FRIEDRICH-ALEXANDER
UNIVERSITÄT
ERLANGEN-NÜRNBERG

TECHNISCHE FAKULTÄT

Department of Materials Science

# Glass and Ceramics

ANNUAL REPORT 2014

# Preface

The Institute of Glass and Ceramics (WW 3) covers the field of inorganic non-metallic materials (INM) including glasses, ceramics, composite and biomimetic materials. Research is focused on fundamental aspects of novel processing techniques and on microstructure-property correlations of materials which are of high relevance for a wide range of applications including medicine, energy and environment, electronics, and transportation. The research groups focus on ceramics (Peter Greil), functional materials (Andreas Roosen), glasses (Dominique de Ligny), biomimetic materials (Stephan Wolf), additive manufacturing (Nahum Travitzky), cellular ceramics (Tobias Fey) and multilayer processing (Ulrike Deisinger). The research work of WW 3 is characterized by strong interactions with the Cluster of Excellence Engineering of Advanced Materials Erlangen, the Energy Campus Nuernberg, the Centre for Advanced Materials and Processes Fuerth, the Max-Planck-Institute for the Science of Light as well as a large number of industrial partners.

The year 2014 was marked by tremendous changes for WW 3. Professor Andreas Roosen retired by October 1st after heading the functional ceramics group for almost 19 years. Ms Alena Schenkel-Rybar, who was in charge of the preparation laboratory, retired after 24 years of continuous service to the institute by September 1st. Starting on February 1st, 2014 we welcomed our new Professor Stephan E. Wolf, who will establish a new research group on Biomimetic Materials. Due to intensive international cooperation with a large number of academic partners in Europe as well as overseas we were proud to host an increasing number of foreign students, postdocs and faculties. More than 30 % of the research associates and doctorate students are from France, Italy, Great Britain, Israel, China, Brazil and Russia.

We would like to thank all members, friends, sponsors and funding institutions of the Institute of Glass and Ceramics for their continuing support and cooperation.

Peter Greil

Outline

***Congratulations to our soccer team***

*for winning the 2014 championship of the Department of Materials Science and Engineering!*

# 1. INSTITUTE OF GLASS AND CERAMICS

## a. Staff

### Faculties

| | |
|---|---|
| Prof. Dr. Peter Greil | Head of Institute |
| Prof. Dr. Dominique de Ligny | Glass |
| Prof. Dr. Andreas Roosen[1] | Functional Ceramics |
| PD Dr. Nahum Travitzky | Ceramic Processing |
| Prof. Dr. Stephan E. Wolf | Biomimetic Materials |

### Administration

Karin Bichler

Candice Iwai

Evelyne Penert-Müller

### Senior Research Staff

| | |
|---|---|
| Dr.-Ing. Ulrike Deisinger | Ceramic Multilayer Processing |
| Dr.-Ing. Tobias Fey | Cellular Ceramics and Simulation |

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[1] *retired*

## Research Staff

Dr. Guo Ping Bei

M. Sc. Alexander Bonet

Ph.D. Maria Rita Cicconi

Dr. rer. nat. Andrea Dakkouri-Baldauf

M. Sc. Benjamin Dermeik

M. Sc. Franziska Eichhorn

M. Sc. Ina Filbert-Demut

M. Sc. Matthias Freihart

M. Sc. Zongwen Fu

M. Eng. Michael Hambuch

M. Sc. Ruth Hammerbacher

Ph.D. Guifang Han

Ph.D. Joseph Harris

Dipl.-Ing. Daniel Jakobsen

M. Sc. Marita Lenhart[2]

Dr.-Ing. Joana Pedimonte

Dipl.-Ing. Lorenz Schlier

Dipl.-Ing. (FH) Tobias Schlordt[2]

Dipl.-Ing. Alfons Stiegelschmitt

M. Sc. Martin Stumpf

Ph.D. Alexander Veber

M. Sc. Moritz Wegener

M. Sc. Bastian Weisenseel

Dipl.-Ing. Bodo Zierath

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[2] *now in industry*

## Technical Staff

Sabine Brungs

Timotheus Barreto-Nunes

Evelyn Gruber

Heiko Huber

Beate Müller

Heike Reinfelder

Peter Reinhardt

Alena Schenkel-Rybar[3]

Eva Springer

Dipl.-Ing. Alfons Stiegelschmitt

Hana Strelec

Andreas Thomsen

*Excursion to a quarry in Mülheim (Middle Franconia)*

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[3] *retired*

## Retirements

**Professor Dr. Andreas Roosen**, head of the Functional Materials group, retired by October 1st, 2014. Born in 1950 Andreas Roosen studied glass and ceramics (Dipl.-Ing.) at the TU Berlin with Prof. H. Hausner. After his Dr.-Ing. in 1984 he joined the Federal Institute for Materials Testing (BAM) at Berlin. From 1985-1986 he visited MIT, Cambridge, Massachusetts as a post doc in the Ceramics Processing Research Laboratory of Prof. H.K. Bowen. In 1986 he joined Hoechst AG at Frankfurt as an executive employee heading the group of Functional Ceramics at the Corporate Research Department.

Andreas Roosen´s research work centred on fundamental as well as applied aspects of synthesis, colloidal processing, shaping and sintering of ceramic powders and multilayer structures. He developed novel approaches for three-dimensional controlled sintering of LTCCs, tape casting of ultrathin transparent oxide films, as well as printing of electronic materials. He became one of the well-recognized experts in the field of multilayer processing of functional ceramics including tape casting, lamination, and micro-engineering. Andreas Roosen published more than 200 research papers and he served as an organizer and co-organizer of a number of national and international conferences on functional ceramics processing. He is a member of the American Ceramic Society, the German Society of Materials Science, the International Microelectronics Assembly and Packaging Society and the German Ceramic Society where he was appointed to executive board member in 2009. Due to his competence and experiences in the field of advanced ceramics processing and functional materials he served as reviewer for a large number of scientific journals as well as funding agencies including DFG, AiF, BMBF, EU, GIF, etc. He received the Boettger Award 2010 of the German Ceramic Society in honour of his outstanding contributions to the interaction between industry, academia and teaching. In 2014 Andreas Roosen has been appointed as an Adjunct Professor of the Danish Technical University (DTU), Department of Energy Conversion and Storage. This was done in recognition of his dedicated research in materials science and engineering as well as his many years of fruitful cooperation with DTU. After almost 19 years of deserving work in research and teaching all members of the Institute of Glass and Ceramics want to express their deep gratitude to Andreas Roosen. Best wishes for him and his family for a healthy and happy time.

*Prof. Peter Greil presents the farewell gift for Prof. Andreas Roosen:*

*A tape casting machine for home – also usable as a pasta maker*

**Ms. Alena Schenkel-Rybar** retired by September 1st, 2014. After joining the Institute of Glass and Ceramics in 1990, Alena initially worked as a technician for several research projects on glass and construction materials. Trained as a glass technician assistant her activities covered the characterization, processing and shaping of powders for melting of glasses and sintering of ceramics. Characterization of materials included measurements of density, mechanical as well as thermal properties, and X-ray analyses.

Since 1998 Alena was in charge of the ceramography workshop. Due to her extensive experience and expertise in surface machining and polishing of ceramics, glasses and composites she was able to contribute significantly to solve even difficult sample preparation problems of many students. She developed sophisticated preparation techniques for inorganic materials to be analysed by optical microscopy, SEM, EPR and mechanical measurements. Furthermore, a continuous process of renewing the basic equipment took place under her leadership in order to serve the changing challenges of complex composite material compositions and surface treatments.

Alena Schenkel-Rybar strongly participated in and contributed to the social life of the institute. She provided great support to the internal events including farewell parties as well as the celebration of anniversaries. Furthermore, she was a member of the first aid team of the institute. Due to her pronounced cooperativeness and responsibility Alena made a continuous and highly appreciated contribution to the growth and prosperity of the institute. All the staff members deeply acknowledge her for her great work and service. We deliver our best wishes to Alena and her family for the time of retirement.

## Welcome to Junior Professor Dr. Stephan Eckehard Wolf

Stephan E. Wolf, born in 1979, graduated in chemistry at the University of Mainz. In 2009 he was promoted to Dr. rer. nat with the thesis work dealing with "*Non-classical crystallization of bivalent metal carbonates*" (biomineralization). After postdoc visits to the Humboldt University at Berlin, the CNRS Bourgogne at Dijon and the Cornell University at Ithaka, NY, he joined the Max-Planck-Institute for Polymer Research at Mainz in 2012. Based on inorganic chemistry background he extended his research interests to the field of material synthesis processes governed by inorganic/organic interfaces as well as in bioorganic environment. His research interests cover concepts of chemical synthesis, high resolution structure analysis and mechanistic modelling of biomimetic materials. Furthermore, he will study the principles of self-organization and properties of biogenic materials.

Since 2014 Stephan Wolf is heading a new DFG funded Emmy Noether Research Group on "*Liquid condensed mineral phases and the mechanism of PILP process: a novel way of morpho-synthesis for the production of nanocomposite materials*". Biological controlled, non-classical crystallization from liquid precursor systems may involve formation of prenucleation clusters, mesocrystals and aggregation controlled assembly structures. The polymer-induced liquid-precursor (PILP) process offers a great potential for generating non-equilibrium morphologies of nanoscale particle structures precipitating from organic modified aqueous precursor systems. It is the aim of the project to transfer the basic principles of the PILP process analysed for carbonate precipitation to other oxidic materials relevant for advanced engineering applications. The Emmy Noether Programme supports researchers in achieving independence at an early stage of their scientific careers. Postdocs gain the qualifications required for a university teaching career during a DFG-funded period, usually lasting five years, in which they lead their own independent junior research group.

# b. Equipment

*Technical hall (600 m²): equipped with facilities for advanced processing, shaping, melting, and sintering as well as molding of glass, ceramics and composites*

## Main Equipment

### Laboratories

- Biomaterials laboratory
- Ceramography workshop
- Functional ceramics laboratory
- Glass laboratory
- Mechanical testing laboratory
- Multilayer processing laboratory
- Polymer processing laboratory
- Powder characterization laboratory
- Processing workshop
- Rapid Prototyping laboratory
- SEM/AFM laboratory
- Simulation laboratory
- X-ray characterization laboratory

## Equipment

**Thermal analysis**

- 3-dimensional optical dilatometer
- Push rod dilatometers (up to 1800 °C)
- Thermal analysis (DTA/TGA/DSC/TMA)
- Thermal conductivity devices
- Viscometry (beam bending)

**Powder characterization**

- ESA acoustophoretic analyser (Zeta-meter)
- Dynamic light scattering particle size analyser
- Gas absorption analyser (BET)
- Laser scattering particle size analyser
- X-ray diffractometers (high-temperature)

**Optical analysis**

- FT-IR spectrometer
- High-resolution fluorescence spectrometer
- Light Microscopes (digital, polarization, in-situ hot stage)
- Scanning electron microscope (variable pressure, ESEM and high temperature with EDX)
- UV-VIS-NIR spectrometers

**Drying stress measurements**

- High precision mechanical testing with optical tracking system (EXAKT)
- Impulse Excitation Measurement (buzz-o-sonic)
- Micro hardness tester
- Servo hydraulic mechanical testing systems (also high temperature)
- Single fibre tensile testing machine
- Viscosimeter and elevated-temperature viscosimeter

**Chemical analysis**

- ICP-OES (Spectro Analytical Instruments)

**Structural analysis**

- 2D laser scanning microscope (UBM)
- 3D Laser scanner
- Atomic force microscope (AFM)
- Electron paramagnetic resonance spectroscopy
- He-pycnometer
- High accuracy weighing scales
- Laser-Flash LFA 457
- Mercury porosimeter
- Micro-CT Sky scan 1172
- Microwave and ultrasonic devices for non-destructive testing
- Raman-microscope with two excitation lasers

**Powder and slurry processing**

- Attrition mills
- Agitator bead mill
- Disc mill
- Intensive mixers (Eirich, powder and inert gas/slurry)
- Jaw crusher
- Overhead mixers
- Pick and Placer
- Planetary ball mills
- Planetary centrifugal mixer (Thinky)
- Rotary evaporators
- Sieve shakers
- Single ball mill
- Thermo kneader
- Three-roll mill
- Tumbling mixers
- Ultrasonic homogenizer

**Cutting and punching devices,**
**slot die coater**

- 3D printers
- Advanced screen printing device
- Calender
- CNC High speed milling machine
- Cold isostatic press
- Electrospinning machine
- Flaring cup wheel grinding machine
- Fused deposition modelling device (FDM)
- High precision cutting device
- Hot cutting device
- Laminated object manufacturing devices (LOM)
- Lamination presses
- Langmuir–Blodgett trough
- Lapping and polishing machines
- Low-pressure injection moulding machine
- Precision diamond saws
- PVD coaters
- Robot-controlled device
- Roller coater
- Screen printer
- Sheet former
- Spin coater
- Tape caster
- Textile weaving machine
- Twin screw extruder
- Ultrasonic drill
- Vacuum infiltration device

**Heat treatment**

- Autoclave
- Dryers
- Furnaces (air, $N_2$, Ar, Vac, High-Vac, forming gas) up to 2500°C for sintering, glass melting, infiltration, debindering, pyrolysis
- Gradient furnace
- High-temperature spray furnace

*Shooting for the famous TV crime series "Tatort" in our technical hall. The main actors Fabian Hinrichs, Andreas Schadt, Dagmar Manzel and director Max Färberböck (left to right) are discussing the key questions, who killed the professor*

# c. International

## International Cooperation

The Institute of Glass and Ceramics maintains connections to a large number of international academic partners in Europe and overseas.

*International academic cooperation with overseas partners*

In recent years, strong links were developed to the Nagoya Institute of Technology, Japan, the Federal University of Santa Catarina at Florianópolis, Brazil, the Northwestern Polytechnical University at Xian, China, the SungKyunKwan University at Suwon, Korea, and the Clemson University, USA.

Nagoya Institute of Technology (NiTech) is a national engineering college with more than 4 060 students located in Japan´s largest industrial area of Aichi prefecture which is one of the world centres in manufacturing and automobile industries. Major fields of common research work centre on piezoceramics, bioceramics, and nanoscale processing of ceramics. More than 15 Japanese students, postdocs and faculties spend a 1 to 6 months research visit to Erlangen and approximately 10 Germans were visiting NiTech. Since 2010 a series of four German-Japanese Seminars on Advanced Ceramic Materials as well as the 6th International Workshop on Advanced Ceramics (IWAC 2014) were organized at Erlangen. In July 2013 the European Liaison Office of NiTech was established at the Engineering Faculty Campus at Erlangen.

SunKyunKwan University (SKKU) in Korea is a private research university with campuses in Seoul and Suwon. Samsung partnered with SKKU. Cooperation with the Materials Engineering Department is focused on ceramics processing and sintering of ultrafine powders for functional, engineering as well as biomedical fields of application. Current research activities of common interests centre on design, manufacturing, characterization and testing of advanced cellular ceramics dedicated for applications in biomedicine and tissue engineering. The cooperation involves exchange of faculties as well as internships of graduate students and postdocs.

Northwestern Polytechnical University (NPU) in Xi´an, China emphasizes on the education and research in aeronautical, astronautical and marine engineering and currently has almost 30 000 students. The cooperation is focused on advanced reaction processing of fibre reinforced ceramic matrix composites. Furthermore, MAX phase composite formation and three dimensional printing of ceramic composites are topics of joint work. Within the frame of the cooperation exchange of faculties and coorganisation of conferences took place. 2014 we host Prof. Fan from the National Key Laboratory of Superhigh Temperature Structural Composite Materials for a one year sabbatical leave.

Federal University of Santa Catarina at Florianópolis (UFSC), Brazil, currently hosts 34 500 students. The long lasting cooperation between WW 3 and the Department of Materials Science and Engineering of UFSC is focused on advanced processing of ceramics and composites. The aim of the current joint research project funded by International Bureau of DLR (BMBF) is the manufacturing of porous calcium phosphate based scaffolds for bone regeneration. While work at WW 3 deals with computer controlled rapid prototyping of the scaffolds (3D printing and LOM), work at UFSC aims to reinforce the mechanical properties by integration of biocompatible fibres. Within the frame of the cooperation WW 3 was hosting several doctorate students and faculties from UFSC.

Clemson University at Clemson, South Carolina, is one of the top ranked public national universities in USA with approximately 22 000 students. Recent initiation of cooperation with the Department of Materials Science and Engineering is focused on manufacturing and properties of porous and multi-layered ceramics for energy applications. Furthermore, polymer derived ceramics and surface modification of ceramics including crack healing ability will be topics of common interest. The cooperation envisages to exchange post-docs and faculties.

## Visiting Students and Scientists

**Mylena Carrijo** (December 2013 – August 2014)
Universidade Federal de Santa Catarina – UFSC, Florianópolis, Brazil

**Prof. Dr. Shangwu Fan** (February 2014 – February 2015)
Northwestern Polytechnical University, Xi’an, P.R. China

**Prof. Dr. Nachum Frage** (September 2014)
Ben-Gurion University of the Negev, Israel

**Jean-Loup Girard** (July 2014 – August 2014)
Ecole Nationale Supérieure d'Ingénieurs de Limoges (ENSIL), Limoges, France

**Mohamed Maaouane** (June 2014 – August 2014)
Ecole Nationale Supérieure d'Ingénieurs de Limoges (ENSIL), Limoges, France

**Laila Mansour** (June 2014 – August 2014)
Ecole Nationale Supérieure d'Ingénieurs de Limoges (ENSIL), Limoges, France

**Hunter Rauch** (February 2014 – May 2014)
Penn State University, Pennsylvania, USA

**Yuta Sumiya** (September 2014 – December 2014)
Nagoya Institute of Technology, Ceramic Research, Nagoya, Japan

# 2. RESEARCH

## a. Project List

Research centres on basic aspects of ceramics, glasses and composites. Materials for applications in microelectronics, optics, energy, automotive, environmental, chemical technologies and medicine were investigated. Research was carried out in close cooperation with partners from national and international universities and industries.

| **Research Projects (in alphabetical order)** | **Funding** | **Principal Investigator** |
|---|---|---|
| Bioactive ceramic cages | IN | P. Greil / T. Fey |
| Development of layered structures and 3D generative processing methods for innovative combustion chamber lining concepts | BMWi + IN | A. Roosen / N. Travitzky |
| Cellular ceramics for heat absorbers | EnCN | P. Greil |
| Deformation and sintering behaviour of preceramic papers | DFG | N. Travitzky |
| Experimental study and simulation of anisotropic effects in cast green tapes | DFG | A. Roosen |
| Flexible manufacturing of preceramic paper based refractory components | DFG | P. Greil |
| Hierarchical cellular ceramics and composites | DFG | P. Greil |
| High temperature stable ignition components based on defined 2D and 3D SiSiC structures | AiF | N. Travitzky |
| Lightweight cellular ceramics | EC | P. Greil |

| | | |
|---|---|---|
| Manufacturing of multilayer refractories by tape casting | DFG | A. Roosen |
| Stable and metastable multiphase systems for high application temperatures | DFG | P. Greil |
| Dispers systems for electronic devices | DFG | A. Roosen |
| Robocasting of macrocellular ceramic 3D-lattice structures with hollow filaments | DFG | N. Travitzky |
| Self healing MAX phase ceramics | DFG | P. Greil |
| Toward smart solar cell glasses: Glass texturing under laser irradiation | EC | D. de Ligny |
| Structured carbon based catalyst support structures for CO hydration | DFG | T. Fey |
| Tape-on-Ceramic Technology | BMBF | A. Roosen |
| Formation of Liquid-condensed mineral phases and the mechanisms of the PILP process (Emmy Noether Group) | DFG | S.E. Wolf |

## Funding organizations:

AiF: Industrial research Cooperation
BMBF: Federal Ministry of Education and Research
BMWi: Federal Ministry of Economics and Technology
DFG: German Research Foundation
EC: Cluster of Excellence (“Engineering of Advanced Materials”)
EnCN: Energy Campus Nuremberg
IN: Industry

## b. Selected Research Highlights

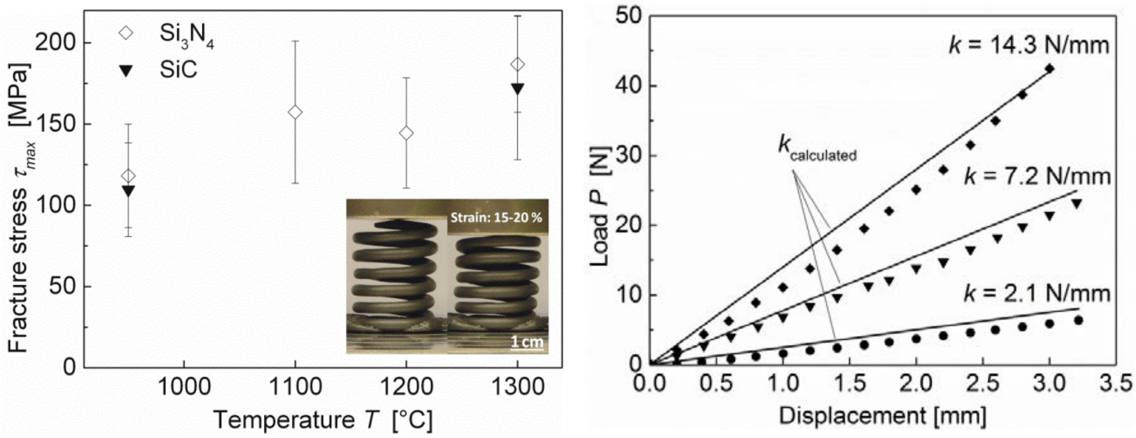
### Polymer Derived Ceramic Springs

Lorenz Schlier, Nahum Travitzky, Peter Greil

A spiral spring is able to store elastic energy on compression loading which is then expelled upon release of the spring. Polymer derived ceramic spiral springs of varying ligament diameter were produced by thermoplastic coiling of extruded filaments. Feedstocks containing polymethlysilsesquioxane binder and fillers (reactive filler: FeSiCr and inert filler: SiC/$Si_3N_4$) were applied. The pyrolytic conversion into composite residue, the surface reactions and the mechanical properties were analysed. After pyrolysis at 1300 °C values of radial and longitudinal shrinkage of 8.2 % and 9.1 %, respectively, were observed. During pyrolysis in a reactive nitrogen atmosphere a multiphase composite material was produced by a complex series of reactions. XRD revealed $Cr_5Si_3C_x$, CrSi, SiC, $Si_2N_2O$ and $Si_3N_4$ as the major crystalline reaction products which are bonded by an amorphous Si-O-C residue phase. High nitrogen concentration on the surface triggered the formation of a dense surface reaction layer. Despite of the small thickness of the surface reaction layer of less than 10 µm, healing of surface cracks and pores is likely to improve the spring´s mechanical behaviour without applying mechanical machining of the surface.

