



Strasbourg (France)

E-MRS Spring Meeting 2004  
May 24-28, 2004

## SYMPOSIUM Q

Polymer derived ceramics (PDCs)

### Symposium Organizers:

Florence Babonneau, LCMC, University of Paris, France

Philippe Miele, LMI, University of Lyon, France

Ralf Riedel, Technical University of Darmstadt, Germany

Gian Domenico Soraru, DIMTI, University of Trento, Italy

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# E-MRS 2004 SPRING MEETING

## SYMPOSIUM Q

Tuesday, May 25, 2004

Morning

Session I : Synthesis

Chairpersons : P. Miele & F. Babonneau

- |              |       |           |   |
|--------------|-------|-----------|---|
|              | 09:00 |           | INTRODUCTION  |
| <b>Q-I.1</b> | 09:10 | -Invited- | <p>THE DESIGN, SYNTHESSES, AND APPLICATIONS OF CHEMICAL PRECURSORS TO NONOXIDE CERAMIC MATERIALS</p> <p><b>Larry G. Sneddon</b>, Mark J. Pender, Kersten M. Forsthoefel, Xiaolan Wei and Upal Kusari, Department of Chemistry, University of Pennsylvania, USA</p> <p>The production of complex structural and electronic materials in useable forms is one of the most challenging problems of modern solid-state chemistry and materials science. The use of a chemical-precursor, in which the precursor is first formed into the desired shape then decomposed to the final material with retention of this shape, is an important new route for producing film, fiber and nanostructured solid-state materials. Our recent work directed at the synthesis, characterization and applications of new boron and/or silicon based polymeric and molecular precursor systems will be presented with a focus on the use of these precursors to generate technologically important nonoxide ceramic materials, such as boron carbide and boron-carbide/silicon-carbide composites, in processed forms. In addition, our recent development of efficient routes to ceramic nanostructured materials, including nanofibers, nanocylinders and nanoporous materials, that employ appropriately designed polymeric and molecular precursors in conjunction with nanoscale templating methods will be discussed.</p>  |
| <b>Q-I.2</b> | 09:50 | -Invited- | <p>SYNTHESIS AND PROPERTIES OF PRECERAMIC Si-B-C-N POLYMERS WITH TUNABLE CHEMICAL COMPOSITION</p> <p><b>M. Weinmann</b>, M. Hörz, A. Müller, S. Bernard and F. Aldinger, Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, 70569 Stuttgart, Germany</p> <p>Thermolysis of organometallic polymers on the basis of silicon, boron, carbon, and nitrogen delivers quaternary Si-B-C-N ceramics. Such materials can be thermally stability up to 2000°C in inert and reactive atmosphere, though thermodynamic calculations predict decomposition below 1500°C. Thermal stability of the ceramic materials is determined to a significant extend by the molecular structure and elemental composition of the polymeric precursors. Even though structurally characterized in much detail, the reasons for the unusual high temperature stability of Si-B-C-N ceramics are still discussed controversial. We found that the thermal stability of Si-B-C-N ceramics is mainly a function of chemical composition i.e. boron and nitrogen concentration and random element distribution in the polymeric precursors.</p> <p>In this context, the paper will report on synthetic approaches, which allow for controlling the chemical composition of Si-B-C-N ceramics by individually tuning the concentration of the constituting elements already in the polymeric precursors. It will be shown, that the amorphous state of polymer-derived Si-B-C-N ceramics can be retained up to 1850 – 1900°C, by simply adjusting proper nitrogen contents. In addition, mechanisms for the devitrification on the basis of TEM and NMR investigations of the amorphous ceramics will be provided.</p> |
|              | 10:30 |           | <b>BREAK</b>  |
| <b>Q-I.3</b> | 11:00 | -Invited- | <p>DESIGN OF PROCESSIBLE BORAZINE-BASED PRECURSORS FOR THE PREPARATION OF BN FIBERS</p> <p><b>D. Cornu</b>, S. Bernard, S. Duperrier, B. Toury and P. Miele, Laboratoire des Multimatériaux et Interfaces, UMR 5615 CNRS – Université Claude Bernard Lyon 1, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France</p> <p>Hexagonal boron nitride (h-BN)-based ceramic matrix composites (CMCs) offer exciting perspectives for use in high-temperature applications. Indeed these materials combine the mechanical properties of the CMCs with the intrinsic properties of h-BN (low density, high-temperature oxidation resistance, chemical and thermal stability). The polymer preceramic route is particularly suited for the formation of high-performance continuous ceramics fibers. The general method consists in the synthesis of a molecular precursor, its polymerization into a processible polymer which can be melt-spun into green fibers and finally the thermally-induced conversion of the shaped product into BN fibers.</p> <p>Among the different precursors used for that application, the borazine derivatives are deemed to be the most promising since they already contain the B<sub>3</sub>N<sub>3</sub> hexagonal pattern of h-BN. A comparative study of the different borazine-based precursors will be reviewed in this state-of-the-art in terms of chemistry, processing abilities of the resulting polymers and characterization of the ensuing ceramic fibers.</p>   |

