fundamental materials properties and to optimise materials for the future. Co-workers Martin van Breukelen and Inge Leermakers guided the participants around in the laboratory, where the magnets, their huge electric wires (as high currents are necessary to generate high magnetic fields) and their just as impressive cooling means were visited.

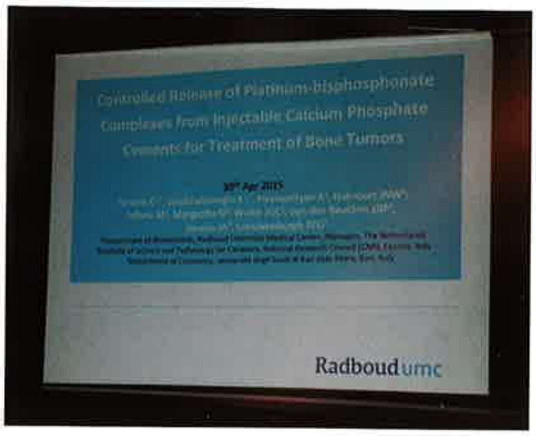
Returning to restaurant Croy-De Goffert, the program continued with 'Research in advanced ceramics'. Six students of Dutch universities presented their research work on ceramics related areas (see somewhere else on this page), and competed with each other within the Dutch edition of the Student Speech Contest. The members of the jury, NKV board members Ries Jeurissen, Mark Welters and Eddy Brinkman, did have a tough job in evaluating the presentations, as the quality of the presentations was high. At the end of the day, during the cold & warm buffet, Patrick de Wit was awarded winner of the Dutch Student Speech Contest. He represents the Netherlands during the European edition of the Student Speech Contest in June in Toledo, with his presentation on the Weibull model for inorganic porous hollow fibers. Those who participated in this day looked back at a versatile program, with something in it for everybody. Especially the interaction between the young MSc/PhD students and the people already working in the ceramic field was very valuable - from both sides - and gives rise to a yearly recurring meeting of this kind.

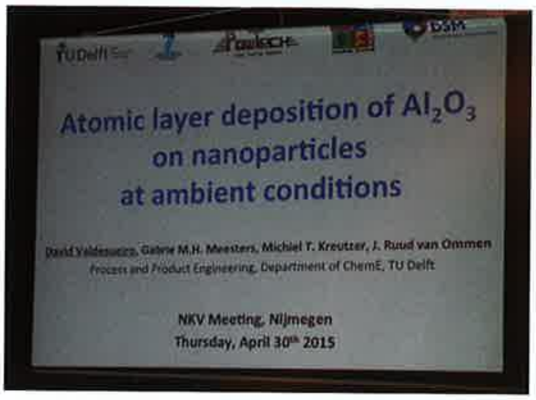


the 3- or 4-point bending method. In his research, Patrick shows that a direct quantitative comparison between different measurement results can only be done when details of the applied method and conditions are mentioned. For example, for porous alumina hollow fibers the flexural strength values highly depend on the measurement geometry and span size when 3- and 4-point bending tests are being performed. Furthermore, for porous ceramic hollow fibers, the fundamental assumptions that form the basis for the Weibull statistics - i.e. the presence of a few defects with no interaction - do not hold. Due to their microstructure, in porous ceramics there are many defects with interactions. This results in a normal or log-normal distribution of the mechanical properties, rather than a Weibull distribution.

Kambiz Farbod of Radboud University Medical Center played a home game in Nijmegen. In his presentation bioceramics entered the stage. Or more specific: injectable, self-setting **calcium phosphate cements**. Originally, these cements were developed as synthetic bone substitutes, as their composition is comparable with the constituents of the mineral component of human bone. Kambiz' research is directed towards the use of these calcium phosphate cements as a container for high concentrations of drugs, to be used within chemotherapeutic strategies after resection of tumors. He presents a new method to incorporate hydroxyapatite nanoparticles loaded with drugs - platinum-bisphosphonate complexes in this case - into apatitic calcium phosphate cements. The results of his research show that these complexes can be released in a sustained way, controlled by varying the binding affinity of hydroxyapatite to the complexes and by varying the concentration of the drug-loaded hydroxyapatite nanoparticles. Moreover, it seems that the released drugs from the injectable calcium phosphate cement formulations are more effective towards certain cancer cells (MG-63s) than towards healthy stem cells (h-BMMSCs). Kambiz concludes that this approach might also work to deliver other biologically active compounds.

That nanotechnology is all around us showed the presentation of David Valdesueiro from Delft University of Technology. Titania nanoparticles with their large surface-to-volume ratio are already tiny pieces of ceramic. By applying **even**





thinner coatings on these particles, it is possible to improve their performance by adding tailor-made functionalities, i.e. to protect or activate the surface. David uses atomic layer deposition, a gas-phase coating technique, to deposit alumina films of (sub)nanometer thickness on titania nanoparticles. For example, by adding a coating to pigment particles made of titania, this coating refrains the particles from reacting with other compounds such as polymers in a paint mixture. Normally, subnanometer alumina layers can be grown successfully by atomic layer deposition at 170 °C and less than 1 mbar. However, this relatively high temperature makes the technique not suitable for heat sensitive materials such as polymers, and such a low pressure brings limitations to scaling-up this technique to an industrial level. Therefore, David investigates the deposition of alumina at ambient conditions, i.e. 27 °C and 1 bar in a fluidized-bed reactor. And although at these conditions self-limitation of the atomic layer deposition reactions is lost, it is still possible to deposit thin and uniform films in a controlled way.

Oil is a common lubricant at room temperature. Going to higher temperatures, graphite or Teflon are solutions. However, partial decomposition of these lubricants at high temperature can cause some problems. Pablo Gonzalez, the third contestant from Twente, showed in which way **'soft ceramics'** - a new generation of inorganic solid lubricants - might help. In his research, he synthesizes, chemically modifies and tests layered titanates of the Lepidocrocite type to design lubricants that are more stable in temperature. In the chemical modification step, he uses amino unodecanoic acid as a precursor resulting in a compound with 'nylon like' functional amide groups, that is applied in between the titanate layers. It may seem that the chemical modification decreases the electrostatic interactions between the titania planes, which makes the layered compound easily deformable, hence improving the lubricating properties. By playing with the pH, Pablo is able to switch between an orderly layered system on one hand, and chaotic loose titanate layers on the other hand. ■