*Polymer derived ceramic springs*

Ceramic springs pyrolyzed at 1300 °C were loaded in compression and attained a fracture stress (without surface treatment) of 175 MPa. Spring constants ranging from 2.1 N/mm (filament diameter 1.5 mm) to 14.3 N/mm (2.5 mm) were measured on the material pyrolyzed at 1300 °C (Young´s modulus 175 GPa), which were in good agreement with expected values calculated according to Whal´s theory.



*Fracture stress of the springs after pyrolysis at varying temperatures (left) and spring constants (right)*

Thermoplastic deformation behaviour of filler loaded polymer composite feedstocks make polymer shaping techniques attractive for ceramic spring manufacturing. Formation of a multiphase reaction composite microstructure combined with a dense surface reaction zone gives rise for enhanced mechanical properties of the polymer derived materials suitable for spiral spring application.

# Hierarchically structured silicon carbide derived carbon catalyst support structures

Bodo Zierath, Tobias Fey

Resources of oil as the common source of transportation fuels tend to decline and the products increase in price. This results in a rising interest in synthetic fuels which can be produced from coal, natural gas or renewable resources. The main advantages of synthetic fuels are the capability to replace common transportation fuel, have a higher purity and decrease the $CO_2$ output. The Fischer-Tropsch process is a key step in the production of synthetic fuels with the catalyst and the catalyst support structure being crucial components.

The challenges for the catalyst support structure are that it should have a high surface area, a high permeability and low pressure drop to provide a high efficiency. Owing to the exothermic reaction behaviour of the Fischer-Tropsch process the catalyst support structure should provide a high heat conductivity and a long live stability (no decrease of surface area and active catalyst material). The current catalyst support structures applied are fixed bed- and slurry bed reactors. The drawbacks of these reactors are low heat conductivity or catalyst degradation and removal. The approach to solve this problem is a monolithic catalyst support based on carbide derived carbon (CDC). The precursor carbide is a biomorphous siliconcarbide produced from paper derived hollow carbon fibres, phenolic resin as binder for the uniaxial hot-pressing process and silicon powder. During pyrolysis up to 900°C organic components decompose leaving solid carbon. During annealing at temperatures exceeding 1300 °C SiC is formed. The porosity of the silicon carbide reaction product can be adjusted between 45 % and 65 % depending on the composition and processing parameters. Finally, SiC is chlorinated in order to remove Si from the surface leaving a microporous carbon skeleton (CDC). This step increases the porosity up to 70 to 90 % and leads to a strong increase in surface area from 25 $m^2/g$ for the silicon carbide to 700 $m^2/$ for the carbide derived carbon. The chlorination, loading with the catalyst and testing was performed at the Institute of Chemical Reaction Engineering (Prof. B. Etzold).

The main advantage of this process is the near net shape process with a shrinkage of less than 5 vol% from the preform to the carbide reaction product. Furthermore, the monolithic structure provides a high heat conductivity and a high mechanical stability.

The reaction product is characterized by a hierarchical pore structure with nanosized pores (< 1 nm) resulting from chlorination and micronsized pores (5-10 µm) produced in the pressed preform. A third level of macropores was introduced by decomposition of polymer grids embedded in the preform.

*Fig. 1: Micro computer tomography reconstruction of silicon carbide catalyst support structure*

# Extra-clear glasses: transition metal elements in silicate glasses

Maria Rita Cicconi, Dominique de Ligny

Transition elements (TE) exhibit different valence states and coordination geometries in glasses and they control the fining processes (the process to obtain bubble free homogeneous glasses) and the final colours. TE are also present at dilute levels (ppm range) in most commercially produced glasses, but yet, the behaviour of TE at ppm level in silicate melts still remains largely unconstrained. Extra-clear (low TE content) silicate glasses are particularly important in the framework of solar energy technologies including photovoltaic and concentrated solar power. In fact, the low TE content aims to minimize absorption and maximize system efficiency. In many other disciplines the understanding of the structural behaviour of transition elements is a key point. For example, in Geosciences, the different behaviour of an element, for different concentration levels, can affect the partition in crystalline phases and the rheology of the melt. Our goals are to better understand i) the local structure of transition metals in glass, ii) the effects of glass composition upon them (because this can strongly influence several physical key properties) and iii) to enhance our understanding of the short-range and medium-range ordering of glasses.

## Case study: Mn-bearing glasses

Manganese is an important transition element. It is commonly found in several oxidation states from +2 to +7 even if the most stable is the divalent one. Because of its abundance (12th most abundant element on earth), and the widespread presence of manganese oxides in nature, Mn has been used as pigments since the Stone Age. Moreover, several studies on ancient glasses (Egyptian, Roman) report the use of Mn both as colorant agent (purple) or to remove colour from glass. At the present time, manganese is widely used in glassmaking industries, and in batteries production.

To understand in detail the Mn speciation and its influence on glass properties, we are going to use Optical Absorption (OA) and Photoluminescence (PL) spectroscopy. Due to electronic transition selection rules OA is sensitive to $Mn^{3+}$ and PL to $Mn^{2+}$ cations. In our samples the OA measurements show mainly the presence of the $Mn^{3+}$ band at 500 nm and the normalized spectra indicates that the amount of trivalent species increases linearly with the total Mn content (Fig. 1). In fact, the increasing purple coloration derives from the absorption band at ~500 nm, and in turn to the increasing amount of $Mn^{3+}$ in 6 fold coordination.

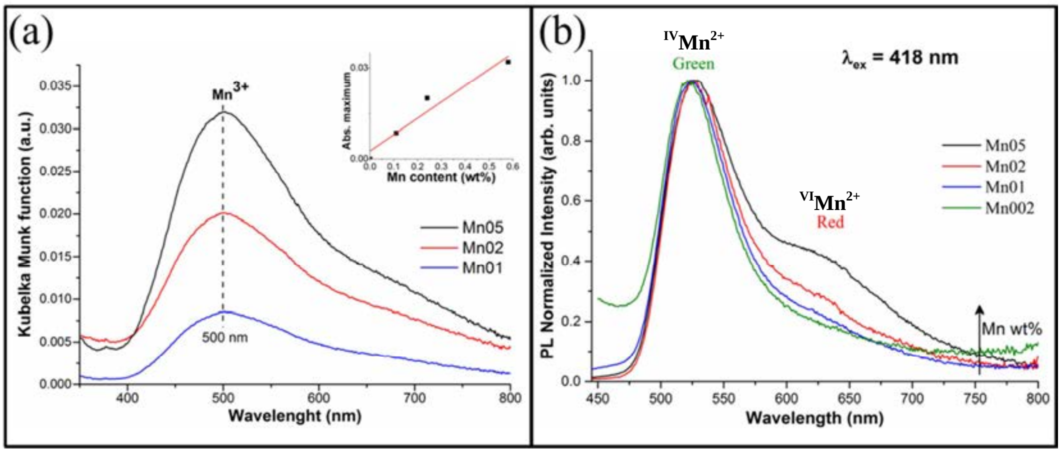


*Fig. 1: Evolution of Mn species with concentration. (a) OA showing a linear decrease of* $Mn^{3+}$ *with composition. (b) PL showing a strong decrease of* $Mn^{2+}$ *6-fold coordinated*

In the recorded PL spectra we observed two emission bands associated with $Mn^{2+}$. There is a predominant green emission (~ 524 nm) and a broad band in the orange/red region (~ 628 nm) (Fig. 2a). The excitation spectra obtained from the two emission maxima are almost overlapped (Fig. 2b), thus we presume that the same absorption bands produced either green or red luminescence and a complete transition assignment was possible in agreement with previous studies.

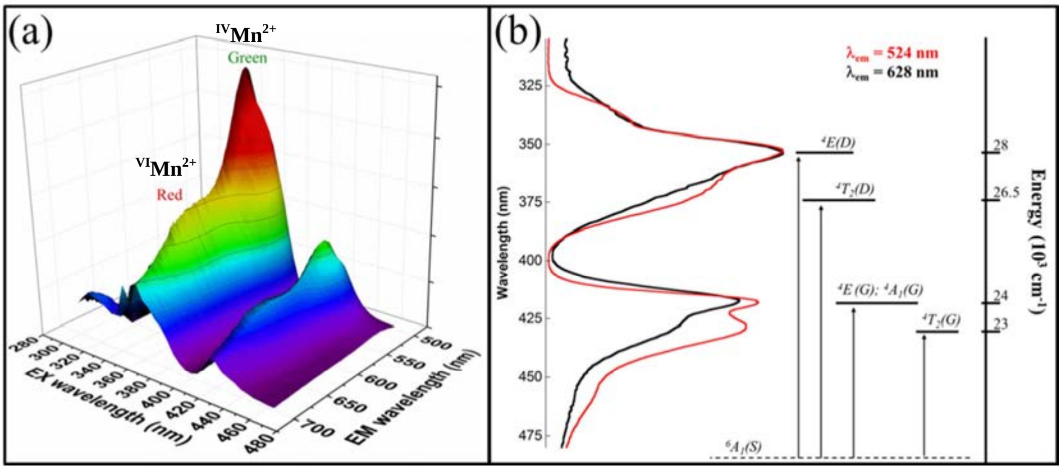


*Fig. 2:* $Mn^{2+}$ *luminescence spectra. (a) 3D spectrum for the NS4 glass doped with 0.2 wt%* $MnO_2$*. There are two predominant emission lines in the green (~ 524 nm) and in the red region (~ 628 nm). (b) Optical excitation spectra and corresponding electronic band structure*

Coupling the two experimental results it is possible to determine that the Mn redox is not affected by its total content but that $Mn^{2+}$ at low concentration has a more specific 4-fold oxygen coordination indicating that the $Mn^{2+}$ environment is composition dependent.

# Glass texturing by demixing under laser irradiation

Alexander Veber, Nahum Travitzky, Dominique de Ligny

Different ways are proposed today to increase efficiency of light emitting and receiving devices, including light-emitting diodes and solar cells. Recent investigations have shown that the efficiency of optoelectronic devices depends not only on the materials but on structural design of a device and proper light management can increase significantly in/out coupling efficiency and improve the overall performance.

Nowadays, laser processing is a powerful technique that allows to create various structures on surfaces and in the whole volume of various media with a desired design, e.g. controllable optical parts such as microlenses etc., optical systems or designed micro/nanostructures. Furthermore, it can be easily implemented on a production line. For direct producing of structures equal or less than vis-NIR range wavelengths, the laser with radiation wavelength of the same order or less is necessary. Taking into account the wide transparency window of pure oxide glasses in this range it requires additional doping of the glasses or UV-laser radiation either high-intense pulsed lasers for initializing of non-linear effects in the glass.

Alternative solution could be obtained by the use of a $CO_2$-laser, which has become already an ordinary machining tool in industry. Using of 10.6 μm radiation allows modifying directly the near-surface layer of a glass, without need of any additional doping element. Despite the fact that the laser spot radius is limited by the diffraction limit, sub wavelength structures can be obtained on the surface by means secondary effects, e.g., laser induce ripples or decomposition/demixing of the initial glass. In this case, the characteristic size of the structures is not only determined by the laser treatment mode but by the initial glass features as well.

In case of $CO_2$ laser induced ripples, structures of ~3 μm were obtained on the surface of barium-borate glasses (Fig. 1). Direction and size of the ripples depend on the laser power and polarization as well as on the glass properties. The process can be controlled quite well and the structures can be used in photonic applications. In that case a variation of the refractive index with the depth is induced by reshaping the surface.

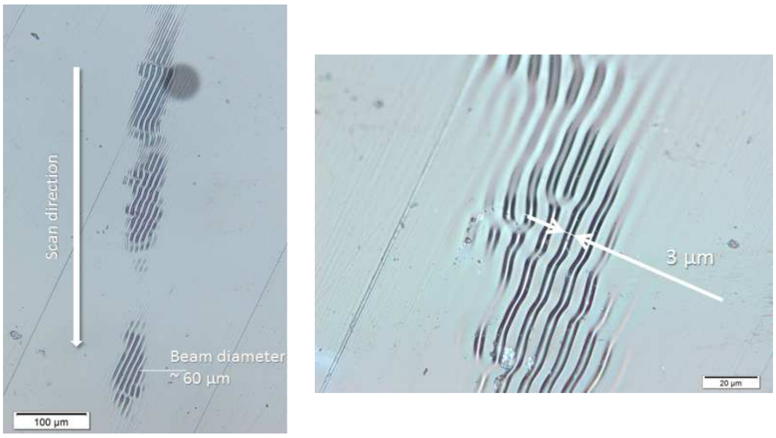


*Fig. 1: $CO_2$ – laser ($\lambda$ = 10.6 µm) induced ripples on the surface of the $BaO$-$B_2O_3$ glass. Laser power 190 mW, beam diameter 60 µm, scanning rate 5 mm/s, the treatment was repeated 20 times*

Another experimental way under investigation is to use phase separation to introduce refractive index modifications (Fig. 2). During decomposition, e.g., spinodal decomposition in soda-borosilicate glasses, it is possible to create structures with characteristic size of ~10 nm – 1 µm. The structures can be used directly. In that case the glass structuring by decomposition should allow creating a local change of the refractive index of the glass without significant modification of the surface roughness, i.e. keeping the initial protective function and reliability. The optical features expected should make this new family of texturized glasses promising devices for in/out light coupling applications in relation with solar energy materials.

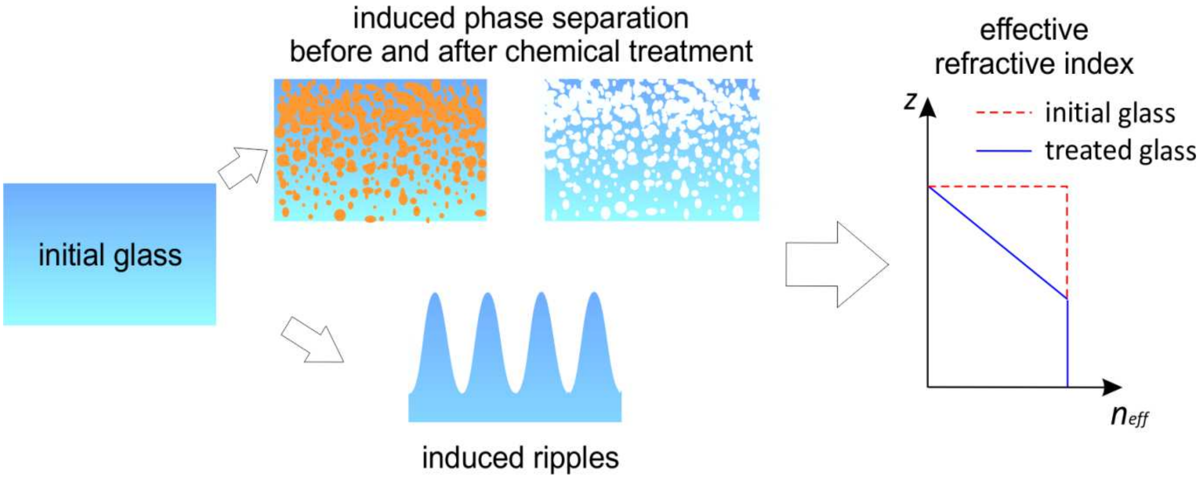


*Fig. 2: Formation of an antireflection coating on the glass surface by laser induced ripples or glass decomposition*

# *In-situ* study of mass loss, shrinkage and stress development during drying of colloidal films

Zongwen Fu, Udo Eckstein, Andreas Roosen

During constrained drying of binder-assisted colloidal coatings on rigid substrates, drying stress-induced defects such as cracks and warpage can be often observed due to the lateral confinement of the film by the substrate. In order to understand the origin of these drying defects and how they can be avoided by the adjustment of slurry composition or processing parameters, an improved cantilever deflection technique was installed to study *in-situ* and simultaneously drying stress, drying shrinkage, drying mass loss and crack formation. Fig. 1 shows the experimental setup. For the measurement, a slurry of defined thickness was spread with a scalpel onto a metallic cantilever beam; the layer thickness was controlled by means of stencils. The cantilever beam was fixed at one end by a supporter placed on an analytical balance, so that the slurry mass loss during drying can be measured, too. At the fixed end of the cantilever beam, the drying shrinkage of the deposited layer was detected by “laser sensor A”; at the free end, the curvature change of the cantilever was recorded by another “laser sensor B” (Fig. 1). The simultaneous measurement of all drying parameters in one trial allowed an exact determination of the critical moment, at which drying cracks occurred.

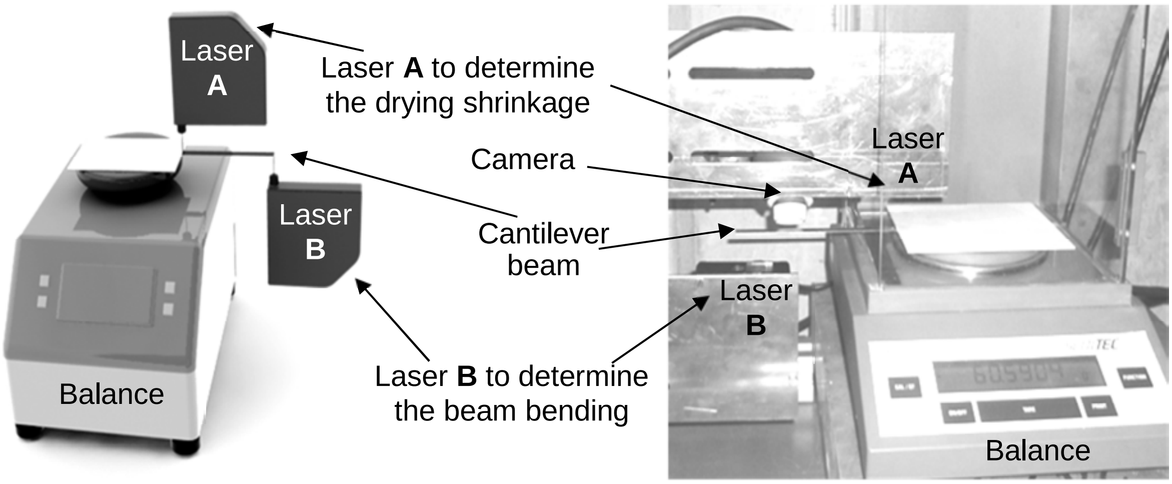


*Fig. 1: Experimental setup of the cantilever deflection method for simultaneous in-situ measurement of in-plane stress, shrinkage and mass loss during drying*

Fig. 2 shows a representative diagram for mass loss, shrinkage and in-plane stress in a binder-assisted $Al_2O_3$-suspension during drying. After ~ 400 s the drying shrinkage levels off, while the equilibrium of mass loss appears after ~ 4000 s drying time. At the same time, two stress maxima are observed in Fig. 2. The first stress maximum is explained by capillary stress and occurs just after the shrinkage has stopped. After this first peak, the drying stress increases continuously until the film mass levels off, and the second stress maximum appears. After drying, a residual stress of ~ 0.3 MPa remains in the green tape.