**Q-I.4**

11:40

**NEW TYPE OF PRECURSOR FOR FIBERS AND MATRICES IN THE SYSTEM SI-C**

J. Clade, E. Seider, D. Sporn, Fraunhofer-Institut für Silicatforschung ISC, Neunerplatz 2, 97082 Würzburg, Germany

Ceramic fibers with compositions in the system Si-C have a great potential for high-temperature applications. In recent years, our efforts have been dedicated to the development of polymers consisting of polysilanes suitable to spin fibers and build up matrices for CMC as well. The polysilanes are synthesized via disproportionation of the so-called disilane fraction [1]. A further thermal treatment yields materials which are soluble in organic solvents, and these solutions can be dry-spun to give fibers which are subsequently pyrolyzed. Solubility and high ceramic yield make this precursor a promising candidate for matrix infiltrations, too.

The chemistry and the adjustment of viscosity and solubility to the requirements of the fiber processing as well as the conversion of the dried fibers to pure SiC fibers by thermal treatment will be reported.

[1] R. Richter, G. Roewer, U. Böhme, K. Busch, F. Babonneau, H.-P. Martin, E. Müller, Appl. Organomet. Chem. 11 (1997) 71

12:00

**LUNCH**

Tuesday, May 25, 2004

Afternoon

Session II : Characterisation

Chairpersons : L. Sneddon & L. Interrante

- Q-II.1** 14:00 -Invited- HIGH RESOLUTION SOLID STATE NMR INVESTIGATION OF VARIOUS PRECERAMIC POLYMERS AND THEIR PYROLYSIS DERIVATIVES  
**Christel Gervais**, Florence Babonneau, Chimie de la Matière Condensée, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France  
In the polymeric route to ceramics, the polymer architecture may strongly influence the structure of the final ceramic. It is therefore essential to rely characterization tools to get a precise description of the polymer structure, and then be able to follow step-by-step the polymer-to-ceramic conversion.  
The samples usually do not present any long range order, which prevents the use of X-Ray diffraction. High resolution solid state magic angle spinning nuclear magnetic resonance (MAS NMR) appears therefore to be extremely useful to characterize the different intermediates. This technique is sometimes challenging because of the lack of sensitivity of the isotope in natural abundance ( $^{15}\text{N}$ ) or a lack of resolution of the spectra due to the quadrupolar character of the isotope ( $^{11}\text{B}$  or  $^{17}\text{O}$ ) or to strong homonuclear interactions ( $^1\text{H}$ ). However, an appropriate combination of solid state NMR techniques such as double resonance experiments ( $\{^1\text{H}\}\text{-}\{X\}$ ,  $X = ^{13}\text{C}, ^{15}\text{N}, ^{29}\text{Si}$ ), multiple-quantum (MQ) MAS sequence for quadrupolar nuclei, use of high magnetic fields or high rotation speed leads to a good description of the various environments present in the structures. The range of structural information that can be obtained through the use of solid state NMR will be illustrated on preceramic polymers and their pyrolysis derivatives in various systems (BN, BCN, SiBCN, SiCO, SiBCO).
- Q-II.2** 14:40 COMPLETE CHARACTERIZATION OF BN FIBRES OBTAINED FROM A NEW POLYBORYLBORAZINE  
**B. Toury**, D. Cornu, F. Chassagneux and P. Miele, Laboratoire des Multimateriaux et Interfaces, UMR CNRS 5615, Université Claude Bernard Lyon 1, 69622 Villeurbanne Cedex, France  
Achievement of boron nitride fibers by the preceramic polymer route generally requires polymers based on the borazine ( $\text{B}_3\text{N}_3$ ) core. These polymers are mostly prepared by thermolysis of borazine-based derivatives such as aminoborazine or borylbrazine. The ensuing polymers always display a complex structure with the presence of two linkage modes: formation of either direct or bridged B-N bonds between the rings. Hence, for a better control of the polymer structure and then of its rheological properties, a new route was investigated which allows the preparation of a "well-defined" polymer at room temperature. Actually, reaction between a di-chloroborazine with a reactive aminoborane leads to a polymer in which the borazine rings are only connected through 3 atoms N-B-N bridges. This connecting mode was evidenced by  $^{15}\text{N}$  solid state NMR.  
This new polymer was processed into a continuous polymer fiber of about 21  $\mu\text{m}$  diameter which was subsequently heat-treated under  $\text{NH}_3 / \text{N}_2$  up to  $1800^\circ\text{C}$  for conversion into BN fibers. The achievement of hexagonal boron nitride was confirmed by X-ray diffraction, FTIR and Raman spectroscopies. Tensile tests were carried out on the ceramics fibers. The average tensile strength is about 1000 MPa and the Young's modulus is close to 200 GPa. Structural characterization of the BN fibers were undertaken by transmission electronic microscopy.
- Q-II.3** 15:00 CARBON-RICH SILICON OXYCARBIDE - SYNTHESIS AND NANOSTRUCTURE CHARACTERIZATION  
**Y.B. Blum** and D.B MacQueen, SRI International, Menlo Park CA, USA, H-J. Kleebe, Colorado School of Mines CO, USA  
The use of the commercially available polyhydridomethylsiloxane (PHMS), as a useful precursor to silica and silicon oxycarbide (SiOC), was found to be very practical for numerous composite and coating applications. A very versatile methodology has been developed to synthesize, modify and cure these polymers, using transition-metal catalyzed dehydrocoupling and hydrosilylation reactions. The modifications allow unique control over the molecular compositions of the derived ceramic formulations.  
A simple, solventless approach to form a highly carbon-rich SiOC is being investigated with the capability to increase the level of "free carbon" at the amorphous stage mixed at the atomic level. These carbon-rich materials demonstrate unexpectedly high thermal and chemical stability at their amorphous stage, oxidation resistance and mechanical integrity relative to other studied SiOC materials, in spite of their high carbon content. Reactivity and nanostructural development of these carbon-rich SiOC will be discussed.

- Q-II.4** 15:20 -Invited- **THE FATE OF CARBON IN POLYMER-DERIVED SiCO CERAMICS**  
**Hans-Joachim Kleebe**(a) and Yigal Blum(b), (a)Colorado School of Mines, Metallurgical and Materials Engineering Dept., Golden CO 80401, USA, (b)SRI international, Menlo Park CA 94025, USA  
 Two polymer-derived SiCO materials with a higher carbon content were processed starting from PHMS and PHMS crosslinked with 60 wt% divinyl benzene (DVB). In both systems, the high carbon content results in the formation of excessive molar content of carbon during the pyrolysis embedded in the overall amorphous network.  
 TEM investigation documented that the PHMS material maintained an almost completely amorphous network up to 1450°C with only a minor amount of turbostratic carbon features. Similarly to other SiCO systems, the PHMS sample underwent phase separation only when heated above 1200 °C.  
 The system with the higher carbon content (60 wt% DVB) showed a homogeneous elemental distribution at low pyrolysis temperature. Energy-filtered TEM studies confirmed a dramatic change of the carbon distribution during heat treatment above 1200°C. In contrast, the microstructure observed at 1450°C showed carbon enriched areas of ~10-15 nm in diameter. Detailed HRTEM imaging revealed that these regions are composed of turbostratic carbon.  
 The above results will be compared with microstructure characterization of materials derived via sol-gel processing. For example, there was no significant SiC nanophase formation in the above systems in contrast to sol-gel derived products, suggesting that *in-situ* carbothermal reduction as well as phase separation of SiOC to Si, C, and SiO<sub>2</sub> are inhibited. Furthermore, results on the carbon distribution in SiCN-based glasses will be presented to emphasize specifics and generalities of the excess free carbon phase in polymer-derived ceramics.
- 16.00 **BREAK**
- Q-II.5** 16:20 **THE MICRO-STRUCTURE OF POLYMER DERIVED AMORPHOUS SILICON CARBIDE LAYERS**  
**A. Hilbig**(a), E .Müller(a), R. Wenzel(b), G. Roewer(b), E. Brendler(c), G. Irmer(d), G. Schreiber(e), Freiberg University of Mining and Technology, Germany: (a)Institute of Ceramic Materials, (b)Institute of Inorganic Chemistry (c)Institute of Analytical Chemistry, (d)Institute of Theoretical Physics, (e)Institute of Physical Metallurgy  
 In order to achieve thin amorphous silicon carbide layers, which are of interest do to their opto-electronic properties, two stage process was applied. The deposition of thin layers from liquid oligomers (chlorovinylsilanes) on various substrates carried out under argon flow using spin-coating-system. Afterwards, the samples were pyrolysed in an alumina furnace in temperature range between 800 C and 1200 C by different hydrogen concentrations in the atmosphere. Additionally, "bulk" material was pyrolysed in order to characterise structural changes by transition oligomer to a-SiC:H.  