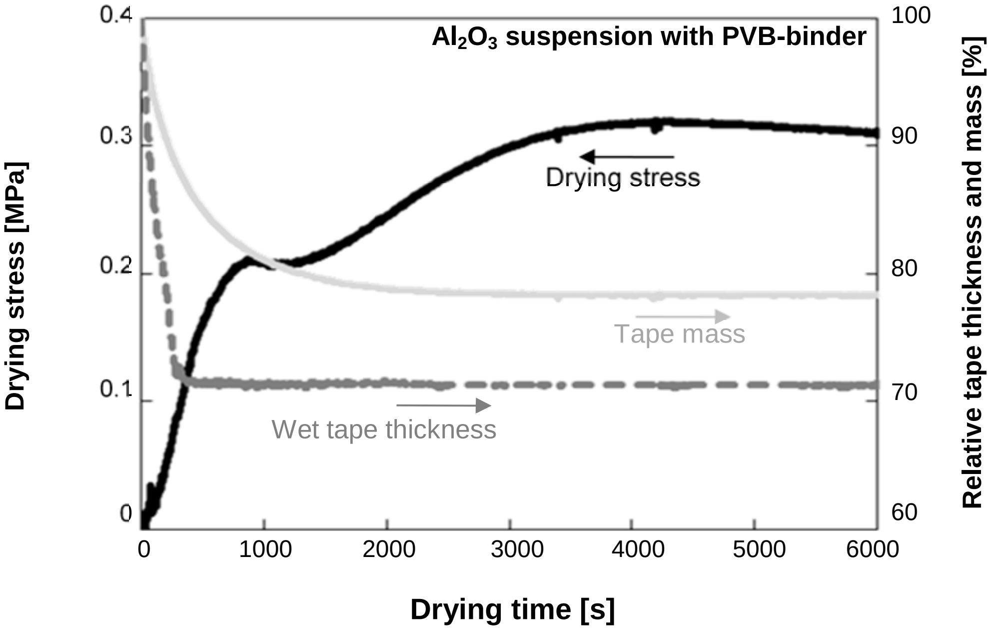
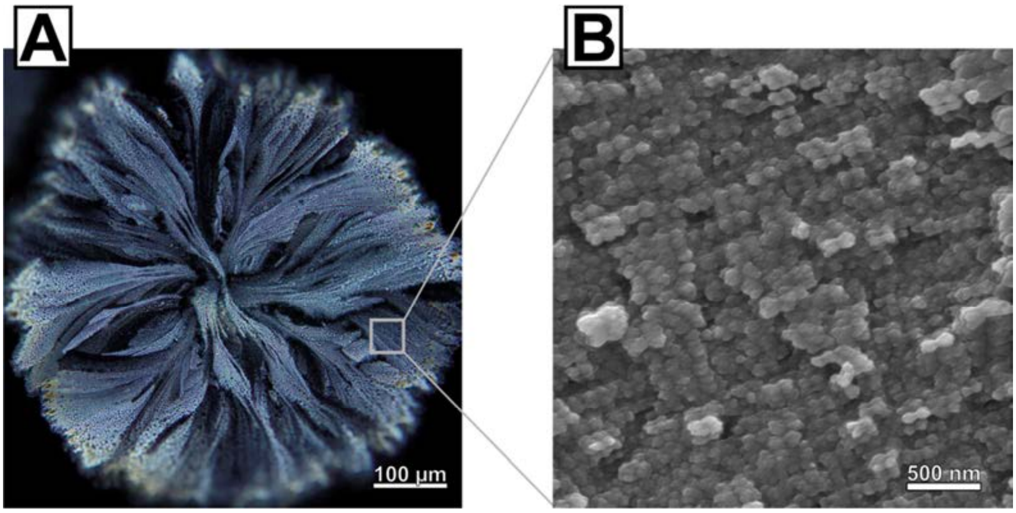


*Fig. 2: Drying shrinkage, mass loss and drying stress of a binder-assisted $Al_2O_3$ slurry measured by beam deflection technique*

## Mechanisms of nonclassical crystallization processes

Stephan E. Wolf

In the recent years, numerous crystallization processes have been reavealed which apparently contradict pertinent models of crystal growth and nucleation. This development recently condensed into the concept of so-called nonclassical crystallization which embraces all crystallization pathways taking place outside of the framework of classical nucleation theories. Since Mai 2014, a new Emmy Noether Research Group under the supervision of Prof. Stephan E. Wolf will focus on mechanistical studies of these processes. The German Research Foundation (DFG) provides 1.26 million euros funding for the project. The research will focus on a specific nonclassical route which is induced by the presence of tiny amounts of a poly-anionic additive during precipitation of a mineral from its supersaturated mother solution at room temperature. These conditions lead to a suppression of classical nucleation. Instead, liquid-liquid phase separation can take place and the liquid-condensed mineral phase serves as the key agent of the precipitation process. Under classical conditions of crystallization, crystal morphology would be dominated by crystal facets that result from the slowest growing crystal faces with lowest surface energy and crystallinity emerges concomitantly to the initial liquid/solid phase separation. But in the polymer-induced liquid-precursor (PILP) process, crystallization proceeds as a solid/solid transformation *after* phase separation and thus downstream to the formation of the transient liquid-amorphous intermediate and its solidification. This union of a solidification process with a final pseudomorphic transformation to crystallinity paves the way for a multitude of non-equilibrium morphologies. The whole process is particle-mediated since classical crystal growth is suppressed by the polymeric additive. As a matter of fact, the obtained mineral bodies still retain a “memory” of this provenance and feature a nanogranular fine structure which mimicks perfectly the nanostructural characteristisc of calcarous biominerals. Inbetween these mineral granules, the polymeric additive is occluded forming an intracrystalline spongy organic network which percolates through the mineral body. PILP materials are thus excellent examples of nanocomposite materials but formed at ambient temperatures. Although the PILP process provides a new synthetical concept for the generation of nanocomposite materials, it is still constrained to few relatively mundane carbonate-based inorganic compounds. The research of this Emmy Noether Research Group is twofold. On the one hand, light shall be shed on the mechanistical foundations of the of the PILP process providing a handy set of empirical rules to transfer the PILP approach to new mineral and polymer systems. On the other hand, the structure-property relationships, which describe the material characteristics of nanogranular composite materials obtained by the PILP process, shall be investigated in order to pave the way for the employment of the PILP process in the design of new nanocomposite materials.



*Exceptional organization of a crystalline film generated in vitro by means of the polymer-induced liquid precursor (PILP) process:* ***[A]*** *The calcium carbonate film appears at first sight as a classical dendritic crystal. However, at second sight and closer inspection, the dendrite branches feature an abnormal gradual tilting of their growth direction. Until now, this feature, the so-called crystal lattice tilting, was only known from calcareous biominerals in which it probably contributes to the increased fracture toughness of the shell. The underlying process is currently under investigation in The Wolf Group.* ***[B]*** *The film is built from singular nanoscopic crystallites which are all aligned in a common crystallographic register. In the current literature, crystalline bodies which show such a prominent crystal ordering on the mesoscale are often subsumed under the elusive term mesocrystal and different pathways of mesocrystallization are hotly debated.*

THE
WOLF
GROUP

# c. Publications

## Papers

(in alphabetical order)

**01/14 M. Adam, S. Kocanis, T. Fey, M. Wilhelm, G. Grathwohl**
Hierarchically ordered foams derived from polysiloxanes with catalytically active coatings
*Journal of the European Ceramic Society 34 (2014) 1715–1725*
DOI: 10.1016/j.jeurceramsoc.2013.12.011

**02/14 A. Bonet, N. Travitzky, P. Greil**
Synthesis of $LaCrO_3$ and $La_{0.9}Ca_{0.1}CrO_3$ by Modified Glycine Nitrate Process
*Journal of Ceramic Science and Technology 5, No.2 (2014) 93-100*
DOI: 10.4416/JCST2013-00024

**03/14 X. Fan, X. Yin, L. Wang, P. Greil, N. Travitzky**
Synthesis of $Ti_3SiC_2$-based materials by reactive melt infiltration
*International Journal of Refractory Metals and Hard Materials 45 (2014) 1-7*
DOI: 10.1016/j.ijrmhm.2014.02.006

**04/14 T. Fey, B. Zierath, A.M. Kern, P. Greil, B.J.M. Etzold**
An advanced method to manufacture hierarchically structured carbide-derived carbon monoliths
*Carbon 70 (2014) 30-37*
DOI: 10.1016/j.carbon.2013.12.052

**05/14 Z. Fu, A. Dellert, M. Lenhart, A. Roosen**
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*Journal of the European Ceramic Society 34 (2014) 2483-2495*
DOI: 10.1016/j.jeurceramsoc.2014.03.002

**06/14 M. Hambuch, A. Roosen, F. Gora, K. Beart, F. Wittmann**
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*Int. J. Appl. Ceram. Technol., 11 (2014) 443-450*
DOI:10.1111/ijac.12200

**07/14 A. Hoppe, B. Jokic, D. Janackovic, T. Fey, P. Greil, S. Romeis, J. Schmidt, W. Peukert, J. Lao, E. Jallot, A.R. Boccaccini**
Cobalt-Releasing 1393 Bioactive Glass-Derived Scaffolds for Bone Tissue Engineering Applications
*ACS Appl. Mater. Interfaces 6 (2014) 2865−2877*
DOI: 10.1021/am405354y

**08/14 A. Hoppe, J. Will, R. Detsch, A.R. Boccaccini, P. Greil**
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*J Biomed Mater Res Part A 102A (2014) 193–203*
DOI: 10.1002/jbm.a.34685

**09/14 D. Jakobsen, R. Hammerbacher, S. Dudczig, T. Fey, A. Roosen**
Manufacture of Rotationally Symmetric Multilayer Refractory Devices for Steel Casting Applications by Spiral Winding of Ceramic Green Tapes
*J. Ceram. Sci. Tech. 5 (2014) 137-144*
DOI: 10.4416/JCST2013-0004

**10/14 S. Krishnan, T. Fey, P. Greil**
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*Journal of the American Ceramic Society 97 (2014) 1638-1644*

DOI: 10.1111/jace.12825

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*Advanced Engineering Materials 16 (6) (2014) 605-606*

DOI: 10.1002/adem.201400130

**13/14 D.R. Neuville, L. Hennet, P. Florian, D. de Ligny**

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*Reviews in Mineralogy and Geochemistry 78 (2014) 779-800*

DOI: 10.2138/rmg.2013.78.19

**14/14 D.R. Neuville, D. de Ligny, G.S. Henderson**

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*Reviews in Mineralogy and Geochemistry 78 (2014) 509-**541***

DOI: 10.2138/rmg.2013.78.13

**15/14 B.J. Pedimonte, G. Bei, D. Pourjafar, T. Fey, P. Greil**

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*J. Ceram. Sci. Tech. 5 (2014) 63-68*

DOI: 10.4416/JCST2013-00044

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*Acta Biomaterialia 10 (2014) 968-974*

DOI: 10.1016/j.actbio.2013.09.023

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*Ceramics International, 40(3) (2014) 4917–4926*

DOI: 10.1016/j.ceramint.2013.10.080

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DOI: 10.1016/j.jeurceramsoc.2014.01.036

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*Journal of Tissue Engineering and Regenerative Medicine 8 (3) (2014) 176–185*

DOI: 10.1002/term.1511

20/14 **N. Travitzky, A. Bonet, B. Dermeik, T. Fey, I. Filbert-Demut, L. Schlier, T. Schlordt, P. Greil,**

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*Advanced Engineering Materials 16 (2014) 729-754*

DOI: 10.1002/adem.201400097

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$Ti_3Si(Al)C_2$-based ceramics fabricated by reactive melt infiltration with $Al_{70}Si_{30}$alloy

*Journal of the European Ceramic Society 34 (2014) 1493–1499*

DOI: 10.1016/j.jeurceramsoc.2013.11.020

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*Materials Science and Engineering A 616 (2014) 214-218*

DOI: 10.1016/j.msea.2014.08.020

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*Rheologica Acta 53, 8 (2014) 635-643*

DOI: 10.1007/s00397-014-0784-0

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*International Materials Reviews 59, 6 (2014) 326-355*

DOI: 10.1179/1743280414Y.0000000037

## Proceedings

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*Proceedings of 16th International Conference on Electromagnetics in Advanced Applications (ICEAA) 2014, Palm Beach, Aruba. Ed. IEEE, USA, 3-8 August 2014, 415-418*

**D. Jakobsen, H. Rauch, A. Roosen**

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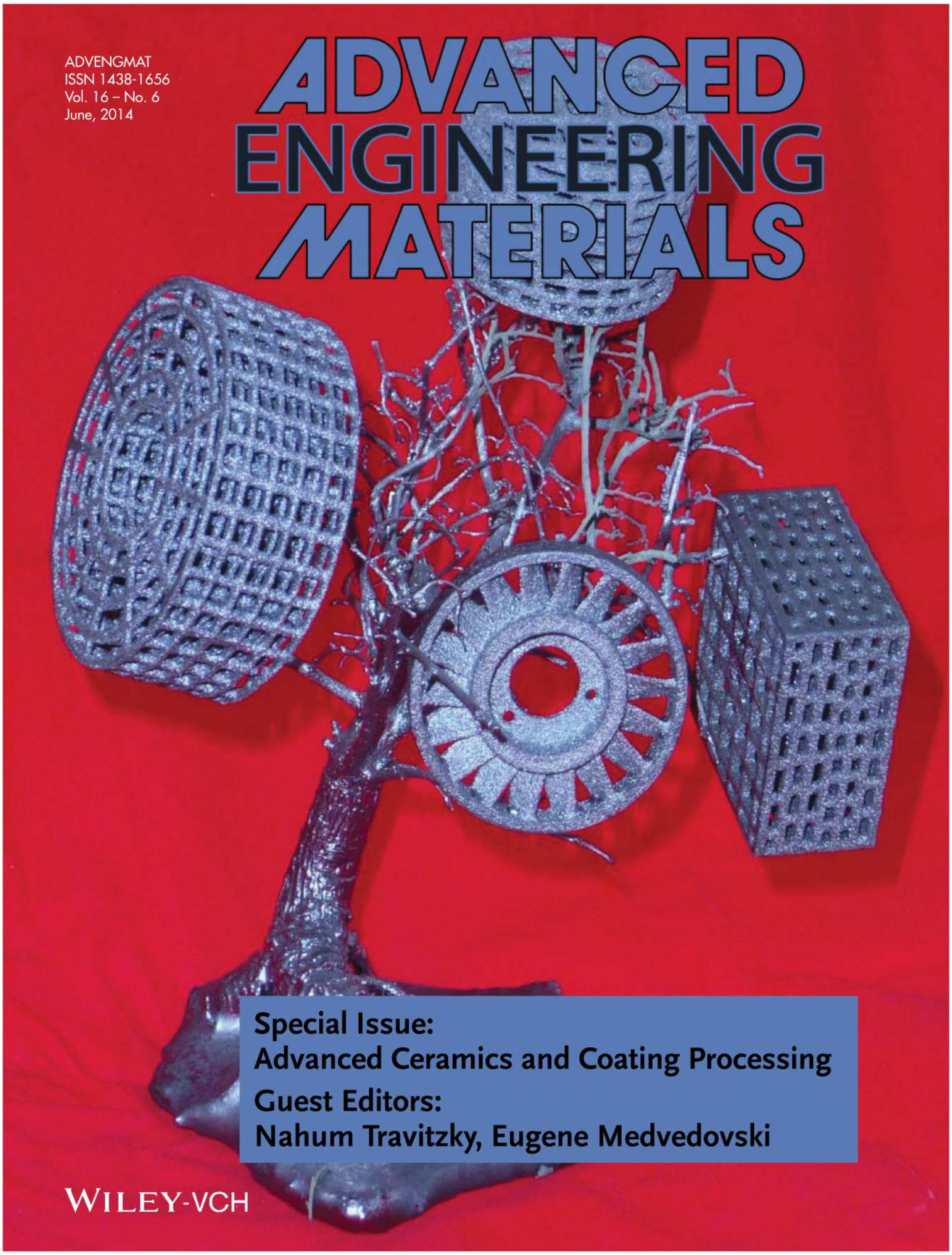
*Proceedings of 57th International Colloquium on Refractories 2014, Aachen, Germany 24-25 September 2014, 171-174*

**R. Hammerbacher, S. Schmiedeke, I. Götschel, F. Lange, A. Roosen**

Influence of lamination techniques on the quality of tape cast refractory multilayer products

*Proceedings of 57th International Colloquium on Refractories 2014, Aachen, Germany, 24-25 September 2014, 178-182*



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Advanced Ceramics and Coating Processing
Guest Editors:
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*SiSiC functionally graded macro-cellular structures and downscaled turbine wheel fabricated by 3D Printing and selective laser curing (SLC), respectively*

Available online at www.sciencedirect.com
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Journal of the European Ceramic Society 34 (2014) 1715–1725
www.elsevier.com/locate/jeurceramsoc

# Hierarchically ordered foams derived from polysiloxanes with catalytically active coatings

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Available online 17 January 2014

**Abstract**

Pt free and Pt containing hierarchically ordered macro/micro porous foams were generated by using polysiloxanes and platinic acid as precursors and expanded polystyrene beads as templates to generate macro pores. By pyrolysis at 500 °C micro porosity and thus high specific surface areas were generated. The foams were analyzed in terms of macro- and microstructures (SEM, micro-computer tomography, TEM, BET) and catalytic properties (CO oxidation). For the crack free foams a method was additionally developed that allows the application of a thin Pt-containing layer only on the cell walls. The well known problems arising from mass transport limitation in micro porous materials can be diminished due to the generation of thin struts and this minimized Pt coating on the cell walls as demonstrated by catalytic experiments.

*Keywords:* Hierarchical structure; Porous materials; Foam; Platinum; CO oxidation

## 1. Introduction

The pyrolytic conversion of preceramic precursors offers a controllable way to generate amorphous and crystalline ceramic materials. Due to the polymer like properties of the precursors, common polymer shaping processes can be applied[1] leading to coatings,[2] bulk materials,[3] tubes[4] and foams.[5–8] Furthermore, by the choice of the versatile precursor materials, but also the addition of active and passive fillers[9,10] the properties of the generated polymer derived ceramics (PDCs) can be influenced. However, the temperature during pyrolytic conversion significantly determines the nature of the materials generated. At temperatures above 1200 °C ceramic materials like SiC and SiCN are generated, whereas at temperatures of 800–1200 °C glassy or amorphous ceramic materials evolve.[11–13]

At moderate temperatures of 400–600 °C the pyrolytic conversion is not complete and surface rich hybrid ceramic/polymer materials are obtained. Due to their high specific surface area (SSA) and adjustable surface properties, these materials are suitable for adsorption and catalytic applications.[14–16] For catalytic applications, besides high SSA, distribution, size and accessibility of the catalytic sites in the material and their stability against sintering are also important requirements.[17,18] Concerning the geometry of catalysts or catalyst supports, geometries are commonly honeycombs and pellets. Honeycombs show low pressure drop combined with low contact of reactant and catalyst but good heat transfer whereas pellets allow good contact of reactant with catalyst but show high pressure drop and poor heat transfer. Therefore foams are found to be promising structures which combine the advantages of honeycombs and pellets.[19,20] Due to the irregular and statistically distributed pore structure the reactants are well mixed and brought into contact with the catalyst. At the same time the monolithic structure improves the heat transfer. Depending on the pore size, the pressure drop can also be adjusted.

For manufacturing of PDC foams, several methods are reported like direct foaming,[6,21] Co-foaming,[5] foaming with volatile components,[7] emulsion processes[22,23] or using sacrificial templates.[8,24–28]

There are a lot of different materials with different shapes that can be used as templates. For example porous SiC was prepared by using filters, carbon nano tubes, carbon fibers and silica beads as sacrificial templates. After pyrolysis and removal of the templates a broad variety of pore structures could be achieved.[24]

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available online at: http://www.ceramic-science.com

# Synthesis of $LaCrO_3$ and $La_{0.9}Ca_{0.1}CrO_3$ by Modified Glycine Nitrate Process

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## Abstract

**$LaCrO_3$ and $La_{0.9}Ca_{0.1}CrO_3$ ceramics were synthesized in the modified glycine nitrate process (MGNP). The effect of the equivalence ratio $\Phi_e$ of precursor mixtures on the combustion reaction was investigated by means of DSC and TG-FTIR analyses. It was found that for $\Phi_e > 0.65$ the combustion reaction proceeds in a self-propagating one-step process, resulting in the formation of well-crystallized single-phase powders. Further glycine addition ($\Phi_e < 0.65$) leads to sluggish multi-step combustion, which is typical for fuel-rich combustion, and the formation of secondary phases such as $La_2CrO_6$. Furthermore it could be found that the ignition temperature of the precursors rises with rising fuel content. An influence of the equivalence ratio on the specific surface area and particle size of synthesized powders could not be detected. The specific surface area of the powders was in the range of 5 – 10 $m^2/g$ and particle size 100 – 150 nm.**

*Keywords: Lanthanum chromite, modified glycine nitrate process, combustion synthesis*

## I. Introduction

Lanthanum chromite, $LaCrO_3$, is a refractory oxide with distorted perovskite structure [1]. Owing to their high electrical conductivity and high-temperature stability in oxidizing and reducing atmospheres, lanthanum-chromite-based ceramics have been investigated extensively as interconnectors in solid oxide fuel cells (SOFC) [2,3,4], as heating elements at high temperatures > 1450 °C in oxidizing atmosphere [5,6,7] and as hot electrodes for MHD power generation [8]. In an oxidizing atmosphere, vaporization of the chromium species gives rise to poor sinterability [9]. The main strategies to improve the sinterability of $LaCrO_3$ are (1) sintering in a reducing atmosphere [10], (2) use of nanoscale powders with high sintering activity [11], (3) Cr-deficient stoichiometry [12,13], (4) doping with earth alkali metals [11,14] and (5) use of sintering aids such as strontium vanadate [15].

Nanoscale powders with a high specific surface area and high packing density may enhance the sintering activity of ceramics. Nanoscale perovskite powders can be synthesized in the glycine nitrate process (GNP) [16]. In this process, metal nitrates and glycine are dissolved in water. Glycine complexes the metal ions with its carboxylic acid and amine group (zwitterionic glycine), to prevent selective precipitation during water evaporation. Furthermore, glycine serves as fuel that is oxidized by the nitrate groups. Heating up the aqueous solution leads at first to evaporation of water and at approximately 180 °C to spontaneous combustion of the viscous liquid, resulting in the formation of an ash containing the perovskite reaction product. Depending on glycine/nitrate ratio, this high exothermic redox reaction reaches flame temperatures up to 1450 °C and is completed in a few seconds. The peak flame temperature (maximum energy release) is reached at a stoichiometric glycine/nitrate ratio of 0.56, forming only $H_2O$, $CO_2$ and $N_2$ with no atmospheric oxygen being required [16]. An example of this combustion reaction for synthesis of perovskite oxides ($A^{3+}B^{3+}O_3$) can be described as follows:

$$\begin{aligned} &3A(NO_3)_3 + 3B(NO_3)_3 + 10C_2H_5NO_2 \\ &\quad \rightarrow ABO_3 + 25H_2O + 20CO_2 + 14N_2 \end{aligned} \tag{1}$$

Compared to the mixed oxide route, GNP is a fast and simple method to produce nanoscale (5 – 50 nm particle size) single- [17,18,19] and multi-oxide powders [20,21,22,23] with a high specific surface area and homogeneous composition [16]. Owing to its high exothermic nature and high amount of released gases, however, this reaction is difficult to control. Bošković *et al.* modified the glycine nitrate process with partial substitution of nitrates by acetates (MGNP) [20] in order to reduce the reaction rate and to facilitate reaction control. For the glycine nitrate process a lot of work has been done to investigate the influence of the glycine/nitrate ratio on the combustion reaction and the resulting powder [23,24,25]. However, owing to substitution of nitrates by acetates, this work is not transferable to the MGNP. In order to control the synthesis reaction, it is essential to understand the effect of partial substitution of nitrates by acetates. Thus, it is the aim of this work to investigate the effect of the fuel/oxidant ratio on the combustion reaction and synthesized $LaCrO_3$-based perovskite in the modified glycine nitrate process.