 In this work we present studies on the structure and chemical composition of the layers and of "bulk" material, which carried out using XRD, NMR MAS and Raman Spectroscopy, in dependence on pyrolysis conditions – temperature and hydrogen content in the atmosphere. Following conclusions can be established: Both, silicon carbide layers and "bulk" material, pyrolysed at 800 C were amorphous. Increase of the temperature to 1200 C leads to a partial amorphous-to-crystalline transition by forming &#946;-SiC. Moreover, derivations from stoichiometric SiC were observed: Free silicon was found in thin layers, whereas in bulk material crystallites of graphite were detected. The amount of excess carbon can be influenced by addition of hydrogen to the pyrolysis atmosphere.
- Q-II.6** 16:40 **CORRELATION BETWEEN STRUCTURAL FEATURES AND MECHANICAL PROPERTIES OF BORON NITRIDE FIBRES DERIVED FROM ALKYLAMINOBORAZINES**  
**P. Miele**(a), B. Toury(a), F. Chassagneux(a), R. Fulchiron(b). (a)Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615 – Université Claude Bernard Lyon 1, 69622 Villeurbanne Cedex, France. (b)Laboratoire des Matériaux Polymères et des Biomatériaux UMR CNRS 5627 – Université Claude Bernard Lyon 1, 69622 Villeurbanne Cedex, France  
 Structural characterisations by X-Ray diffraction, Raman spectroscopy, Transmission Electronic Microscopy and Optic Microscopy with polarised light were performed on boron nitride fibres prepared from a series of different molecular precursors. Conclusions have exemplified a correlation between the structural features and the mechanical properties of the studied hexagonal boron nitride fibres. In the case of BN fibres with good mechanical properties, the structural analyses reveal that the c axis of a BN crystallites is roughly in a plane perpendicular to the fibre axis whereas the a axis is in a plane parallel to the fibre axis. That means that the covalent B-N bonds are along the fibre axis which can be correlated with the good mechanical properties of this BN fibres. Hence, better the orientation of the BN crystallites in the fibre axis is, better the mechanical properties of the derived fibres are.
- Q-II.7** 17:00 -Invited- **MODELING OF POLYMER-DERIVED AMORPHOUS CERAMICS**  
**Peter Kroll**, Inorganic Chemistry, RWTH Aachen, Germany  
 We present an overview of our computational research on structure and properties of some polymer-derived ceramics. In a first step, we concentrate on our approach of modeling such covalent binary and multinary compounds through network structures and simple empirical potentials. We emphasize the chemically perfectly ordered random network as a reference structure of such systems, suitable to study effects of large distortions, impurities, segregations, and increasing crystallinity.  
 In a second step, we apply density functional theory methods to investigate network structures of ternary silicon oxide and silicon nitride based ceramics. Models consisting of 100 to 400 atoms are relaxed and, subsequently, annealed at elevated temperatures. Stability and/or change of a network, both within the geometrical and chemical structure, are monitored through extensive (ab initio) Car-Parrinello molecular dynamics simulations. The combination of empirical and quantum mechanical techniques allows an efficient study of structure and properties with highly accurate methods and facilitates an understanding of chemical processes that may govern the evolution of polymer-derived ceramics.

Wednesday, May 26, 2004

Afternoon

Session III : Processing and Properties

Chairpersons : R. Riedel & G.D. Soraru

- Q-III.1** 14:00 -Invited- CERAMIC PROCESSING WITH FILLER-LOADED PRECERAMIC POLYMERS  
**Michael Scheffler**, Department of Materials Science & Engineering, University of Washington, Seattle WA, USA  
Preceramic polymers offer a set of unique properties for ceramic manufacturing. Their rheological and chemical properties make them suitable for shaping of ceramic green parts in a temperature range from room temperature to 300°C. Subsequent temperature increase (800°C – 1600°C) in inert or reactive atmosphere results in a thermal transformation into an inorganic material. When particulate fillers are present shape retention and near net shaping is possible, and the materials properties can be designed for a wide variety of applications.  
In the first part, capabilities for shaping with polysiloxanes will be reported and ceramic parts such as tapes, tubes and foams will be presented. The second part addresses interfacial reactions and resulting structure property relations of silicon-filled and transition metal doped ceramics from polysiloxanes. A special feature of these systems is the pore space which can act as a microreactor for the direct in situ formation of carbon nanotubes and nanowires in the Si-O-C-N system. Finally, novel applications of polymer derived ceramics in chemical and automotive industry will be discussed.
- Q-III.2** 14:40 SPRAY WINDING, A NOVEL ONE-STEP SPRAY-TECHNOLOGY TO PERFORM CMC'S FROM PRECERAMIC POLYMERS  
O. Goerke, E. Feike, H. Schubert, Institute for material science and -technology, Technical University Berlin, Germany  
Ambitious CMC materials are usually processed by very elaborated techniques. Especially high potential composites derived from various silicon based preceramic polymers are already in demand but very costly. We developed a novel spray-technology in order to establish an one-step-process which enables to decrease the process time along with saving of costs. Our manufacturing route combines the traditional formation of composites (fibers plus preceramic matrix) with the thermal treatment to transfer the preceramic polymers into an inorganic matrix. The applied metalorganic polymers vary from commercial polysiloxanes to silsesquioxanes precursors which can be easily handled in air. A solution or suspension can be produced by adding a reactive or an inert filler (AlN, SiC, Cu or WC) to minimize volume shrinkage and to improve the properties of the composites. A rotating tapered spindle for winding SiC or carbon fibers is sprayed with the polymer solution. A heatable two flux nozzle is positioned perpendicular above the rotating spindle and coats the surface continuously. An ellipsoid mirror furnace which cures and pyrolyses the matrix (at least partly) is 180° displaced focusing the radiation onto the surface. Temperatures up to around 900 °C in an inert gas stream were applied, resulting in an amorphous SiOC-matrix. So coating and heating takes place at the same time to form the CMC tube layer by layer. The anisotropic shrinkage of these thin layers means that most of the typical strains and stresses within the matrix can be avoided to produce tubes with rather small porosity. This process offers a perspective of low cost CMC's away from well established materials in space applications to open up the broad field of structural high performance components.
- Q-III.3** 15:00 NOVEL APPLICATION OF PRECERAMIC PRECURSORS FOR THE FABRICATION OF COMPOSITES  
Andreas Herzog, Maik Thuenemann, Ulrich Vogt, Olivier Beffort, EMPA, Duebendorf, Switzerland  
Preceramic polymers are enabling the development of a variety of advanced shaping methods which, in turn, make possible new and cost-effective approaches for the fabrication of composite materials. This opens new perspectives for the mass production of composites which might, for example, be used in cost-sensitive areas of application in the machine and automobile industries. In two examples it will be shown how preceramic polymers can be used to obtain both metal matrix composites (MMC's) and ceramic matrix composites (CMC's) and their properties will be discussed in particular with respect to the usage of a preceramic polymer.  
The first example shows an approach to manufacture short-fibre-reinforced CMC by means of a plastic forming technique which involves mixing of either carbon or SiC fibres, ceramic fillers and a viscous ceramic precursor. The precursor permits a fibre-reinforced ceramic with a low porosity to be obtained. The role of the precursor in the whole process and the resulting material properties will be discussed. The second example shows a method for fabricating porous SiC ceramic preforms which are subsequently infiltrated with aluminium to form a MMC. By using the precursor route, a machinable perform with tailored porosity can be produced. Correlations between precursor, preform and MMC properties will be drawn.