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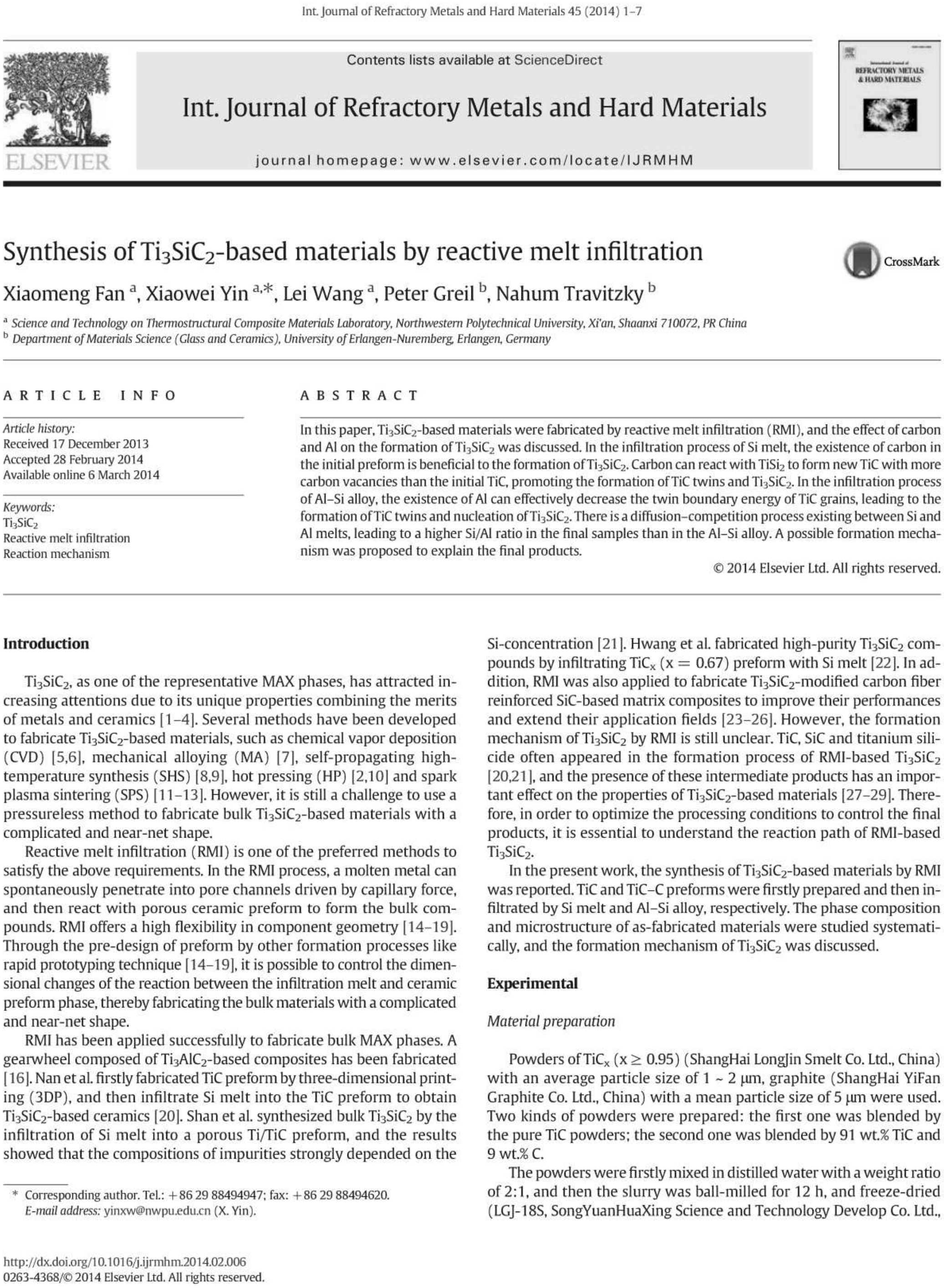

Int. Journal of Refractory Metals and Hard Materials 45 (2014) 1–7

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# Synthesis of $Ti_3SiC_2$-based materials by reactive melt infiltration

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ABSTRACT

In this paper, $Ti_3SiC_2$-based materials were fabricated by reactive melt infiltration (RMI), and the effect of carbon and Al on the formation of $Ti_3SiC_2$ was discussed. In the infiltration process of Si melt, the existence of carbon in the initial preform is beneficial to the formation of $Ti_3SiC_2$. Carbon can react with $TiSi_2$ to form new TiC with more carbon vacancies than the initial TiC, promoting the formation of TiC twins and $Ti_3SiC_2$. In the infiltration process of Al–Si alloy, the existence of Al can effectively decrease the twin boundary energy of TiC grains, leading to the formation of TiC twins and nucleation of $Ti_3SiC_2$. There is a diffusion–competition process existing between Si and Al melts, leading to a higher Si/Al ratio in the final samples than in the Al–Si alloy. A possible formation mechanism was proposed to explain the final products.

## Introduction

$Ti_3SiC_2$, as one of the representative MAX phases, has attracted increasing attentions due to its unique properties combining the merits of metals and ceramics [1–4]. Several methods have been developed to fabricate $Ti_3SiC_2$-based materials, such as chemical vapor deposition (CVD) [5,6], mechanical alloying (MA) [7], self-propagating high-temperature synthesis (SHS) [8,9], hot pressing (HP) [2,10] and spark plasma sintering (SPS) [11–13]. However, it is still a challenge to use a pressureless method to fabricate bulk $Ti_3SiC_2$-based materials with a complicated and near-net shape.

Reactive melt infiltration (RMI) is one of the preferred methods to satisfy the above requirements. In the RMI process, a molten metal can spontaneously penetrate into pore channels driven by capillary force, and then react with porous ceramic preform to form the bulk compounds. RMI offers a high flexibility in component geometry [14–19]. Through the pre-design of preform by other formation processes like rapid prototyping technique [14–19], it is possible to control the dimensional changes of the reaction between the infiltration melt and ceramic preform phase, thereby fabricating the bulk materials with a complicated and near-net shape.

RMI has been applied successfully to fabricate bulk MAX phases. A gearwheel composed of $Ti_3AlC_2$-based composites has been fabricated [16]. Nan et al. firstly fabricated TiC preform by three-dimensional printing (3DP), and then infiltrate Si melt into the TiC preform to obtain $Ti_3SiC_2$-based ceramics [20]. Shan et al. synthesized bulk $Ti_3SiC_2$ by the infiltration of Si melt into a porous Ti/TiC preform, and the results showed that the compositions of impurities strongly depended on the Si-concentration [21]. Hwang et al. fabricated high-purity $Ti_3SiC_2$ compounds by infiltrating $TiC_x$ ($x = 0.67$) preform with Si melt [22]. In addition, RMI was also applied to fabricate $Ti_3SiC_2$-modified carbon fiber reinforced SiC-based matrix composites to improve their performances and extend their application fields [23–26]. However, the formation mechanism of $Ti_3SiC_2$ by RMI is still unclear. TiC, SiC and titanium silicide often appeared in the formation process of RMI-based $Ti_3SiC_2$ [20,21], and the presence of these intermediate products has an important effect on the properties of $Ti_3SiC_2$-based materials [27–29]. Therefore, in order to optimize the processing conditions to control the final products, it is essential to understand the reaction path of RMI-based $Ti_3SiC_2$.

In the present work, the synthesis of $Ti_3SiC_2$-based materials by RMI was reported. TiC and TiC–C preforms were firstly prepared and then infiltrated by Si melt and Al–Si alloy, respectively. The phase composition and microstructure of as-fabricated materials were studied systematically, and the formation mechanism of $Ti_3SiC_2$ was discussed.

## Experimental

### *Material preparation*

Powders of $TiC_x$ ($x \geq 0.95$) (ShangHai LongJin Smelt Co. Ltd., China) with an average particle size of 1 ~ 2 μm, graphite (ShangHai YiFan Graphite Co. Ltd., China) with a mean particle size of 5 μm were used. Two kinds of powders were prepared: the first one was blended by the pure TiC powders; the second one was blended by 91 wt.% TiC and 9 wt.% C.

The powders were firstly mixed in distilled water with a weight ratio of 2:1, and then the slurry was ball-milled for 12 h, and freeze-dried (LGJ-18S, SongYuanHuaXing Science and Technology Develop Co. Ltd.,

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# An advanced method to manufacture hierarchically structured carbide-derived carbon monoliths

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ABSTRACT

The preparation of carbide-derived carbon (CDC) monoliths with a hierarchically structure in the nm and μm range is presented. Basis is the manufacturing of porous cellular SiC ceramics based on a biomorphous approach with μm porosity and subsequent conformal conversion to CDC by reactive extraction with chlorine. The SiC ceramics can be sintered at low temperatures and short times (1500 °C, 2 h) compared to classical preparation methods. The SiC ceramics show a macro pore volume (1–10 μm channel size) of 0.56 ml $g^{-1}$, which corresponds to 1.5 ml $g^{-1}$ in the resulting CDC. The final carbon material exhibits an additional nano pore volume of 0.525 ml $g^{-1}$ with a mean slit pore size of 0.86 nm. Mechanical stabilities of the highly porous CDC are excellent (bending strength 2.1 ± 0.2 MPa, corrected Weibull modulus 8.7, characteristic strength 2.2 MPa and Youngs modulus 10.0 ± 0.5 GPa). The reactive extraction of the carbide monoliths shows very high reaction rates, approx. two dimensions faster (95×) compared to non-porous samples. Thus the manufacturing of the structured carbide and CDC can be performed at lower costs.

## 1. Introduction

Carbide-derived carbons (CDCs) attract the attention as porous carbons. Their high purity, pore size control and reproducible material properties from batch to batch is interesting for several applications like e.g. gas storage and separation [1–3], electrical energy storage [4–7] or as catalyst support [8–12]. CDCs are prepared by the reactive extraction of the non-carbon components from carbides [13]. Mainly chlorine is used as reactant. In a conformal process the overall texture does not change, but inner porosity is created [14,15]. The resulting pore structure can be varied by the precursor carbide and extraction temperature from ultramicroporous to mesoporous. While controlling the micro- or mesoporosity is well established, methods to add a secondary porosity are less reported [16–23]. This could be necessary for porous monolithic structures, which can be advantageous in several applications as solely microporous material would suffer pore diffusion limitations for most applications. CDC with micro- and mesoporosity results from using binary metal carbides [24,25]. Kaskel et al. presented a hard- and soft-templating method to produce monolithic and mesoporous SiC from preceramic polymers and subsequently monolithic and mesoporous CDC [16,18,20,26,27]. They introduced not only random mesoporosity, but the templating results in well-ordered structure.

We reported recently that for carbides containing a free metal phase like commercial SiSiC, the reactive extraction results in the nm porosity know for CDC and an additional porosity in the micrometer ranger originating from the extraction of the free metal phase [26]. Extraction rates were shown to be approx. 20 times higher compared to compact SiC. Nevertheless, the common SiSiC material is cost-intensive due to liquid silicon infiltration (wick/capillary) operating at high temperatures (T > 1550 °C), long sintering times [29] and high postprocessing (grinding/polishing) costs. Also for

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# Effect of pore orientation on anisotropic shrinkage in tape-cast products

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**Abstract**

During tape casting, an anisotropic shrinkage can be observed, which is attributed to particle alignment during the casting process. The understanding of the relationship between green body microstructure and shrinkage anisotropy is of great importance for further miniaturization of multilayer ceramics. In the current study, four alumina powders with different particle shape (spherical, standard, plate-like and extreme plate-like) were used to cast green tapes. The sintering shrinkage behavior and the microstructure were analyzed. In particular, the pore orientation was determined quantitatively by using a modified linear intercept method. The relationship between pore alignment and anisotropic sintering shrinkage of cast green tapes is discussed in all three spatial directions. The shrinkage anisotropy could be correlated quantitatively with the pore anisotropy. Furthermore, this correlation was verified by mathematical modeling based on elongated particles and pores.

*Keywords:* Tape casting; Anisotropic shrinkage; Pore orientation; Linear intercept method; Sintering

## 1. Introduction

Tape casting is used for the manufacture of large areas of thin ceramic sheets.[1–3] These ceramic green tapes can be further processed via punching, metallization, and lamination to build up complex multilayer devices, e.g., capacitors, inductors, actuators, gas sensors and high integrated multilayer circuits based on LTCC (low temperature co-fired ceramics).[3–5] The current trend toward further miniaturization and higher integration of functions requires high accuracy of the position of printed structures in each layer. Any shrinkage anisotropy of the green tapes can lead to device failure.[6–10] Therefore, in order to guarantee a high reproducibility in dimension and in physical properties, the origin of anisotropic shrinkage in tape-cast ceramic sheets must be well understood.

Recently, anisotropic shrinkage behavior of tape-cast products is intensively studied and has been reported in several publications.[6,10–17] Shrinkage anisotropy is caused by a non-isotropic microstructure of the green tape, which is formed during processing. During casting, e.g., the slurry is sheared while passing the blade of the tape casting head, which results in an orientation of non-equiaxed particles and binder molecules.[16–19] This particle orientation is increased during lamination of green tapes.[15] In addition, during the drying process, the solvent evaporation is only carried out on the top surface. Owing to the capillary forces, which transport the solvent to the surface, an increased amount of the dissolved binder can be found at the top surface of the tape.[20] Moreover, due to the adhesion forces between slurry and carrier tape, drying shrinkage occurs only in the $z$-direction, which is the direction perpendicular to the casting plane.[15–17] All these effects cause a non-uniform green microstructure, which gives rise to an anisotropic shrinkage behavior during firing. This anisotropy already develops in the early stages of sintering.[14,16]

Based on sintering theory some papers describe the densification of such inhomogeneous microstructures. Raj et al. simulated the densification of a two-dimensional arrangement of oriented elliptical particles based on surface and grain boundary diffusion. They showed that the shrinkage is faster in the direction perpendicular to the long axis of elliptical particles.[21] Travitzky et al. observed an anisotropic shrinkage during the sintering of preceramic paper-derived ceramics with elongated pores which can be ascribed to oriented cellulose-based wood fibers.[22] The primary cause of anisotropic shrinkage in all these systems is

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# Joining of Sintered Alumina Substrates and LTCC Green Tapes via Cold Low-Pressure Lamination

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Common technologies for the manufacture of ceramic-based microelectronic devices are thick-film hybrid technology and LTCC technology. The first one uses sintered ceramic substrates, mostly $Al_2O_3$, to provide very good heat conductivity, for example of 25 W/mK for alumina substrates; but there are only two sides to carry a metallization. An improved miniaturization can be accomplished by multilayer systems using the LTCC technology. A drawback of LTCCs is their low heat conductivity of typically 3 W/mK due to the high glass content. By combining hybrid and LTCC technology, the advantages of both methods can be joined. Because the failure rate is too high to laminate sintered substrates and ceramic green tapes via thermo compression, cold low-pressure lamination (CLPL) has been used. CLPL is a lamination method, where the joining is performed at room temperature by application of very low pressure (<5 MPa) using a double-sided adhesive tape. During heat treatment, the adhesive film keeps the tapes together until the adhesive is completely decomposed; during further temperature increase, the tapes are joined by sintering. The study describes the materials used and processing steps and discusses effects which occur during firing. These effects like edge curl and crack formation are mainly due to stresses which occur during constrained sintering.

## Introduction

In microelectronic devices for automotive applications, power electronics, and other applications with high thermal dissipation losses, the requirements for thermal management are increasing. The hybrid technology, in which sintered substrates are metallized via screen printing, followed by drying and firing of these pastes at 850°C, offers high heat dissipation if alumina ($Al_2O_3$) substrates with a thermal conductivity of 25 W/mK are used. With the use of VIAs, there are two sides available for metallization. Higher integration can be achieved by multilayer systems, for example the low-temperature co-fired ceramics (LTCC) technology. LTCC is a composite material composed of fillers such as $Al_2O_3$, which are surrounded by a glass matrix from a glass of low glass transition temperature. This allows densification at relatively low sintering temperatures of 850°C. After VIA punching, screen printing, and stacking, the green tapes are laminated using thermocompression, followed by co-firing of the multilayer stack. During thermocompression, the stacked green sheets are joined by applying pressure at a temperature above the glass transition point of the binder—plasticizer system of the green tape to provide mass flow.[1] This is typically performed around 80°C and 30 MPa. A drawback of the LTCC technology is the poor thermal conductivity of app. 3 W/mK,[2] due to the high content of glass phase.

By combining hybrid and LTCC technology, the advantages of both methods can be joined. Joining of hybrid and LTCC technology is not obvious. The combination of a sintered material with a green sheet is normally difficult to accomplish because of the high failure rate due to breakage during thermocompression. In the past, some techniques for joining green tapes with solid substrates were developed. With the tape-on-substrate (TOS) technology, LTCC green tapes are uniaxially pressed onto sintered alumina substrates using a lamination die at a pressure of 5.9 MPa and a temperature of 50°C. Above the tape, several layers of Mylar and a sheet of polyurethane are placed to ensure a homogeneous pressure distribution. TOS, however, is a serial process, and each single layer has to be laminated and fired to accomplish a multilayer stack.[3] In another

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# Cobalt-Releasing 1393 Bioactive Glass-Derived Scaffolds for Bone Tissue Engineering Applications

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*Supporting Information*

ABSTRACT: Loading biomaterials with angiogenic therapeutics has emerged as a promising approach for developing superior biomaterials for engineering bone constructs. In this context, cobalt-releasing materials are of interest as Co is a known angiogenic agent. In this study, we report on cobalt-releasing three-dimensional (3D) scaffolds based on a silicate bioactive glass. Novel melt-derived "1393" glass (53 wt % $SiO_2$, 6 wt % $Na_2O$, 12 wt % $K_2O$, 5 wt % MgO, 20 wt % CaO, and 4 wt % $P_2O_5$) with CoO substituted for CaO was fabricated and was used to produce a 3D porous scaffold by the foam replica technique. Glass structural and thermal properties as well as scaffold macrostructure, compressive strength, acellular bioactivity, and Co release in simulated body fluid (SBF) were investigated. In particular, detailed insights into the physicochemical reactions occurring at the scaffold–fluid interface were derived from advanced micro-particle-induced X-ray emission/Rutherford backscattering spectrometry analysis. CoO is shown to act in a concentration-dependent manner as both a network former and a network modifier. At a concentration of 5 wt % CoO, the glass transition point ($T_g$) of the glass was reduced because of the replacement of stronger Si–O bonds with Co–O bonds in the glass network. Compressive strengths of >2 MPa were measured for Co-containing 1393-derived scaffolds, which are comparable to values of human spongy bone. SBF studies showed that all glass scaffolds form a calcium phosphate (CaP) layer, and for 1393-1Co and 1393-5Co, CaP layers with incorporated traces of Co were observed. The highest Co concentrations of ~12 ppm were released in SBF after reaction for 21 days, which are known to be within therapeutic ranges reported for $Co^{2+}$ ions.

KEYWORDS: *cobalt, hypoxia, bioglass, bioactive, scaffold, bone tissue engineering, angiogenesis*

## 1. INTRODUCTION

Bioactive glasses (BGs), such as "45S5 Bioglass" (45 wt % $SiO_2$, 25 wt % CaO, 25 wt % $Na_2O$, and 6 wt % $P_2O_5$)[1] and "1393" (53 wt % $SiO_2$, 6 wt % $Na_2O$, 12 wt % $K_2O$, 5 wt % MgO, 20 wt % CaO, and 4 wt % $P_2O_5$) compositions,[2] have been widely used for bone tissue engineering applications. BGs allow strong bonding to hard as well as soft tissue and have been shown to promote osteogenesis via the activation of several relevant genes.[3] Bioactive glass-derived three-dimensional (3D) scaffolds have been extensively researched in tissue engineering approaches for restoring damaged tissue.[4] Hereby, a porous 3D network is seeded with cells that are stimulated toward proliferation and differentiation, resulting in the formation of bone tissue *in vitro*. However, after implantation *in vivo*, the new bone tissue needs a functioning blood supply, making neovascularization of bone constructs a critical issue.[5] Since it has become clear that highly vascularized tissue is essential for successful clinical application of engineered bone constructs,[5,6] research efforts have been focusing on enhancing the angiogenic potential of biomaterials by incorporating inorganic therapeutics into a carrier matrix.[7,8]

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# Formation and *in vitro* biocompatibility of biomimetic hydroxyapatite coatings on chemically treated carbon substrates

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**Abstract:** Carbon derived materials such as pyrolytic carbon or carbon-carbon composites (CCCs) exhibit excellent mechanical properties making them promising candidates for bone replacement. However, these materials are considered bioinert and not to induce bone formation *in vivo*. In this study, a two-step chemical surface treatment including etching with $HCl/HNO_3$ solution and subsequent soaking in $CaCl_2$ solution was applied to carbon substrates in order to activate the materials surface towards bioactive behavior. The bioactivity was proven by soaking the samples in simulated body fluid (SBF) and formation of carbonated hydroxyapatite layer (HCA), which indicates the ability of the material to bond to bone *in vivo*. The materials surface is shown to be functionalized through the chemical etching creating $COO^-Ca^{2+}$ complexes on the surface as confirmed by FTIR and XPS analyses. These ionic complexes provide nucleation sites for HAp precipitation. After similar immersion time in SBF under the condition of local supersaturation the thickness and homogeneity of the HAp layer were found to depend on the chemical pretreatment with $HCl/HNO_3$. Homogenous HAp layers with a thickness ranging from ~ 6 to ~ 17 μm were achieved. The proposed bioactivating treatment of carbon stimulates HAp formation *in vivo* and can be considered an easy biomimetic approach for coating carbon derived materials with bone-like hydroxyapatite. *In vitro* cell assay with osteosarcoma cells (MG-63) showed increased cell viability (+70%) on HAp coated carbon substrates as compared to uncoated reference while both materials induced ALP expression in MG-63 cells confirming the osteoblastic phenotype. © 2013 Wiley Periodicals, Inc. J Biomed Mater Res Part A: 102A: 193–203, 2014.