Q-III.4 15:20

#### FABRICATION OF POLYMER DERIVED CERAMIC PARTS BY SELECTIVE LASER CURING

T. Friedel(a), N. Travitzky(a), F. Niebling(b), A. Otto(b) and P. Greil(a), (a)University of Erlangen-Nuernberg, Dept. of Materials Science, Erlangen, Germany, (b)University of Erlangen-Nuernberg, Dept. of Manufacturing Technology, Erlangen, Germany

Polymer derived ceramic parts of complex shape were fabricated by Selective Laser Curing (SLC). The ceramic parts were built in the layer by layer fashion. Either Al<sub>2</sub>O<sub>3</sub> or SiC loaded polysiloxane thin powder layers, were sequentially cured by a CO<sub>2</sub>-laser (10.6µm) beam. After building the part, the excess powder, which was supporting the product, was removed. The cured bodies were converted to Si-O-C/Al<sub>2</sub>O<sub>3</sub> and Si-O-C/SiC ceramic parts in a subsequent pyrolysis treatment at 1200 °C in nitrogen atmosphere. Due to the filler loading (40, 50 or 60 vol%) the linear shrinkage after pyrolysis was less than 2 %. Thus, the SLC approach can be considered as a near-net-shape forming process of ceramic components with complex geometries.

The properties of the produced parts were dependent both upon the composition of the starting powder and the parameters of the laser radiation. The scanning speed and the power of the CO<sub>2</sub>-laser beam were varied, leading to pronounced differences in material properties. Laser irradiating a powder mixture containing 50 vol-% polymer and 50 vol-% Al<sub>2</sub>O<sub>3</sub> lead to relative green densities of 45% to 65%. Relative densities increased to 53% - 69% after pyrolysis. The average pore diameters of pyrolyzed materials ranged between 1.0 and 3.1 µm. A subsequent infiltration with liquid silicon was carried out in order to produce dense parts. A turbine wheel was successfully produced as a demonstrator.

Q-III.5 15:40

#### MICROSTRUCTURING PRECERAMIC POLYMERS BY APPLICATION OF UV- AND DEEP X-RAY LITHOGRAPHY

Michael Schulz(a,d), Martin Börner(b), Jost Göttert(c), Thomas Hanemann(a,d), Richard Heldele(d), Günter Motz(e), Jürgen Haußelt(a,d), (a)Forschungszentrum Karlsruhe, Institut für Materialforschung III, (b)Forschungszentrum Karlsruhe, Institut für Mikrostrukturtechnik, (c)CAMD, Baton Rouge, Louisiana, USA, (d)Universität Freiburg, Institut für Mikrosystemtechnik, (e) Universität Bayreuth, Lehrstuhl Keramik und Verbundwerkstoffe (IMA), Germany

The fabrication of micro components made from ceramic materials is becoming more and more important because of their outstanding chemical stability. Different replication methods like low or high pressure ceramic injection molding of ceramic feedstocks have been established. Various lithographic methods are being widely used for the direct fabrication of very precise plastic or metal microstructured surfaces.

Silicon organic compounds containing the elements silicon, nitrogen and carbon in the polymer backbone, can serve as precursors for Si<sub>3</sub>N<sub>4</sub>, SiC or Si-C-N ceramics depending on the pyrolysis atmosphere. Our work deals with the direct manufacturing of microstructures by using ceramic precursors in combination with the UV- and deep X-ray lithography. This allows for a rapid fabrication of high temperature stable (400 °C) and chemical resistant transparent microstructured plastic components. Pyrolysis of these parts yields amorphous SiCN or Si<sub>3</sub>N<sub>4</sub> ceramics. The applicability of different preceramic polymers based on polysilazane for direct structuring with UV- and synchrotron radiation was investigated. Resist materials, partially doped with photoactive compounds have been developed. The application of those materials in lithographic processes allows for the fabrication of microstructures. First X-ray exposures of ceramic Si<sub>3</sub>N<sub>4</sub> powder filled polysilazane polymer have been carried out, showing that it is possible to microstructure those composites. By inserting ceramic fillers a reduction of the pyrolysis shrinkage was possible. Further investigations were made to determine the maximum filler content and required exposure dose. As established in the LIGA technique with PMMA, resist layers up to 1 mm should be possible by deep X-ray lithography on preceramic polymers.

Q-III.6 16:00

#### MANUFACTURE AND PROPERTIES OF LONG FIBRE REINFORCED CERAMICS CONTAINING AL AND TI FILLERS BASED ON THE PIP PROCESS

G. Stantschey, M. Frieß, W. Krenkel, R. Kochendörfer, German Aerospace Center, DLR, Stuttgart, Germany

Silicon based preceramic polymers are attractive candidates for the manufacture of high temperature and corrosion resistant ceramics, particularly in regard to the formation of a ceramic matrix in long fibre reinforced ceramic matrix composites (CMCs). The manufacture of CMCs constitutes of the infiltration of fibre preforms followed by a subsequent crosslinking and pyrolysis of the Si-precursor, yielding to a SiCN Matrix. However, due to the inherent shrinkage of ceramic precursors, a high number of polymer impregnation and pyrolysis (PIP) cycles is required to obtain dense composites. Nevertheless, their microstructure is characterized by large interbundle pores which show a negative impact on the mechanical properties.

In order to improve the performance of the long fiber reinforced CMCs as well as to accelerate the manufacturing process, a novel approach was investigated. Thereby, powders of Al and Ti are used as active fillers. The powders were strewed between the plies and infiltrated by the resin transfer moulding (RTM) technique. Since reactions with the polymer matrix are associated with a volume increase during pyrolysis, a more compact ceramic matrix is obtained. The processing of the CMCs employs the commercial polysilazanes CERASET SN and VL20 as preceramic precursors. The reinforcement constitutes of Tyranno SA fibers. To densify the composites, up to four PIP cycles were performed. CMC samples were aged in air to evaluate the impact of oxidation on microstructure and mechanical properties. Microstructural characterization was conducted using both optical and electron microscopy. The conversion of the filler particles was analysed by means of EDX and XRD.

16:20

**BREAK**

- Q-III.7** 16:40 **IMPROVED DURABILITY OF SI/B/N/C RANDOM INORGANIC NETWORKS**  
 Th. Jäschke, M. Jansen, Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany  
 The inherent high temperature durability as well as the hardness of random inorganic networks composed of Si, B, N and C, can be raised using new single source precursors with rigid structure elements (e.g. borazine rings). Since in these special monomers all cations are fixed by strong covalent bonds via a bridging methylene group the backbone of the precursor survives the whole sequence of processing (polymerization and pyrolysis) leading to a highly homogeneous distribution of all elements in the final ceramic. In fact, following the well known 'polymer route', crosslinking of the borazine precursors with methylamine provides highly homogeneous preceramic polymers, in which the introduced borazine rings become a fixed part of the network, being interconnected by -C-Si-N-Si-C- linkages. Subsequent pyrolysis at 1500 °C converts the as-obtained inorganic polymers into the desired Si/B/N/C ceramic materials, which still contain the embedded cyclic units, and exhibit enhanced material properties compared to ceramics derived from related acyclic single source precursors: the high temperature stability of the borazine derived ceramics is raised up to at least 2000 °C, and, at the same time, the mechanical strength of these materials has increased. The amorphous Si/B/N/C networks have been characterized by elemental analysis, XRD, IR spectroscopy, MAS NMR and DTA/TG. Furthermore, the density of the ceramics as well as their hardness and stiffness (Young modulus) has been determined.
- Q-III.8** 17:00 **MECHANICAL PROPERTIES OF CERAMIC MATRIX COMPOSITES WITH SILOXANE MATRIX AND LIQUID PHASE COATED CARBON FIBER REINFORCEMENT**  
 R. Gadow, F. Kern, H. Ulutas, Institute for Manufacturing Technologies of Ceramic Components and Composites, University of Stuttgart, Allmandring 7b, 70569 Stuttgart Germany  
 Commercial carbon fibers were coated with various ceramic and carbon layers by means of continuous liquid phase coating (CLPC). 12 k rovings were thermally desized and infiltrated with diluted precursor solutions. The precursors were subsequently cured and pyrolyzed in order to obtain homogeneous ceramic monofilament coatings. HT and IM-carbon fibers with coatings of SiCN, SiCO, glassy and graphite-like carbon were produced. Coated fabrics were produced by a similar batch process. For a comparative study CMCs with different types of fiber coatings and fiber architecture (UD, 2D) were produced by lamination of siloxane coated prepreps. The matrix polymer was thermally cured and the CMCs were calcined at 750°C. The CMCs were densified by subsequent polymer infiltration and calcinations cycles. The mechanical properties of the composites were determined by 4-point bending tests. The application of coated fibers in composite manufacturing led to improved composite strength and toughness compared to reference samples with uncoated reinforcement fibers.
- Q-III.9** 17:20 **FORMATION KINETICS OF NANO-CRYSTALLINE SiC IN AMORPHOUS SI-(B-)C-N**  
H. Schmidt, W. Gruber, G. Borchardt, FB Physik, Metallurgie und Werkstoffwissenschaften, TU Clausthal, Robert-Koch-Str. 42, 38678 Clausthal-Zellerfeld, Germany and A. Müller, J. Bill, Institut für Nichtmetallische Anorganische Materialien, PML, U Stuttgart, Heisenbergstr. 3, 70569 Stuttgart, Germany  
 Precursor derived ceramics of type Si-(B-)C-N show attractive high temperature properties, making them interesting for various technological applications. For these materials which are amorphous after thermolysis, thermal treatment at temperatures between 1400 and 1750 °C leads to crystallization and the formation of nano-crystalline SiC (grain size 3-40 nm) embedded in an amorphous matrix. In order to reach an optimised stability of the amorphous state and to obtain tailor-made microstructures, it is necessary to understand and quantitatively specify the kinetics of phase formation. Crystallization can be described by the classical theory of Johnson-Mehl-Avrami-Kolmogorov (JMAK) as a diffusion controlled growth process with a time dependent nucleation rate. A superimposed slower coarsening process allows to manipulate the crystallite size of SiC in a wide range. The rate constants and activation enthalpies of crystallization are determined and compared to the activation enthalpy of self-diffusion. This enables an insight into the role of element mobility for the growth and coarsening of crystallites. The results are discussed for Si-C-N and Si-B-C-N ceramics with different chemical composition.