**Key Words:** carbon, hydroxyapatite, bioactive, osteoblast, functionalization

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## INTRODUCTION

Carbon based materials exhibit a high potential for use in orthopedic implant devices because of their appropriate biological and mechanical properties. The biocompatibility of carbon derived materials has been proven by *in vitro* and *in vivo* studies, which showed carbon materials to allow cell attachment and growth.[1] Furthermore, carbon derived materials such as pyrolytic carbon and carbon reinforced carbon composites (CFC) have been considered for hard tissue replacement due to excellent mechanical properties and fatigue resistance matching or even exceeding the properties of human cortical bone.[2,3] Carbon fibers were demonstrated to support growth of bone derived cells. Coating of the carbon fibers with HAp even improved the biocompatibility and accelerated enhanced osteoblast growth.[4] Carbon coatings on Ti implants show bone integration *in vivo* resulting in an improved bone bonding shear strength.[5] Diamond like carbon (DLC) was reported to be effectively used in biomedical fields because of high wear resistance, hardness, and good biocompatibility.[6] More recently, the use of nano and submicron sized carbon fibers has emerged as a wide field for carbon applications as biomaterials including fabrication of carbon derived scaffolds for bone tissue engineering.[7] Aoki et al.,[8] for instance, introduced carbon fiber based scaffolds via electro spinning method for bone tissue engineering as an synthetic alternative to natural polymers like collagen. These scaffolds provided new bone formation when tested *in vivo* making this materials highly potential for tissue engineering applications.

Dense carbon materials (neglecting carbon nanotubes, CNT), however, are considered to be bioinert in contrary to bioactive glasses and ceramics and do not form a strong bonding to bone when exposed to the human body.[9] Moreover, some studies reported possible toxic effects of carbon derived materials.[10] Since HAp is known for its high biocompatibility HAp coatings have been applied in order to

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# Manufacture of Rotationally Symmetric Multilayer Refractory Devices for Steel Casting Applications by Spiral Winding of Ceramic Green Tapes

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## Abstract

**In order to create rotationally symmetric refractory devices from ceramic green tapes, the spiral winding method, which is mainly known from the paper industry, was applied. Different green tapes with varying properties with regard to shrinkage, porosity and Young's modulus were used to generate multilayer tubes with the spiral winding and the cold low pressure lamination technique. The tubes were fired in air and their microstructure was investigated. Thermal shock tests were conducted to evaluate the applicability of the fabricated structures for refractory applications. The correlation between the microstructure and thermal shock behaviour of the tubes is discussed.**

*Keywords: Spiral winding, green tapes, refractories, thermal shock*

## I. Introduction

The reduction of greenhouse gas emissions has become a major issue in almost every technical and industrial field. Many commercial refractories are carbon-bound, and thus release CO and $CO_2$ gases during the steelmaking process [1,2]. Therefore, substituting carbon-free raw materials for the carbon-bound ones is very interesting in terms of "clean steel technology". However, the absence of carbon also involves a decline in thermal shock and corrosion resistance [1]. Therefore, the development of advanced refractories to compensate for this disadvantage is of great interest. Ceramic multilayer technology, which is based on cast green tapes, has the potential to generate such advanced structures [3,4]. The technique of multilayer composites allows the generation of structures with improved mechanical and thermal properties [5,6]. One concept is based on combining different layers exhibiting different shrinkage behavior and/or coefficients of thermal expansion (CTE) in order to generate internal stresses which could counteract the thermal stresses resulting from thermal shock. Another way, which is the goal of this work, is based on the generation of weak bonds at interfaces, which was described in literature as yielding excellent thermal shock behaviour [7]. Regardless of which method is employed, the use of the green tape multilayer technology for refractory applications generally requires the ability to manufacture rotation-symmetric devices from green tapes; it is obvious to use winding as a manufacturing technique for such devices.

Winding is a well-known technology in different applications, e.g. winding of thermoplastics, inductors, or superconductors [8–10]. Depending on the direction of the winding axis relative to the direction in which the material is moved, a distinction is generally made between parallel, vertical and spiral winding. As the axis of rotation, a core or a mandrel may be used [11]. Offering the possibility of endless winding, spiral winding is the most widespread method. This technique is often used in the paper industry to fabricate devices, like paper rolls [12–14]. Reports about winding ceramic green tapes are rare, but there have been attempts to fabricate some structures, such as piezoelectric multilayer actuators in the shape of a double helix structure [15]. Spiral winding of ceramic green tapes was conducted by Scheithauer *et al.* using zirconia and calcium aluminate tapes to manufacture tubes for energy, environmental, and high-temperature applications [16]. Götschel *et al.* combined the winding of preceramic papers and ceramic green tapes to prepare a rotation-symmetric structure for refractory applications [17]. They used the non-continuous parallel winding technique and a cold low pressure lamination technique and obtained crack-free structures after firing. However, in parallel winding, the length of the tube is limited by the width of the green tape. To lengthen the wound tube, a second winding step has to be started next to the first one. This interface is a weak point in the green body and will probably cause cracking during firing.

To avoid this disadvantage, the applicability of the spiral winding process to ceramic green tapes will be demonstrated in this study as a continuous method to manufacture rotation-symmetric nozzles for steel casting ap-

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# SILICONBORONOXYCARBIDE (SIBOC) FOAM FROM METHYL BOROSILOXANE

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## ABSTRACT

Siliconboronoxycarbide (SiBOC) foams were prepared from borosiloxane precursors by sacrificial pu foam template method. Methyl borosiloxane oligomer was synthesized from boric acid and methyltriethoxysilane. This SiBOC precursor (methylborosiloxane) was pyrolyzed at 1000°C in argon with a ceramic yield of amorphous SiBOC of ~78%. Compressive strength of the foam sample achieved values of 410kPa at a total porosity of 85% and a mean pore cell diameter of approx. 700 µm. Annealing at 1400°C in argon resulted in β-SiC crystallization and a SiC/SiBOC nano composite foam was formed.

## INTRODUCTION

Ceramic foam materials have gained much momentum over the past few years. Low density, high surface area, high permeability and low specific heat have enabled these materials to find application as catalyst supports, filters for molten metals and hot gases, thermal protection materials and heat exchangers[1]. The production of ceramics from the pyrolysis of filler free polymeric precursors has already claimed a pivotal position as it provides many advantages over the conventional methods. The advantages include low temperature processability, high purity of the ceramics, the ability to control the composition of the ceramics at the molecular level, easiness in the preparation of shaped objects and the ability to generate products in a variety of forms such as coatings, films, joints, monolithic bodies, foams and fibers[2]. The preparation of ceramics from polymers involves the following steps:

a) synthesis of preceramic polymers from monomers

b) shaping and curing of green body at temperatures <250°C

c) pyrolysis in the temperature range 500 to 1600°C under inert or reactive gas.

During pyrolysis decomposition of cross-linked polymer takes place in the temperature range 400 to 800°C, followed by conversion to amorphous ceramic and crystallization of the ceramic occurs in the temperature range 1300 and 1600°C. The ceramics obtained by polymer pyrolysis is amorphous in nature owing to its unique chemical composition and the low processing temperature. For crystallizing this amorphous ceramics, high temperature annealing is required. One of the advantages of the polymer-derived ceramic materials is their ability to remain amorphous at high temperatures thereby retaining their mechanical properties. Detailed micro-structural / compositional analysis of the ceramics shows that the transformation of amorphous ceramics to crystalline material is not via purely crystalline intermediates. The materials are in-homogeneous in phase distribution consisting segregates of metastable intermediates[3]. With increase in temperature, size of these metastable phases increases and leads to the formation of a crystalline material. The type of metastable phase formed during pyrolysis depends strongly on the chemical composition of the precursor. This is the major advantage of precursor route to ceramics that the composition and properties of the ceramics can be defined by the structure and composition of the polymer.

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journal

# Microstructure Development of PZT Ceramics by Doping with Small Amounts of $Al_2O_3$, $SiO_2$, and $Fe_2O_3$

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**Lead zirconate titanate (PZT) ceramics are used in a wide range of applications as sensors and actuators. Typically, they are formulated by the mixed oxide route, using several mixing and milling steps. Due to wear, these processes introduce impurities into the ceramic mass, which on their part can strongly influence densification behaviour and final properties of the PZT. In this study, the effect of such impurities, such as iron oxide, alumina, and silica, on the sintering behaviour and microstructure development of PZT ceramic is evaluated. A commercial Nb-doped PZT powder was used and doped by adding $Al_2O_3$, $SiO_2$, and $Fe_2O_3$ with an amount of up to 0.001 mol%. Bulk samples were prepared and sintered in air. The mass loss, density, and grain size were correlated by regression analysis using the doping elements and levels, respectively. Due to the complex interactions between the oxides and the ceramic properties, the experiments were performed with the design-of-experiment method (DoE). The results showed a significant influence of these low amounts of doping levels on the microstructure development. Moreover, it was shown that doping after calcination affects the microstructure in a similar way to doping before calcination. Thus, a possibility to compensate concentration variations in the calcined ceramic mass is demonstrated, to homogenize the chemical composition and the final microstructure of the sintered PZT ceramic in the manufacturing processes.**

## I. Introduction

The wide use of lead zirconate titanate (PZT) ceramics in sensor and actuator applications is based on their excellent piezoelectric properties. This is due to the crystallographic structure and polarization behaviour coexistence of two crystallographic phases in the morphotropic phase boundary region (MPB),[1,2] a tetragonal and a rhombohedral ferroelectric phase. The width of the MPB depends on the chemical homogeneity of the PZT ceramics and its grain size.[3,4] In addition, the desired piezoelectric properties of the ceramic can be adjusted by doping. The doping alters the ceramic microstructure and its electrical properties and shifts the behaviour to soft or hard PZT behaviour, respectively.

Soft PZT is obtained by doping with donors, such as, e.g., $Nb^{5+}$, $La^{3+}$, $Nd^{3+}$, substituting ions of lower valence. Soft PZT offers a higher dielectric permittivity, higher loss tangent, and is easier to polarize.[1] These ceramics are typically used for sensors, high strain actuators, or for electro acoustic applications.[5] Doping with acceptor ions, e.g., $Al^{3+}$, $Ag^{+}$, $Fe^{3+}$, which exhibit a lower valence than the substituted ion, leads to hard PZT ceramics. For charge compensation, oxygen vacancies are formed in the PZT.

However, during powder synthesis or processing there is always a certain degree of undesired change in the composition due to impurities. These impurities can result from the raw materials or from wear during ceramic processing, e.g., abrasion during milling and mixing. Typical wear products are $Al_2O_3$ and $SiO_2$ from alumina components or Fe from steel components.

This study investigates the effect of the impurities Al, Si, and Fe on the microstructure development. From the literature it is known that the doping of pure PZT ceramics with Al leads to a decrease in the grain size and an increase in the density. $Al^{3+}$ is incorporated on the Zr/Ti site. However, in a soft doped PZT, the $Al^{3+}$ enhances the grain size by compensating the donor inhibition effect, which results from the formation of rather immobile donor-vacancy complexes.[6,7] For Si doping, the formation of a glassy phase with PbO is reported, which decreases the sintering density.[8] Therefore, the Si is assumed to stay at the grain boundaries and is not incorporated into the PZT lattice. The Fe doping tends to increase the density and the grain size in soft Nb-doped PZT and exhibits behaviour similar to that of $Al^{3+}$.[9,10] The Fe is also incorporated on the Zr/Ti site as an acceptor ion and can compensate the Nb donor ion.

The aim of this study was to investigate the influence of doping with $Al_2O_3$, $SiO_2$, and $Fe_2O_3$ on the sintering behaviour of a soft PZT ceramic in dependence on the PbO partial pressure of the sintering atmosphere. The difference from former studies is that less than 0.001 mol% (~0.04 Ma.%) of the dopants are mixed into the PZT after the calcination to simulate the introduction of process impurities, e.g., by milling the powder after calcination. The sintering behaviour of the prepared samples was investigated with respect to density, grain size, and mass loss. The latter is an equivalent variable for the PbO loss of the PZT ceramic during sintering. To resolve the complex interactions between the dopants and the microstructure, the design-of-experiment method (DoE) was used. Therefore, it is possible to get simultaneous access to interrelations between the influencing factors and to the effects of the single influencing factors on the response variables. In this study, the influencing factors were the amount of $Al_2O_3$, $SiO_2$, and $Fe_2O_3$, and the PbO partial pressure of the sintering atmosphere. The response variables were the sintering density, mass loss, and grain size. The relations between the dopants and the microstructure properties yielded by the DoE were discussed by considering the micrographs and the phase ratio and were verified with respect to the results from literature.

## II. Experimental Procedure

For the investigation, a commercial soft PZT material with 2 mol% $SrKNbO_3$ and 1.75 mol% PbO excess was used. The material characteristics are similar to the PZT ceramic which was studied by Helke *et al.*[11] and Donelly *et al.*[12] As

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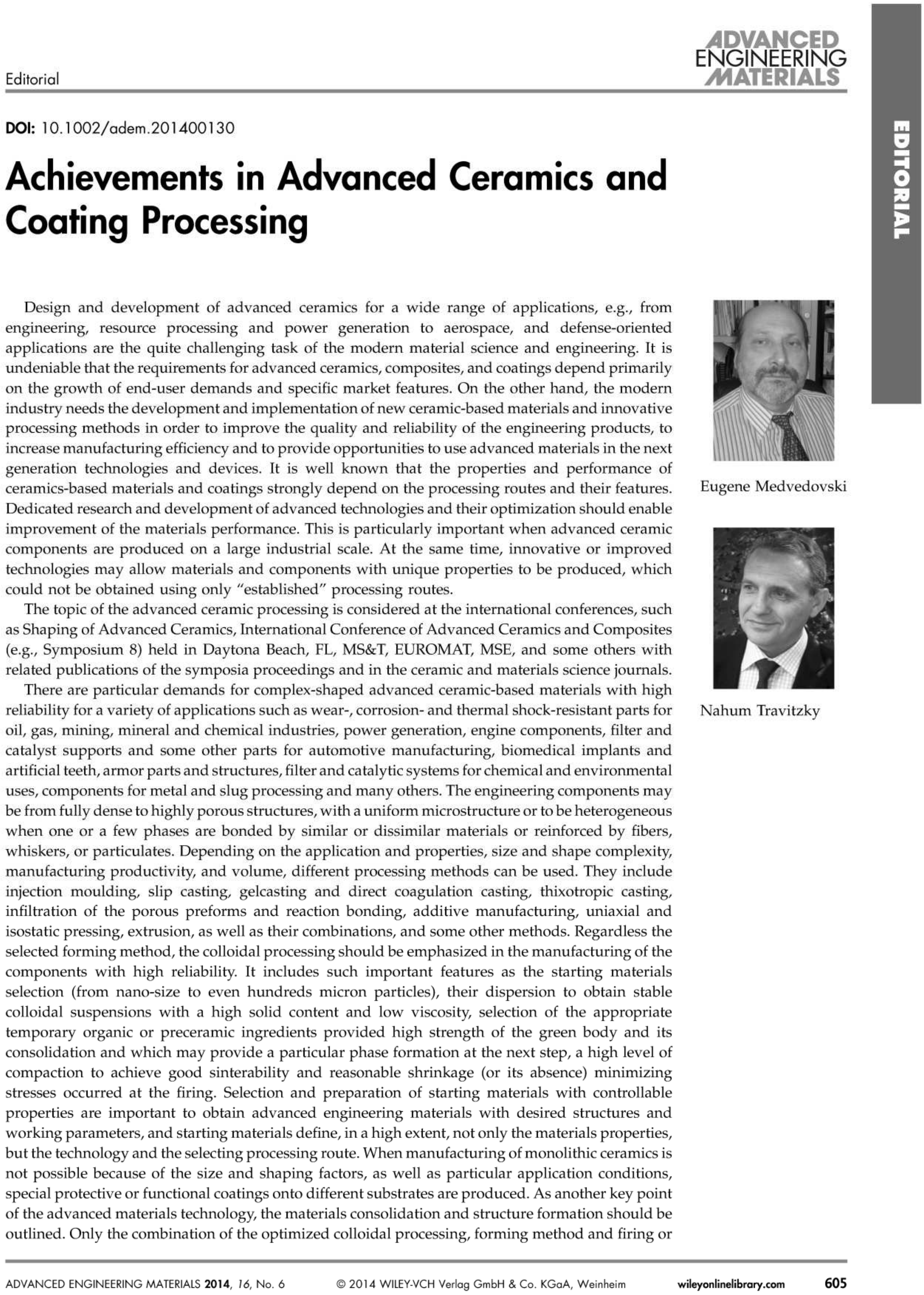

Editorial

ADVANCED ENGINEERING MATERIALS

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# Achievements in Advanced Ceramics and Coating Processing

Eugene Medvedovski

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Design and development of advanced ceramics for a wide range of applications, e.g., from engineering, resource processing and power generation to aerospace, and defense-oriented applications are the quite challenging task of the modern material science and engineering. It is undeniable that the requirements for advanced ceramics, composites, and coatings depend primarily on the growth of end-user demands and specific market features. On the other hand, the modern industry needs the development and implementation of new ceramic-based materials and innovative processing methods in order to improve the quality and reliability of the engineering products, to increase manufacturing efficiency and to provide opportunities to use advanced materials in the next generation technologies and devices. It is well known that the properties and performance of ceramics-based materials and coatings strongly depend on the processing routes and their features. Dedicated research and development of advanced technologies and their optimization should enable improvement of the materials performance. This is particularly important when advanced ceramic components are produced on a large industrial scale. At the same time, innovative or improved technologies may allow materials and components with unique properties to be produced, which could not be obtained using only "established" processing routes.

The topic of the advanced ceramic processing is considered at the international conferences, such as Shaping of Advanced Ceramics, International Conference of Advanced Ceramics and Composites (e.g., Symposium 8) held in Daytona Beach, FL, MS&T, EUROMAT, MSE, and some others with related publications of the symposia proceedings and in the ceramic and materials science journals.

There are particular demands for complex-shaped advanced ceramic-based materials with high reliability for a variety of applications such as wear-, corrosion- and thermal shock-resistant parts for oil, gas, mining, mineral and chemical industries, power generation, engine components, filter and catalyst supports and some other parts for automotive manufacturing, biomedical implants and artificial teeth, armor parts and structures, filter and catalytic systems for chemical and environmental uses, components for metal and slug processing and many others. The engineering components may be from fully dense to highly porous structures, with a uniform microstructure or to be heterogeneous when one or a few phases are bonded by similar or dissimilar materials or reinforced by fibers, whiskers, or particulates. Depending on the application and properties, size and shape complexity, manufacturing productivity, and volume, different processing methods can be used. They include injection moulding, slip casting, gelcasting and direct coagulation casting, thixotropic casting, infiltration of the porous preforms and reaction bonding, additive manufacturing, uniaxial and isostatic pressing, extrusion, as well as their combinations, and some other methods. Regardless the selected forming method, the colloidal processing should be emphasized in the manufacturing of the components with high reliability. It includes such important features as the starting materials selection (from nano-size to even hundreds micron particles), their dispersion to obtain stable colloidal suspensions with a high solid content and low viscosity, selection of the appropriate temporary organic or preceramic ingredients provided high strength of the green body and its consolidation and which may provide a particular phase formation at the next step, a high level of compaction to achieve good sinterability and reasonable shrinkage (or its absence) minimizing stresses occurred at the firing. Selection and preparation of starting materials with controllable properties are important to obtain advanced engineering materials with desired structures and working parameters, and starting materials define, in a high extent, not only the materials properties, but the technology and the selecting processing route. When manufacturing of monolithic ceramics is not possible because of the size and shaping factors, as well as particular application conditions, special protective or functional coatings onto different substrates are produced. As another key point of the advanced materials technology, the materials consolidation and structure formation should be outlined. Only the combination of the optimized colloidal processing, forming method and firing or

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# *In situ* High-Temperature Experiments

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## PREFACE

When Frank Hawthorne (1988) edited the *Reviews in Mineralogy* volume on "Spectroscopic Methods in Mineralogy and Geology," all the experiments presented had been performed at room pressure and room temperature because, at that time, vibrational and X-ray techniques were already quite difficult at ambient conditions so more sophisticated sample environments were not a priority. However, it has now become somewhat easier to perform experiments *in situ* at high temperatures (HT), high pressures (HP) or under combined high temperature and pressure (HP-HT). These types of experiments are becoming routine on crystals, glasses and liquids (see Shen and Wang 2014, this volume).

High-temperature experiments are important because most of the physical properties of high-temperature liquids, such as magmas and melts, are related to their atomic structure. Consequently, it is important to probe the local environment of the atoms in the sample under the conditions noted above (e.g., HT). However, at very high temperatures (~≥ 1200 °C) it is difficult to use conventional furnaces because of a number of experimental difficulties associated with their use: temperature regulation, thermal inertia and spatial obstruction of the sample. Due to the progress made in the development of lasers and X-ray, neutron and magnetic sources it is now possible to perform experiments *in situ* at HT, HP and HT-HP on samples of millimeter or micron size.

## INTRODUCTION

In this chapter, we discuss some of these noncommercial methods used in performing experiments at HT, and outline the best choices for heating systems with regard to the experimental requirements. Different commercial heating systems are available such as the systems available from Linkam® (*http://www.linkam.co.uk/*) or Leica® (*http://www.leica-microsystems.com/*) for example. These two systems are well adapted to performing experiments at HT including

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# Advances in Raman Spectroscopy Applied to Earth and Material Sciences

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## BRIEF HISTORICAL PERSPECTIVE AND SIMPLE THEORY

When monochromatic radiation $\nu_o$, is incident on a system (gas, solid, liquid, glass, whether colored or transparent) most of the radiation is transmitted through the system without change, but some scattering of this radiation can also occur (approximately 1 in $10^7$ photons). The scattered radiation corresponds to $\nu' = \nu_o \pm \nu_m$. In molecular systems, the energy of the scattered light (in wavenumbers, $\nu_m$) is found to lie principally in the range associated with transitions between vibrational, rotational and electronic energy levels. Furthermore, the scattered radiation is generally polarized differently from that of the incident radiation with both scattered intensity and polarization dependent upon the direction of observation.

During the 1920's different physics groups worked on this subject around the world: 1) an Indian group composed of Raman and Krishnan (1928), who made the first observations of the phenomenon in liquids in 1928 (Raman won the Nobel Prize in Physics in 1930 for this work); 2) Landsberg and Mandelstam (1928) in the USSR reported the observation of light scattering with change of frequency in quartz and finally 3) Cabannes and Rocard (1928) in France confirmed the Raman and Krishnan (1928) observations while Rocard (1928) published the first theoretical explanation.

The principle of Raman spectroscopy is the illumination of a material with monochromatic light (laser) in the visible spectral range followed by the interaction of the incident photons with the molecular vibrations or crystal phonons which induces a slight shift in the wavelength of the scattered photons. Scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. If the scattering is elastic and the incident photons have the same energy as the scattered photons, the process is called Rayleigh scattering and this is the dominant scattering interaction. If the scattering is inelastic (the scattered photons have a

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Short Communication

# Oxidative Crack Healing in $Al_2O_3$ Composites Loaded with $Ti_2AC$ (A = Al, Sn) Repair Fillers

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## Abstract

**Crack healing of alumina composites loaded with 5, 10, and 20 vol% $Ti_2AC$ (A = Al or Sn) MAX phase was investigated. Surface cracks were prepared by means of indent loading and the modulus of rupture was measured on virgin, indented, and healed specimens. The MAX phase particles serve as repair filler which reacts with oxygen penetrating along a surface crack and filling disrupted crack surfaces with the oxidation reaction products. After annealing for 3 h composites loaded with 20 vol% $Ti_2AlC$ showed full recovery at a healing temperature of approximately 900 °C, whereas lower temperatures of 700 °C were observed for specimens loaded with 10 and 20 vol% $Ti_2SnC$. The enhanced healing response of $Ti_2AC$-loaded composites containing Sn instead of Al on the A-position offers high potential for providing crack healing capability to ceramic matrix composites applied at moderate temperatures below 1000 °C.**

*Keywords: MAX phase composites, crack healing, repair filler, alumina, oxidation*

## I. Introduction

Engineering ceramics able to repair cracks upon heat treatment have gained increasing attention[1, 2]. Recovery of mechanical properties depleted by overloading, slow crack growth, or thermal shock damage may offer high potential for improving the reliability and prolonging the lifetime of ceramic components subjected to mechanical loading at elevated temperatures. Crack healing behaviour of $Al_2O_3$ was observed at temperatures exceeding 1400 °C where sintering phenomena driven by the reduction of surface energy may trigger perturbation and closure of pores and cracks[3]. Significantly lower healing temperatures $\leq 1200$ °C were achieved by loading $Al_2O_3$ with SiC particles and whiskers that may undergo oxidation in near-surface cracks thereby filling the crack space with $SiO_2$-based oxidation products[4–7]. Different parameters affecting the healing ability were investigated including phase composition, atmosphere, e.g. oxygen partial pressure, crack dimension as well as stress[2]. For example, a 100 µm surface crack prepared in $Al_2O_3$ composites loaded with 20 vol% SiC-whiskers could be completely recovered upon annealing in air at 1200 °C for 1 h[5]. Healing temperatures < 1000 °C, however, require repair fillers with higher reactivity than SiC.

MAX phases are ternary nitrides and carbides, with the general formula $M_{n+1}AX_n$ (n = 1 to 3), where M is a transition metal, A is an A group element, and X is either carbon or nitrogen[8]. Owing to the stronger M-X bonds and weaker M-A bonds associated with the nanolayered nature of the structure, MAX phases possess a unique combination of metal and ceramic properties. For example, they are resistant to oxidation and corrosion, elastically stiff, but at the same time, they also demonstrate high thermal and electrical conductivities and superior machinability[9]. Recent work has shown that MAX phases such as $Ti_3AlC_2$, $Ti_2AlC$ and $Cr_2AlC$ possess an interesting crack healing ability[10–12]. Cracks with a length of 7 mm and a width of 5 µm in $Ti_3AlC_2$ could be fully healed after heat treatment at 1100 °C for 2 h in air. Superior healing capability observed on $Ti_2AlC$ and $Cr_2AlC$ ceramics was attributed to the formation of adhesive $Al_2O_3$ filling the space between the disrupted crack surfaces. Furthermore, repeatable crack healing was demonstrated on $Ti_2AlC$, indicating that MAX phases offer a multiple crack-healing ability.

We have reported on the oxidation behaviour of $Ti_2Al_{(1-x)}Sn_xC$ MAX phases solid solution[13]. It was found that for a reasonable healing period of a few hours the oxidation temperature of A elements decreased from $Ti_2AlC$ to $Ti_2SnC$ from 900 °C to 460 °C. Accelerated crack healing was attributed to the higher mobility of Sn compared to Al (or Si) on the A position in the $Ti_2AC$ crystal structure, which may be favourable to promote crack healing at lower temperatures. Furthermore, MAX phase particles may serve as repair filler providing crack healing capability when dispersed in a ceramic matrix composite. It is the aim of the present work to explore oxidation-induced crack healing behaviour of $Al_2O_3$ composite loaded with $Ti_2AlC$ or $Ti_2SnC$, respectively. Composite specimens with various repair filler loading from 5, 10, and 20 vol% were prepared. Strength recovery of specimens containing indent surface cracks was analyzed for different healing temperatures.

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# Morphological zeta-potential variation of nanoporous anodic alumina layers and cell adherence

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## ABSTRACT

Nanoscale surface modification of biomedical implant materials offers enhanced biological activity concerning protein adsorption and cell adherence. Nanoporous anodic alumina oxide (AAO) layers were prepared by electrochemical oxidation of thin Al-seed layers in 0.22 M $C_2H_2O_4$, applying anodization voltages of 20–60 V. The AAO layers are characterized by a mean pore diameter varying from 15 to 40 nm, a mean pore distance of 40–130 nm, a total porosity of ~10% and a thickness of 560 ± 40 nm. Zeta potential and isoelectric point (iep) were derived from streaming potential measurements and correlated to the topology variation of the nanoporous AAO layers. With decreasing pore diameter a shift of iep from ~7.9 (pore diameter 40 nm) to ~6.7 (pore diameter 15 nm) was observed. Plain alumina layers, however, possess an iep of ~9. Compared to the plain alumina surface an enhanced adherence and activity of hFOB cells was observed on the nanoporous AAO after 24 h culture with a maximum at a pore size of 40 nm. The topology-induced change of the electrochemical surface state may have a strong impact on protein adsorption as well as on cell adhesion, which offers a high potential for the development of bioactive AAO coatings on various biomaterial substrates.

## 1. Introduction

Bioceramics applied to bone replacement and regeneration should trigger minimal inflammatory responses while stimulating osteoblast adhesion, proliferation and differentiation [1]. It has long been known that substrate topography, including grooves, ridges, islands, nodes and pores, can affect cell response and osseointegration behavior of a bioceramic implant in contact with bone [2]. Interaction with nanotopographies can alter cell morphology, adhesion, motility, proliferation, endocytotic activity, protein abundance and gene regulation [3,4]. Among diverse cell types (fibroblasts, osteoclasts, endothelial, smooth muscle, epithelial) osteoblasts were observed to interact with nanotopographical features of substrate materials [5].

Nanoporous $Al_2O_3$ surfaces offer a high potential for a load-bearing implant in contact with bone due to excellent chemical and mechanical stability as well as biocompatibility [6,7]. The topology of nanoporous alumina can be easily controlled by changing the pore diameter, shape, periodicity and density by applying anodic oxidation of an Al-seed layer in a variety of polyprotic acids at voltages ranging from 10 to 200 V [8,9]. Anodic alumina oxide (AAO) is subtly different from conventional alumina in that it has a regular self-organized porous nanostructure with pores orthogonal to the surface and pore diameters ranging from 5 nm to 10 μm [10]. Previous work on the biomedical application of AAO mainly referred to AAO membrane structures serving as a tissue engineering scaffold for cultivating different types of human cells (hepatoma, osteoblasts, epithelium), as an immune-isolation for cell carrier devices, as a sensor array for cellular diagnostics as well as for immobilizing enzymes [11]. AAO surface coatings, however, may offer further potential for improving the interface bonding of load-bearing implants to bone [12] and for enhancing osseointegration [13]. Favorable osteoblast adhesion was observed on AAO membranes fabricated using a two-step anodization process in phosphoric acid with a pore size ranging from 30 to 80 nm [6,14]. Nanotopography with pores ranging from 20 to 200 nm was reported to affect monocyte/macrophage behavior with the 20 nm pores, resulting in a reduced pro-inflammatory response compared to the large pore surface [15]. Furthermore, nanoporous alumina surfaces were modified by physically absorbing vibronectin protein and covalently immobilizing the arginine–glycine–aspartic amino-acid sequence (RGD) peptide to enhance adhesion of bone-forming osteoblast cells [14].

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# Influence of calendering on the properties of paper-derived alumina ceramics

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## Abstract

The effect of calendering of alumina loaded preceramic papers in a hard nip laboratory calender at various temperatures, line loads and times of nip passes on their green and sintered properties was investigated. The main objective was to achieve a maximum densification, which resulted in a maximum reduction of thickness of 45%, a green density of 80.5% of the theoretical density and a sintered density of 81% of the theoretical density. The ring-on-ring flexural strength of sintered specimen could be increased from 71 ± 11 MPa to 138 ± 33 MPa. The surface roughness of green samples could be diminished to a value for $R_a$ of below 2 μm compared to an $R_a$ of 13.2 μm for an uncalendered paper, whereas the $R_a$ value of the sintered samples was much higher due to the burn-off of the cellulose fibers. Preceramic papers manufactured by the dynamic hand-sheet-forming process exhibit a fiber-orientation which causes anisotropic effects regarding the sintering shrinkage, the surface roughness and Young's modulus.

*Keywords:* B: Porosity; B: Surfaces; C: Mechanical properties; Preceramic paper

## 1. Introduction

Commonly available shaping techniques for ceramic structures such as pressing, tape-casting, injection molding or extrusion techniques can be used to create complex light-weight structures. However, these techniques are costly and have a low throughput compared to papermaking machines. Preceramic papers offer a new view on the shaping of ceramic lightweight structures. They exhibit the shapeability and cost-efficiency and production output of common paper while still maintaining the ability to create complex structures with unique properties. Preceramic papers differ considerably from common paper products. Travitzky et al. [1] stated that preceramic papers have to be loaded with at least 75–90 wt% of ceramic powder while common printing and writing papers contain 20–30 wt% of inorganic fillers such as kaolin, alumina or titania. The increased filler content of preceramic papers ensures the successful conversion from preceramic paper to ceramic components, as dense particle-packing is necessary. It has been shown that preceramic papers can be converted into the ceramic state via adapted thermal treatment. Preceramic paper is a fiber enhanced composite material whose properties are significantly defined by the filler that is used. The manufacture of preceramic paper can be performed on commonly used paper machines. The process can be described as a three-stage-process and involves:

a. Preparation of an aqueous suspension containing ceramic powder and pulp at a fixed ratio.
b. Coagulation and flocculation of filler and pulp within the suspension by means of adding organic additives which alter surface charges and interconnect the suspended solids.
c. Formation of paper sheet by dewatering (filtration), followed by wet pressing and drying.

Paper properties such as bending stiffness, porosity and pore size distribution, density and smoothness are heavily influenced by the filler grade, the particle size of the filler and the type of cellulosic fibers that are used.

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# Multiphase ceramic composites derived by reaction of Nb and SiCN precursor

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**Abstract**

In this work multiphase Nb(C,N)/$Nb_5Si_3$ ceramic composites containing niobium silicide, nitride and carbide phases were designed by using the polymer derived ceramic (PDC) route to avoid the complicated shaping of refractory metal compounds. Starting from polycarbosilazane (PCSZ) precursor powder and metallic niobium as reactive filler green compacts were manufactured by uniaxial warm pressing and stabilized by subsequent crosslinking. Due to the reactivity of both the Nb and the rearrangements within the forming amorphous SiCN phase a porous ceramic material is generated via solid-state reaction during thermal treatment. Depending on the amount of PCSZ as well as on the pyrolysis conditions the particles within this network reveal a core/rim structure containing submicron-sized $Nb_2CN$, NbC as well as coarse-grained $Nb_2N$ phases in the core and $Nb_5Si_3$ or alternatively metastable $Nb_5Si_4C$ phase at the particle surface.

*Keywords:* Refractory metal; Precursor; Ceramic composite; Solid-state reaction

## 1. Introduction

Refractory metal based composites containing ultrahigh temperature stable carbide, nitride and silicide phases have gained attention in the last years because they seem to be potential candidates for structural components or matrix materials for high temperature (HT) or ultrahigh temperature (UHT) applications [1–3]. Thereby, much attention is paid on advanced intermetallics or silicide based composites because these materials provide high strength and melting points in combination with improved oxidation stability at temperatures exceeding 1000 °C [3,4]. In addition, binary niobium silicide phases like $Nb_5Si_3$ show very good creep behavior at high temperatures [5,6]. Furthermore, mechanical properties of ceramic composites can be improved by adding binary niobium nitride or carbide phases due to their remarkable properties like very high hardness, high stiffness and strength as well as a comparatively low density (7–8 g/cm$^3$) [7,8].

Because of the high melting points of refractory metal carbides, nitrides and silicides there is a need for processes like self-combustion high temperature synthesis (SHS), spark plasma sintering (SPS) or reactive hot pressing (RHP) [9–13] to manufacture bulk composites. In the past alternative processing routes were developed to simplify manufacturing of ceramics using the route of polymer derived ceramics (PDC) to generate bulk ceramic materials or coatings [14–19]. Based on the high reactivity of the used oxide or non-oxide precursors and refractory metals, ceramic composites were in situ generated containing refractory metal carbide, nitride, oxide and silicide phases. Furthermore, the PDC route provides the possibilities for a complex shaping and to form a ceramic binder phase which benefits the consolidation [20].

For niobium based ceramic composites derived from active and passive filled polysiloxane precursors (Si–C–O) a lot of work has been published already [7,21–23] whereas for composites based on non-oxide precursor systems like poly(carbo)silazanes (Si–(C)–N) only few work was done in the recent years [15,24].

The focus of this work is to design a multiphase Nb(C,N)/$Nb_5Si_3$ composite material derived by powder

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# Induction of bone formation in biphasic calcium phosphate scaffolds by bone morphogenetic protein-2 and primary osteoblasts

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## Abstract

Bone tissue engineering strategies mainly depend on porous scaffold materials. In this study, novel biphasic calcium phosphate (BCP) matrices were generated by 3D-printing. High porosity was achieved by starch consolidation. This study aimed to characterise the porous BCP-scaffold properties and interactions of osteogenic cells and growth factors under *in vivo* conditions. Five differently treated constructs were implanted subcutaneously in syngeneic rats: plain BCP constructs (group A), constructs pre-treated with BMP-2 (group B; 1.6 μg BMP-2 per scaffold), seeded with primary osteoblasts (OB) (group C), seeded with OB and BMP-2 (group D) and constructs seeded with OB and pre-cultivated in a flow bioreactor for 6 weeks (group E). After 2, 4 and 6 weeks, specimens were explanted and subjected to histological and molecular biological analyses. Explanted scaffolds were invaded by fibrovascular tissue without significant foreign body reactions. Morphometric analysis demonstrated significantly increased bone formation in samples from group D (OB + BMP-2) compared to all other groups. Samples from groups B-E displayed significant mRNA expression of bone-specific genes after 6 weeks. Pre-cultivation in the flow bioreactor (group E) induced bone formation comparable with group B. In this study, differences in bone distribution between samples with BMP-2 or osteoblasts could be observed. In conclusion, combination of osteoblasts and BMP-2 synergistically enhanced bone formation in novel ceramic scaffolds. These results provide the basis for further experiments in orthotopic defect models with a focus on future applications in orthopaedic and reconstructive surgery. Copyright © 2012 John Wiley & Sons, Ltd.

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**Keywords** **biphasic calcium phosphate; bioreactor; BMP-2; bone morphogenetic protein; flow perfusion; osteoblasts; scaffolds**

## 1. Introduction

Since the late 1980s, tissue engineering has been one of the key technologies in regenerative medicine. With regard to bone tissue, an approach based on a patient's own cells, suitable growth factors and 3D scaffolds has been proposed (Bruder and Fox, 1999; Pneumaticos *et al*., 2010). For this purpose, scaffolds were used as carriers for cells and growth factors. Scaffold material properties and porosity must allow cell adhesion, migration, proliferation and differentiation.

Biphasic calcium phosphate (BCP) ceramics consist of a mixture of hydroxyapatite (HA) and beta-tricalcium phosphate (β-TCP). HA and β-TCP play an important role in hard tissue repair because of their similarity to the minerals in human bone and their outstanding bioactivity (Pilliar *et al*., 2001; Eyckmans *et al*. 2010). Combining the reactivity of β-TCP and the stability of HA enhances bioactivity with retained degradability (Hutmacher *et al*., 2007). To realise complex and controllable internal structures, 3D-printing as a manufacturing technique is widely used in biomaterial fabrication (Seitz *et al*., 2005).

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ADVANCED ENGINEERING MATERIALS

**DOI:** 10.1002/adem.201400097

# Additive Manufacturing of Ceramic-Based Materials**

By *Nahum Travitzky,* Alexander Bonet, Benjamin Dermeik, Tobias Fey, Ina Filbert-Demut, Lorenz Schlier, Tobias Schlordt* and *Peter Greil*

*This paper offers a review of present achievements in the field of processing of ceramic-based materials with complex geometry using the main additive manufacturing (AM) technologies. In AM, the geometrical design of a desired ceramic-based component is combined with the materials design. In this way, the fabrication times and the product costs of ceramic-based parts with required properties can be substantially reduced. However, dimensional accuracy and surface finish still remain crucial features in today's AM due to the layer-by-layer formation of the parts. In spite of the fact that significant progress has been made in the development of feedstock materials, the most difficult limitations for AM technologies are the restrictions set by material selection for each AM method and aspects considering the inner architectural design of the manufactured parts. Hence, any future progress in the field of AM should be based on the improvement of the existing technologies or, alternatively, the development of new approaches with an emphasis on parts allowing the near-net formation of ceramic structures, while optimizing the design of new materials and of the part architecture.*

## 1. Introduction

The design and development of advanced ceramics for high-performance applications ranging from automotive to aerospace, defense-oriented, energy, environmental, and biomedical applications is one of the most challenging tasks of modern engineering. Examples of current and future applications of advanced ceramics are given in Ref.[1] The need for advanced ceramics primarily depends on the growth of end-use markets. On the other hand, technological innovations have continuously contributed to performance and productivity improvements, which have stimulated the expansion of the use of advanced ceramics in key sectors.[1] It is an incontrovertible fact that the wide industrial use of advanced ceramic materials depends on the technological availability to fabricate near-net-shaped three-dimensional ceramic-based parts with the required geometry. The latter is of great importance because the post-hard machining of ceramics is time-consuming and an expensive process that generally requires diamond tools. Thus, in many cases, it incurs up to 80% of the overall manufacturing costs of a ceramic product.[2] In addition, since for small-scale manufacturing and prototyping the expenses for models and molds are crucial factors in the production costs, it is difficult to implement new designs quickly in test parts. The inability of current technology-related methods to produce complex-shaped ceramic-based parts with the desired compositions, microstructures and properties directly from computer aided design (CAD) files or data obtained using reverse engineering methods including scanners and computer tomographs (CT or μ-CT) without hard tooling, dies or molds has led to novel techniques such as additive (generative) manufacturing (AM), solid freeforming (SFF), rapid prototyping (RP), rapid manufacturing (RM), rapid tooling (RT), layer manufacturing (LM), and direct digital manufacturing (DDM) that are becoming increasingly more

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# $Ti_3Si(Al)C_2$-based ceramics fabricated by reactive melt infiltration with $Al_{70}Si_{30}$ alloy

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**Abstract**

Dense $Ti_3Si(Al)C_2$-based ceramics were synthesized using reactive melt infiltration (RMI) of $Al_{70}Si_{30}$ alloy into the porous TiC preforms. The effects of the infiltration temperature on the microstructure and mechanical properties of the synthesized composites were investigated. All the composites infiltrated at different temperatures were composed of $Ti_3Si(Al)C_2$, TiC, SiC, Ti(Al, Si)$_3$ and Al. With the increase of infiltration temperature from 1050 °C to 1500 °C, the $Ti_3Si(Al)C_2$ content increased to 52 vol.% and the TiC content decreased to 15 vol.%, and the Vickers hardness, flexural strength and fracture toughness of $Ti_3Si(Al)C_2$-based composite reached to 9.95 GPa, 328 MPa and 4.8 MPa m$^{1/2}$, respectively.

*Keywords:* Reactive melt infiltration; Al-Si alloy; $Ti_3Si(Al)C_2$

## 1. Introduction

$Ti_3SiC_2$, as one of the nanolaminated ternary carbides called as MAX phases,[1] has been extensively studied due to the combined properties of metal and ceramic, such as high melting point, low density (4.53 g/cm$^3$), low hardness (Vickers hardness of 4 GPa), excellent thermal shock resistance, and high strength (flexural strength of 475 MPa).[2,3] Therefore it shows a great application prospect to be used as high temperature structural material. In recent years, many methods have been developed to further improve the properties of $Ti_3SiC_2$. On one hand, multiphase $Ti_3SiC_2$-based composites incorporated with hard materials such as TiC and SiC have been fabricated to improve its mechanical properties.[4–6] On the other hand, some studies demonstrate that $Ti_3Si(Al)C_2$, in which a part of Si atoms of $Ti_3SiC_2$ are substituted by Al atoms, possesses similar mechanical properties with $Ti_3SiC_2$, but exhibits a better oxidation resistance than $Ti_3SiC_2$.[7–9] $TiAl_3$ possesses attractive characteristics, such as low density, high modulus, good oxidation resistance and high melting point,[10,11] Combining $TiAl_3$ with tough ceramic such as MAX phases is considered as a necessary method to get improved mechanical properties.[12] In consideration of these methods, a composite composed of $Ti_3Si(Al)C_2$, SiC, TiC and $TiAl_3$ may possess high mechanical properties and good oxidation resistance.

Reactive melt infiltration (RMI) is an effective way to fabricate bulk materials with near-net-shape manufacturing,[13,14] and also can be applied to prepare bulk MAX phases.[15–21] During RMI process molten metal infiltrates and reacts with porous preform, leading to the formation of bulk materials. Shan et al. synthesized $Ti_3SiC_2$ bulk material by infiltrating molten Si into porous TiC/Ti precursor.[15] Hwang et al. fabricated high-purity $Ti_3SiC_2$ by infiltrating molten Si into $TiC_x$ preform.[16] In our previous work, based on a joint process of three-dimensional printing (3DP) and RMI, $Ti_3SiC_2$-based composites were fabricated by reactive infiltration of molten Si into TiC preform,[17] and $Ti_3AlC_2$-$TiAl_3$-$Al_2O_3$ composites were synthesized by reactive infiltration of molten Al into TiC/$TiO_2$ preform.[18,19] Up to now, however, no report on the fabrication of $Ti_3Si(Al)C_2$-based ceramic by RMI was found. The previous results demonstrated that Si melt reacted with TiC to form $Ti_3SiC_2$-TiC-SiC composites,[17] and the addition of Al promoted the formation of $Ti_3SiC_2$ by reducing the twin boundary energy of TiC.[22–25] Therefore, it can be supposed that $Ti_3Si(Al)C_2$-based composites can be fabricated by infiltration of TiC preform with molten Al-Si alloy.

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# Preparation and mechanical properties of *in situ* $TiC_x$–Ni (Si, Ti) alloy composites

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ABSTRACT

Novel in situ $TiC_x$ reinforced Ni (Si, Ti) alloy composites with superior mechanical properties were prepared at 1250 °C for 30 min by pressureless sintering $Ti_3SiC_2$ (10 and 20 vol%) and Ni as precursors. The $Ti_3SiC_2$ particles decomposed into substoichiometric $TiC_x$ phase, while the additional Si and partial Ti atoms derived from $Ti_3SiC_2$ diffused into Ni matrix to form Ni (Si, Ti) alloy. The *in situ* formed $TiC_x$ phases are mainly dispersed on the grain boundaries of the Ni (Si, Ti) alloying, forming a strong skeleton and refining the microstructures of the metal matrix. The hardness, the yield stress $\sigma_{0.2\%}$ and ultimate compressive strength of 20.6 vol%$TiC_x$–Ni(Si, Ti) composite can reach 2.15 ± 0.04 GPa, 466.8 ± 55.8 MPa and 733.3 ± 78.4 MPa, respectively. The enhanced mechanical properties of $TiC_x$–Ni(Si, Ti) composites are due to the *in situ* formation of $TiC_x$ skeleton, the refined microstructures of Ni (Si, Ti) alloys and solid solution effects as well as good wettability between $TiC_x$ and Ni (Si, Ti) matrix.

## 1. Introduction

Particulate reinforced Metal Matrix Composites (MMCs) have gained considerable attention recently. MMCs combine metallic properties (ductility and toughness) with ceramic properties (high strength and modulus) leading to greater strength in shear and compression and higher service temperature [1–4]. Interest in MMCs for aerospace, automotive and other structural applications has increased in the past few decades. Metals such as Al, Mg, Cu, Ni or based alloys were often selected as the matrix, and the reinforcement materials for the MMCs include carbides (e.g., SiC, TiC), nitrides (e.g., $Si_3N_4$, AlN), oxides (e.g., $Al_2O_3$, $SiO_2$) as well as elemental materials (e.g., C, Si) [1–4].

As one of the typical reinforcements, TiC was widely used in Ni-based MMCs because of its high hardness (32 GPa), high melting point (3147 °C), high modulus and low density (4.95 g/cm$^3$) [1]. Loading TiC particles into the nickel alloy matrix can remarkably improve the properties of the alloy. In order to produce fine and thermodynamic stable reinforcement with improved interfacial characteristics, *in situ* formation of TiC in Ni matrix was extensively investigated [5–8]. Among those *in situ* techniques, Self-propagating High-temperature Synthesis (SHS) techniques combined with various densification techniques were applied to fabricate dense TiC reinforced Ni composites. For example, fully dense TiC–Ni cermets could be obtained by combustion synthesis coupled with impact forging [5]. Large scale TiC–Ni cermets were prepared by means of SHS/PHIP methods [7]. Previous studies on *in situ* reaction formed TiC–Ni composites have concentrated on the high content of carbides ranging from 40 to 90 wt%. There is limited work on the fabrication of the TiC–Ni cermets with lower content of TiC by *in situ* technology.

MAX phases are a group of ternary compounds with a general formula $M_{n+1}AX_n$ ($n = 1–3$), where M is a transition metal, A is an A group element (from IIIA to VIA), and X is either carbon or nitrogen [9]. MAX phases are distinguished by a set of remarkable properties which derive from their nanolayered structure through the strong covalent M–X bonds which are interleaved with A layers through weak M–A bonds. Because of this unique structure, they exhibit lower Vickers hardness and stiffness at room temperature, high strength at high temperatures, good resistance to thermal shock and oxidation, high thermal and electrical conductivities and they are lightweight and easily machinable [9–12]. Such unique properties make them interesting candidates to be used as structural components for high-temperature applications, oxidation-resistant coatings on alloy surfaces, conducting ceramic in harsh environments, and reinforcement for soft metals in MMCs [13–16]. Indeed, the incorporation of $Ti_3SiC_2$ or $Ti_3AlC_2$ into Cu metal matrix was demonstrated to increase strength and modulus

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ORIGINAL CONTRIBUTION

# Gelation of polyvinylbutyral solutions by the addition of tetrabutyl orthotitanate

**Moritz Wegener · Joachim Kaschta ·**
**Helmut Münstedt · Andreas Roosen**

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**Abstract** This paper discusses the gelation of polyvinylbutyral (PVB) solutions by the addition of tetrabutyl orthotitanate. The addition of around 0.10 vol.% tetrabutyl orthotitanate to an ethanol-based PVB solution already causes a pronounced gelation. For the characterization of this gelation reaction, different rheological measurements are used. The characterization is mainly performed in the linear viscoelastic regime. Time sweeps prove the stability of the samples during the measuring time. Frequency sweeps are used to investigate the state of gelation after different reaction times as well as the dependence of the degree of the gelation on the tetrabutyl orthotitanate concentration. Furthermore, the gelation point is determined by measuring the loss factor tan $\delta$ as a function of frequency. A strong influence of water on the degree of gelation is shown; by the addition of different amounts of water, the gelation can be controlled or even avoided. Amplitude sweeps reveal the breakdown of certain network structures at high amplitudes which recover after the strain is lowered.

**Keywords** Polyvinylbutyral (PVB) · Gelation with titanate · Dynamic mechanical analysis (DMA) · Network characterization · Gel point

## Introduction

The sol-gel process is a low-cost process for the manufacture of high-purity oxide materials with a wide variety of shapes (Chen and Kumar 2012; Meulenkamp 1998); typically, a precursor sol is converted by a post treatment into a crystalline material (Macwan et al. 2011; Periyat et al. 2011; Hafizah and Sopyan 2009).

Mostly, metal-organic molecules are used to build up gels via condensation processes and to synthesize nanoparticles (Zou et al. 2008; Burda et al. 2005; Cushing et al. 2004). Tailored organic/inorganic hybrid materials can also be obtained by the sol-gel processing route (Huang 1985, 1987; Wen and Wilkes 1996; Schubert et al. 1995; Schottner 2001; Sanchez et al. 2005). Titania is intensively used as an inorganic component in such hybrid materials, e.g., in polytetramethylene oxide/titania (Glaser and Wilkes 1989; Wang and Wilkes 1991; Brennan et al. 1991), cellulose acetate/titania (Kurokawa et al. 1994; Hatayama et al. 1996), or poly(*n*-butyl methacrylate)/titania hybrids (Mauritz and Jones 1990). Nakane et al. (1999) published a paper about the system polyvinylbutyral (PVB) and titania; they produced a $TiO_2$ sol and mixed the sol with PVB solutions to obtain PVB/titania composites after drying. They observed a gelation of the PVB/titania solution, but comprehensive investigations and deeper discussions about the gelation effect of PVB by the addition of titania were not presented. This paper focuses on the gelation of PVB solutions by the addition of tetrabutyl orthotitanate and not by the addition of titania sols. Furthermore, intensive characterizations of the rheological behavior of the gels were performed. The aims of this paper are to contribute to a better understanding of the gelation effect of PVB solutions by the addition of tetrabutyl orthotitanate and to find measures to control this behavior.

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# Electromagnetic properties of Si–C–N based ceramics and composites

**Xiaowei Yin***[1], **Luo Kong**[1], **Litong Zhang**[1], **Laifei Cheng**[1], **Nahum Travitzky**[2] **and Peter Greil**[2]

Besides the excellent high-temperature mechanical properties, $Si_3N_4$ and SiC based ceramics containing insulating or electrically conductive phase are attractive for their tunable dielectric properties, which may vary from electromagnetic (EM) wave transparent to absorption and shielding. Consequently, SiC, $Si_3N_4$, SiON, SiBN, SiBC, SiCN and SiBCN ceramics have attracted extensive interest in recent years. $SiO_2$, $Si_3N_4$, $Si_3N_4$–$SiO_2$, $Si_3N_4$–BN, and $Si_3N_4$–$SiO_2$–BN are promising EM wave transparent materials for applications in microelectronic packaging, microwave transparent reaction chamber, radome and antenna window. C, SiC, SiC–C, $Si_3N_4$–C and $Si_3N_4$–SiC are potential EM wave shielding materials, which can be used as electronic packaging of highly integrated circuits, and be used in wireless communication system, telecommunication base stations and the other electronic devices. $Si_3N_4$–SiBC, $Si_3N_4$–SiCN and $Si_3N_4$–SiBCN are attractive EM wave absorbing materials for potential applications in amplifier, accelerator, microwave heating, anechoic chambers, stealth aircraft and ship. Other potential harsh environment or high-temperature applications will also benefit from the Si–C–N ceramic system. The concept of hybrid structure and EM metamaterials (MMS) opens up new avenues in developing EM wave absorption materials. The key developments and future challenges in this field are summarised. The main issues regarding permittivity of high-temperature structural ceramics are discussed, with an emphasis on the EM wave transparent, shielding and absorbing mechanisms that are responsible for the EM wave properties.

**Keywords:** Ceramic matrix composites, Porous ceramics, Polymer-derived ceramics (PDC), Chemical vapour infiltration (CVI), Dielectric properties, Microwave absorbing, Electromagnetic interference (EMI) shielding, Electromagnetic wave transmission

## Introduction

High frequency electromagnetic (EM) wave with wavelength varying from $2{\cdot}4\times10^{-2}$ to $3{\cdot}7\times10^{-2}$ m is used in various environments, especially for critical electronic equipments in wireless communication, medical and aerospace applications, which require EM transparent materials as well as EM shielding and absorbing dielectric materials. These applications include Doppler, weather radar, TV transmission, and telephone microwave relay systems, which work at gigahertz frequencies.[1–6] The commercial wireless communication band was relatively at the early stage of gigahertz range, but the frequency band of newly developed commercial devices has been increased to tens of gigahertz. Therefore, the target frequency range of the above applications is set as 8·2–12·4 GHz (*X*-band). Recently, EM absorbing properties of magnetic materials, nanomaterials and metamaterials (MMs) have been summarised by Kong *et al.*[7] EM absorption properties in polymer composites filled with carbonaceous particles have been reviewed by Brosseau *et al.*[8] Si–B–C–N ceramic has attracted wide attention due to its excellent structural stability, oxidation resistance, creep resistance and high-temperature mechanical properties, etc. The preparation method, microstructure, mechanical, electrical, and optical properties, oxidation resistance, and potential application of Si–B–C–N ceramic have been summarised by Jia *et al.*[9] The present review will focus on the recent progress in EM properties of Si–C–N based ceramics and composites, which are non-magnetic and thermostructural materials.

When EM wave is incident on a material surface, it experiences three processes: reflection, absorption and transmission, obeying the laws of optics, Fig. 1. When EM wave is incident on the surface of a non-magnetic dielectric material, the electric field induces two different electrical currents within the material, i.e. the conduction and displacement currents, respectively. In dielectric materials, most of the charge carriers are bound and cannot

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# 3. TEACHING

The Department of Materials Science and Engineering offers Bachelor and Master programmes in Materials Science and Engineering and in Nanotechnology.

The Bachelor course is a three years programme (six semesters) which qualifies for the Master programme (four semesters). The curriculum consists of the "*Grundstudium*" (basic studies) during the first 2 years, devoted to the fundamental scientific education. It introduces the student very early into materials science and engineering concepts by offering courses on materials structures, properties, thermodynamics, kinetics, chemistry, processing, product manufacturing, analysis and testing as well as practical training. Examinations follow immediately after each semester.

The subsequent advanced programme in the 5th and 6th semester broadly deepens the entire field of materials science and engineering. Courses on economics, management and other soft skills are obligatory. This period ends with a Bachelor Thesis of nine weeks duration. Additionally, the student has to perform an industrial internship of 12 weeks.

The Master programme in the 7th, 8th and 9th semester specializes in a selected "*Kernfach*" (core discipline), including corresponding practical courses, seminars and courses in materials computational simulation. In addition the students select a *“Nebenfach”* (minor subject) from the Department of Materials Science and a *“Wahlfach”* (elective subject) from other Departments of the University, which offers the possibility of specialization. Finally, the programme is completed by a Master Thesis of six month duration.

In addition to this Materials Science and Engineering programme, the Institute of Glass and Ceramics is involved in the Bachelor and Master programmes “Energy Technology”, “Medical Technology” and the Elite course “Advanced Materials and Processes”.

## a. Courses

(L) = lecture, (E) = exercise

### 1st Semester

- Introduction to Inorganic Non-metallic Materials (L); P. Greil

*Students enjoying an experiment with a superconducting ceramic (P. Greil, Introduction to Inorganic Non-metallic Materials, 1<sup>st</sup> semester)*

- Materials Science I (MB) (L); N. Travitzky

### 2nd Semester

- Materials Science (CBI and CEN) (L); T. Fey
- Materials Science II (MB); A. Roosen

### 4th Semester

- Materials Characterization and Testing (L); A. Roosen
- Basics in Programming (L/E); T. Fey, E. Bitzek

## 5th Semester

- Glass and Ceramics (L); A. Roosen, D. de Ligny
- Instrumental Analytics (L); U. Deisinger
- Nanocomposites (L/E); T. Fey

## 7th to 9th Semester

- Physics and Chemistry of Glasses and Ceramics I: Thermodynamics of Condensed Systems (L); P. Greil
- Physics and Chemistry of Glasses and Ceramics II: Physicochemical Principles of Non-Crystalline Materials (L); D. de Ligny

- Structure and Properties of Glasses and Ceramics I: Electrical and Magnetic Properties (L); A. Roosen
- Structure and Properties of Glasses and Ceramics II: Optical Properties (L); D. de Ligny
- Structure and Properties of Glasses and Ceramics III: High Temperature Properties (L); P. Greil
- Structure and Properties of Glasses and Ceramic IV: Mechanoceramics (L); P. Greil

- Functional Ceramics: Processing and Applications (L); A. Roosen
- Glasses and Ceramics for Energy Technology, (L); D. de Ligny
- Glass Ceramics (L); D. de Ligny
- Glass Formulation (L); D. de Ligny
- Vibrational and Optical Spectroscopy of Glasses and Ceramics (L); D. de Ligny
- Biomimetic Materials and Processes (L); S.E. Wolf
- Ceramic Materials in Medicine (L); S.E. Wolf
- Innovative Processing Techniques for Advanced Ceramic Materials (L); N. Travitzy
- Silicate Ceramics (L); N. Travitzky
- Powder Synthesis and Processing (L); U. Deisinger
- Stresses and Mechanical Strength (L/E); T. Fey
- Computational Calculation of Crack Probabilities (E); T. Fey
- Non-Destructive Testing (E); T. Fey
- Mechanical Testing Methods (E); T. Fey

# b. Graduates

## Bachelor Thesis

**Michael Bergler**

Effect of fictive temperature on titanosilicates

**Jonas Biggermann**

Ceramic foams from alkali niobates

**Florens Bach**

Preparation and properties of 3D printed $Ti_3AlC_2$

**Benedikt Diepold**

Generating 3D structures of ceramic buildings blocks by using the pick and placer

**Udo Eckstein**

The drying behaviour of ceramic films

**Theresa Eder**

Manufacturing of piezoelectric micro-grids

**Julia Carolin Groppweis**

Manufacturing of wound multilayer structures based on preceramic papers

**Florian Holzheimer**

Optimization of the adhesive system for laminating preceramic, paper-derived ceramics

**Christoph Hutzler**

Optimization of the cold low-pressure lamination process for joining of LTCC green sheets and sintered $Al_2O_3$ substrates

**Felix Kalkowski**

Prince Rupert’s drops: Looking at the stress field using Raman spectroscopy

**Björn Kleemann**

Manufacturing of ceramic MAX phase foams

**Simone Kellermann**

Piezoelectric hybrid materials

**Moritz Knorr**

Cellular ceramic $BaTiO_3$ foams

**Andreas Kastner**

Manufacturing of ceramic laminates based preceramic paper

**Georg Lechner**

Vibration-controlled generation of 3D structures from ceramic building blocks

**Georg Menge**

Sintering properties of doped $LaCrO_3$ ceramics

**Paul-Erich Öchsner**

Production of thermal shock resistant multi-layer structures by deliberate generation of residual stresses

**Carsten Polzer**

Coating of carbon nanotubes on heterogeneous SiC surfaces with optically active nanoparticles

**Kevin Rieß**

Influence of process parameters on the properties of thin ceramic films manufactured by slot die casting

**Samuel Schmiedeke**

Influence of different laminating techniques on the sintering behaviour of tape cast refractory multilayer oxides

**Jonas Schatz**

FE analysis of the mechanical behaviour of real structural models from µCT images

**Philipp Schnierstein**

Manufacturing of porous TiC ceramics and their chlorination

**Felix Sturm**

Dielectric and piezoelectric properties of tape cast $BaTiO_3$

## Master Thesis

**Werner Aumayr**

Influence of the redensification on the mechanical properties of 3D printed ceramics

**Özlem Duman**

Cellular $Al_2O_3$ oxide ceramics by metal oxidation

**Tobias Früh**

The effects of $Na_2O$, MgO and $SiO_2$ dopants on sintering of $\alpha$-alumina

**Matthias Freihart**

Co-extrusion of highly viscous pastes

**Hannes Lorenz**

Tape casting of thin glasses

**Marita Lenhart**

Investigation and characterization of the gelation and tape casting behaviour of PVB-based ITO slurries

**Jan Schultheiß**

Processing and characterization of paper-derived MAX Phase ceramics

**Martin Stumpf**

Aluminium chlorohydrate gel for surface modification of 3D printed $Al_2O_3$ ceramic

**Lukas Weiß**

Influence of chromium silicide on polymer-derived ceramics

# Ph.D. Thesis

**Michael Götz**

*Modular composites with periodic micro-structure*

**Kai Gutbrod**

*Photocatalytic decomposition of organic substances with ceramics from the system Ti-Mo-O*

**Nadja Kölpin**

*Processing of ITO and ZnO nanoparticles to ultrathin films and miniaturized structures*

**Anne-Kathrin Meier**

*Three-dimensional printing of porous calcium phosphate ceramics for biomedical applications*

## Tobias Kühnlein

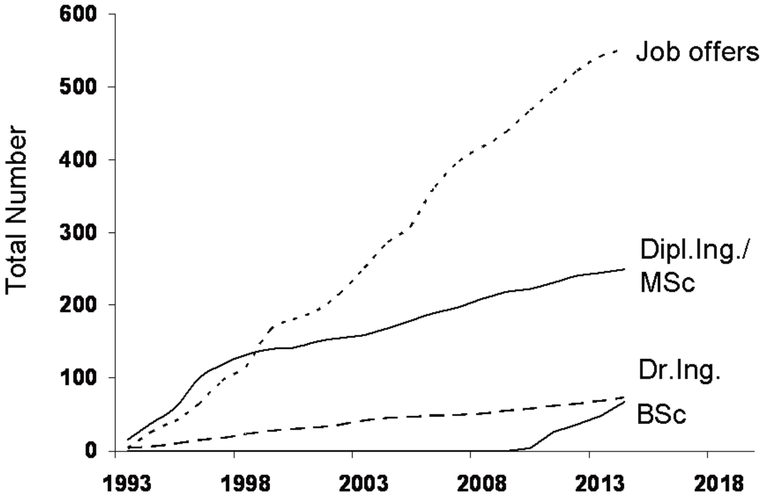
*Properties of PZT ceramics depending on material composition and sintering parameters*

## Martin Steinau

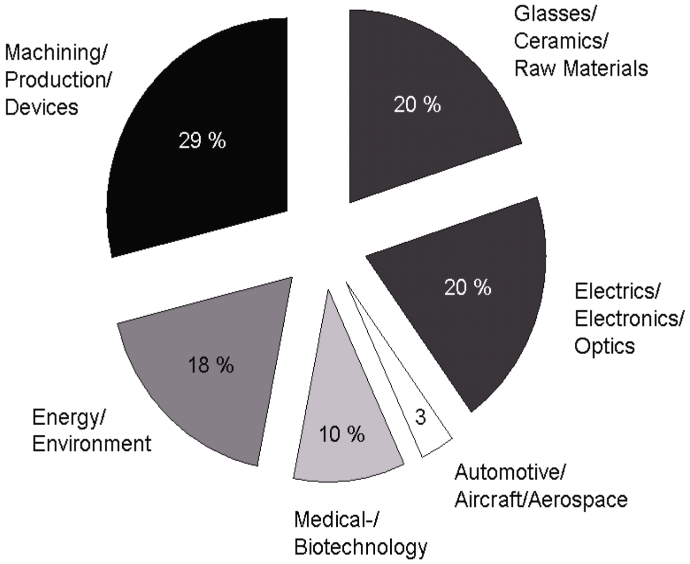
*Laminates on the basis of preceramic polymers for tribological applications*

## c. Alumni

In 2014 the number of alumni graduated from the Institute of Glass and Ceramics since 1993 reached 249 Dipl.-Ing. + MSc, 67 BSc, and 73 Dr.-Ing. After implementation of Bologna reform first BSc were graduated in 2010 whereas graduation of Dipl.-Ing. ceased in 2012. At the same time period more than 550 job offers were submitted to the institute.



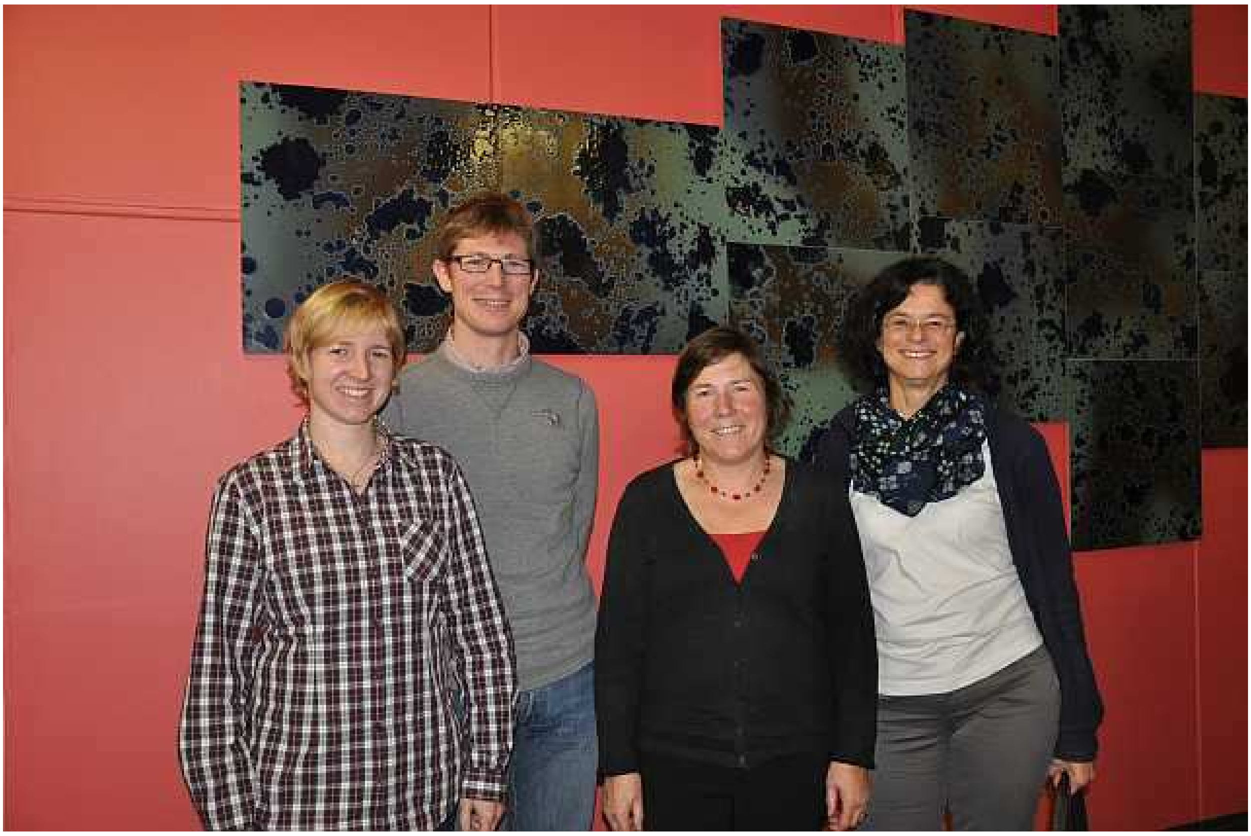
The industrial fields of work cover a wide range. While in the seventies and eighties more than 50 % of the alumni went into glass, ceramics and construction materials producing industries, this number has dramatically decreased in the nineties. The majority of alumni is now going into advanced technologies fields.



## Alumni Association of Friends and Supporters of WW 3 (FV-WW 3)

The FV-WW 3 is an association of alumni graduated from the Institute of Glass and Ceramics (http://www.foerderverein-ww3.de). The aims of the association are to foster the scientific and cultural exchange as well as to promote young scientists by offering scholarships, financial support for abroad studies and consulting. Annually, a master award and a bachelor award are donated for appreciation of the best thesis of undergraduate and graduate students. These students are invited to the members meeting to present their work.

After the members meeting all invited alumnis and students of WW3 meet to enjoy a typical franconian dinner (buffet) alumnis. The number of alumni association members reached 149 by 2014.



*Members of the FV-WW3 executive board*

# 4. ACTIVITIES

## a. Conferences and Workshops

**T. Fey**

Member of the Organizing Committee, “CellMAT 2014”, Dresden, Germany, 22-24 October 2014

**T. Fey**

Member of the Organizing Committee, Annual Meeting of the “Deutsche Keramische Gesellschaft”, Clausthal-Zellerfeld, Germany, 24-26 March 2014

**A. Roosen**

Organization of the 7th Advanced Training Course on ”Tape Casting and Slot-Die Casting as well as Aspects of Multilayer Processing”, University of Erlangen, Erlangen, Germany, 19 February 2014

**A. Roosen**

Member of the Program Committee and Session Chair, Annual Meeting of the “Deutsche Keramische Gesellschaft”, Clausthal-Zellerfeld, Germany, 24-26 March 2014

**A. Roosen**

Member of International Advisory Board of Symposium “Ceramic Powders” of 13th CIMTEC, Montecatini Terme, Italy, 8-13 June 2014

**A. Roosen**

Member of the Program Committee and Session Chair of the DKG-Symposium “Processing of ceramic powders“, Erlangen, Germany, 26-27 November 2014

## b. Invited Lectures

**U. Deisinger**, J. Hartmann, G. Ziegler

Selective Laser Melting of Calcium Phosphate Glass/Hydroxyapatite-Composites

*12th Meeting of the DGG-DKG Working Committee „Amorphous-crystalline Multi-functional Materials“, Erlangen, Germany, 27-28 February 2014*

**T. Fey**

Cellular ceramics – processing, characterization and simulation

*3rd International Symposium on Ceramics Nanotune Technology, Nagoya Institute of Technology, Nagoya, Japan, 3-5 March 2014*

**T. Fey**

Cellular ceramics – processing, characterization and simulation

*BaCaTec, HRL Labs, Malibu, USA, 15 April 2014*

**T. Fey**, B. Ceron-Nicolat, B. Zierath, M. Stumpf, F. Eichhorn, J. Schatz, A. Koshravani, P. Greil

Modelling of cellular structures on the basis of computer tomographical data

*CIMTEC 2014, Montecatini Terme, Italy, 8-13 June 2014*

**T. Fey**, M. Götz, B. Diepold, P. Greil

Cellular Ceramic – Polymer Composites of Ceramic Building Blocks

*CellMAT Conference, Dresden, Germany, 22-24 October 2014*

**T. Fey**, B. Ceron-Nicolat, B. Zierath, M. Stumpf, R. Kaiser, J. Schatz, A. Koshravani, P. Greil

Microstructural characterization and simulation of cellular ceramics materials

*Syntactic and Composite Foams IV, Santa Fe, NM, USA, 2-7 November 2014*

**P. Greil**

Preceramic Paper Derived Lightweight Ceramics

*MSE 2014, Darmstadt, Germany, 23-25 September 2014*

**P. Greil**

Cellular Ceramics – Processing, Properties and Applications

*6th FEZA-Pre-School: Hierarchically-ordered Materials: From Theory to Applications, Lichtenfels, Germany, 5-7 September 2014*

**P. Greil**

Crack Healing Ceramics

*Materials Science Seminar, Nagoya Institute of Technology, Nagoya, Japan, March 2014*

**D. de Ligny**

Glasses at extreme conditions: high pressure and hyper-quenching

*1st Joint Meeting of DGG-Acers GOMD, 2014, Aachen, Germany, 25-30 May 2014*

**A. Roosen**

Thickness limitations during tape casting and how to overcome them

*Vision Ceramic 2014, Dresden, Germany 16-17 January 2014*

**A. Roosen**

Printing and coating techniques for the manufacture of particulate structures in the micrometer range

*Establishment of the NITech-Europe Liaison Office Kickoff Symposium, Nagoya, Japan, 20 March 2014*

**A. Roosen**

Manufacture of Particulate Structures in the Micrometer Range by Printing and Coating Techniques

*Technical University of Denmark (DTU), Risø, Denmark, 9 May 2014*

**A. Roosen**, M. Wegener

Continuous manufacture of thin and ultrathin particulate coatings on flexible carriers

*3rd International Symposium on Disperse Systems for Electronic Applications, Erlangen, Germany, 11-12 September 2014*

**N. Travitzky**, T. Fey, P. Greil

10 Years of Paper-Derived Ceramics

*DKG Annual Meeting 2014, TU Clausthal, Clausthal-Zellerfeld, Germany, 24-26 March 2014*

**N. Travitzky**, P. Greil

Additive Manufacturing of Ceramic-Based Composites

*MSE 2014, Darmstadt, Germany, 23-25 September 2014*

**N. Travitzky**

Paper-Derived Ceramics

*Materials Science Seminar, Beijing Jiaotong University, Beijing, China, December 2014*

**M. Wegener**, A. Roosen

Printing of structured layouts based on nanoparticulate ITO inks

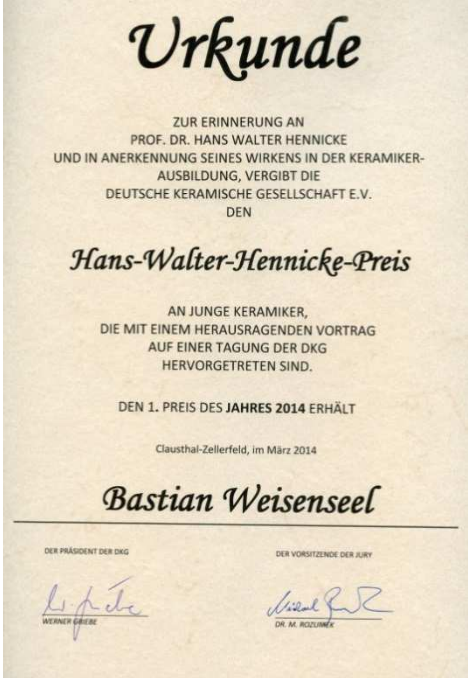
*3rd International Symposium on Disperse Systems for Electronic Applications, Erlangen, Germany, 11-12 September 2014*

**M. Wegener**, A. Roosen

Processing properties of nanoparticles in dispersions and slurries for tape casting applications

*DKG Symposium of the Technical Committee Process Engineering "Processing of ceramic powders“, Erlangen, Germany, 26-27 November 2014*

## c. Awards



Urkunde

ZUR ERINNERUNG AN
PROF. DR. HANS WALTER HENNICKE
UND IN ANERKENNUNG SEINES WIRKENS IN DER KERAMIKER-AUSBILDUNG, VERGIBT DIE
DEUTSCHE KERAMISCHE GESELLSCHAFT E.V.
DEN

Hans-Walter-Hennicke-Preis

AN JUNGE KERAMIKER,
DIE MIT EINEM HERAUSRAGENDEN VORTRAG
AUF EINER TAGUNG DER DKG
HERVORGETRETEN SIND.

DEN 1. PREIS DES **JAHRES 2014** ERHÄLT

Clausthal-Zellerfeld, im März 2014

Bastian Weisenseel

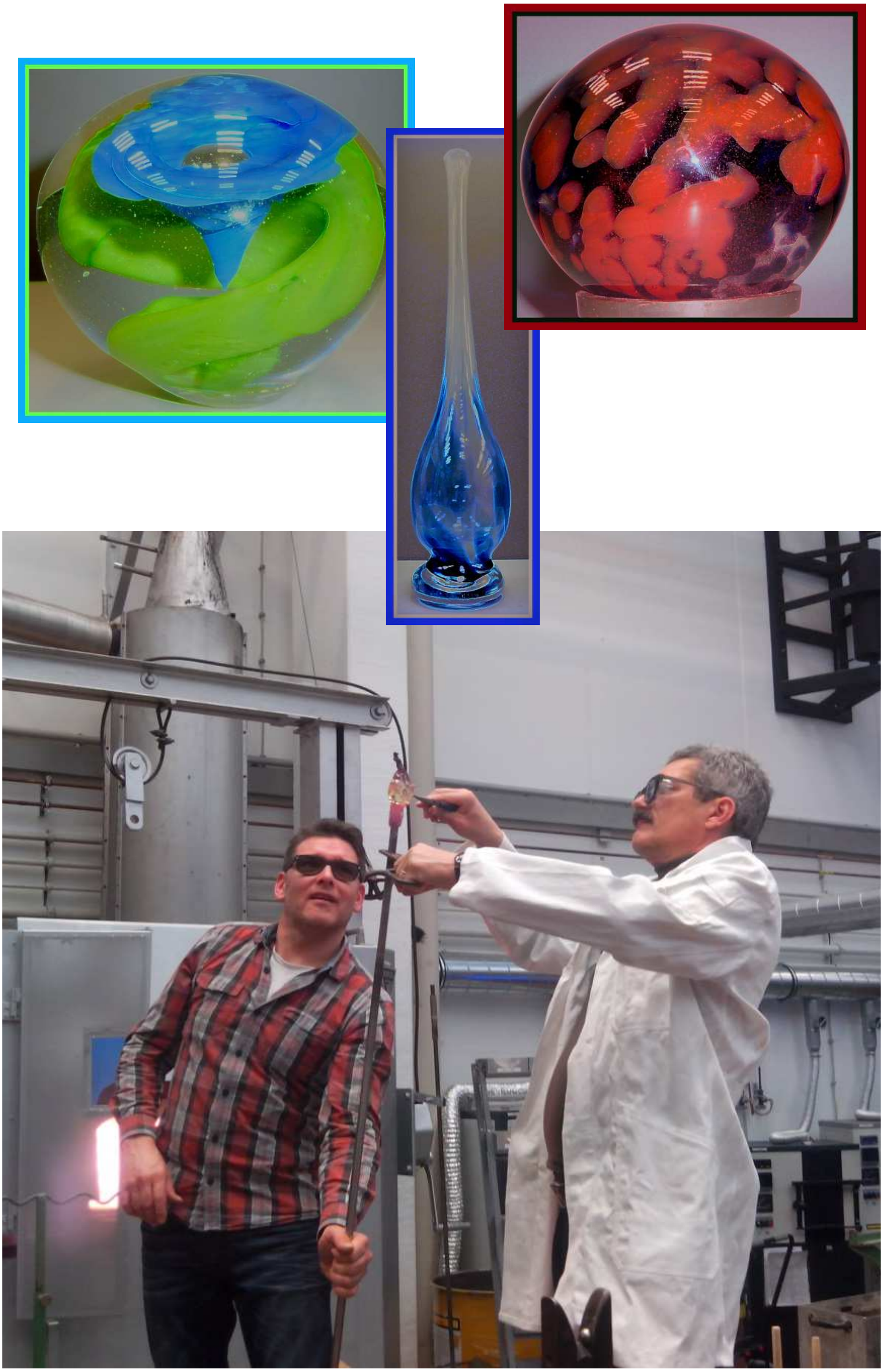
DER PRÄSIDENT DER DKG
WERNER GRIEBE

DER VORSITZENDE DER JURY
DR. M. ROZUMEK

**Bastian Weisenseel**

Hans-Walter-Hennicke Award:

1st place for his Master thesis *"Ceramic Loop Heat Pipes with microporous SiC wicks"*



*Annual glass week: Peter Greil tries to create some artistic glass ware with the help of Andreas Thomsen*

# 5. ADDRESS AND IMPRESSUM

## Department of Materials Science - Glass and Ceramics

Friedrich-Alexander University of Erlangen-Nuremberg

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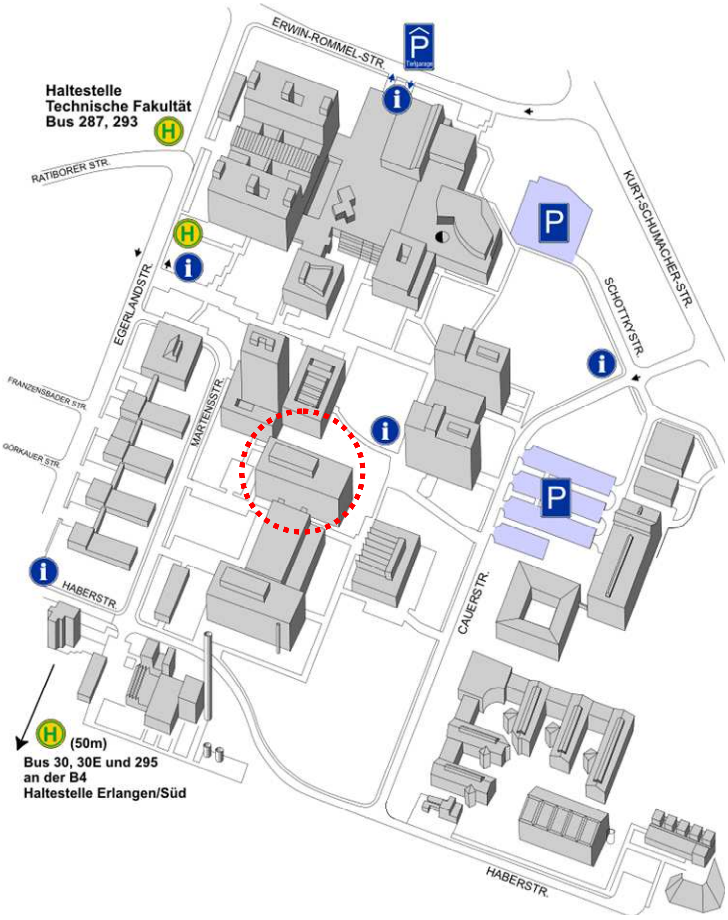
Fax: ++49-(0) 9131-852-8311

E-mail: ww3@ww.fau.de

Internet: http://www.glass-ceramics.fau.de/



By car:

Highway A3 exit **Tennenlohe**; direction to Erlangen (B4).

Follow the signs "**Universität Südgelände**".

After junction "**Technische Fakultät**" please follow the map.

By train:

Railway station **Erlangen**.

Bus line No. 287 direction "**Sebaldussiedlung**".

Bus Stopp "**Technische Fakultät**". 50 meters to a layout plan; search for "**Department Werkstoffwissenschaften**".

http://www.glass-ceramics.fau.de/Home/contact.htm

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Dr.-Mack-Strasse 81

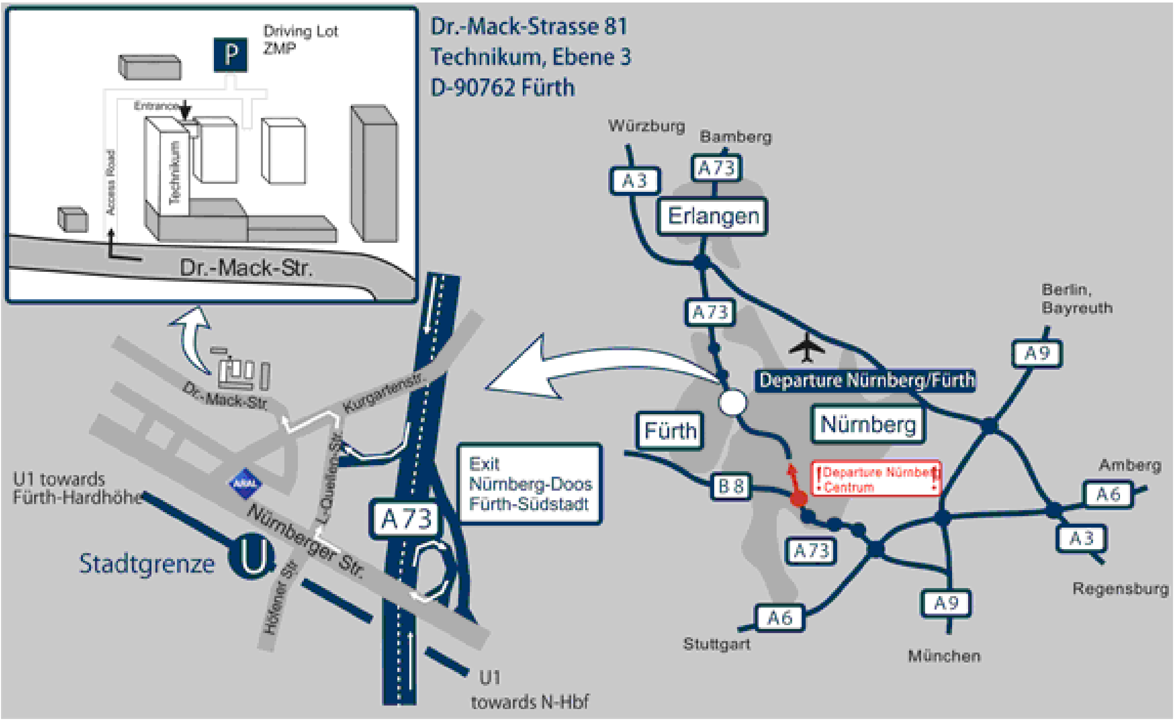
Technikum, Ebene 3

D-90762 Fürth

Tel.: ++49-(0) 911-950918-10

Fax: ++49-(0) 911-950918-15

Internet: http://www.zmp.fau.de/



http://www.zmp.fau.de/anfahrt/

# Impressum

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Dr. Andrea Dakkouri-Baldauf

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