## Session IV : Products I

Chairpersons : Y. Blum &amp; H.J. Kleebe

- Q-IV.1** 09:00 -Invited- METHYLENE-BRIDGED CARBOSILANES AND POLYCARBOSILANES AS PRECURSORS TO SILICON CARBIDE - FROM SiC NANOTUBES TO BULK CERAMIC OBJECTS  
**Leonard V. Interrante**(a), Michael Lienhard(b), Qing-Min Cheng, Kevin Moraes, Walter Sherwood(c) and Steve Atmur(c), (a)Chemistry Department, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, (b)NASA Glenn Research Center, MS 77-1, Cleveland, OH 44135, and (c)Starfire Systems Inc., Saratoga Technology & Energy Park, 10 Hermes Road, Malta, NY 12020, USA  
 Our research in organosilicon chemistry over the past 18 years has centered on the synthesis, study, and application of a broad class of carbosilane oligomers and polymers that contain bridging Si-CH<sub>2</sub>-Si groups. In addition to single-source CVD precursors to silicon carbide, this research has led to the development of a commercial polymer precursor to SiC (AHPCS) and SiC nanotubes, as well as various other potential applications that involve structurally modified polycarbosilanes as materials, such as low k films, liquid crystalline materials and ionic electrolytes. This talk will center on the synthesis, characterization and application of these cyclic and polymeric carbosilanes, including the use of 1,3-disilacyclobutane and other volatile carbosilanes, to prepare SiC nanotubes via CVD inside of alumina templates, the use of polycarbosilane-based co-polymers and polymer blends to prepare nanoscale and micro-phase separated ceramic composites, and the use of the commercial precursor, AHPCS, to fabricate bulk ceramic composites by Polymer Infiltration and Pyrolysis.
- Q-IV.2** 09:40 MICRO-CELLULAR POROUS CERAMICS FROM PRECERAMIC POLYMERS: FABRICATION, PROPERTIES AND APPLICATIONS  
 Paolo Colombo(a), Lisa Biasetto(b) and Enrico Bernardo(b). (a)Università di Bologna, Dipartimento di Chimica Applicata e Scienza dei Materiali, V.le Risorgimento 2, 40136 Bologna, Italy and Department of Materials Science and Engineering, The Pennsylvania State University, University Park PA 16802, USA. (b)Università di Padova, Dipartimento di Ingegneria Meccanica – Settore Materiali, via Marzolo 9, 35131 Padova, Italy  
 Cellular ceramics possess an unique combination of favorable properties, like low density, thermal conductivity, dielectric constant and high thermal shock resistance, specific strength and chemical resistance, which make them good candidates for both structural or functional applications.  
 We recently developed a novel process for obtaining micro-cellular ceramic foams with a cell size in the range ~1-100 micron starting from a preceramic polymer and sacrificial fillers. The process is simple, economical and versatile, and large bodies with various shapes can be produced. The fillers, comprised of PMMA spherical microbeads with a dimension of about 1.5, 5, 10, 25, 50 or 100 micron, were dry-mixed with a thermosetting silicone resin, and were burned out in air at 250-350°C before pyrolysis at 1200°C in nitrogen. The high temperature polymer-to-ceramic conversion yielded a highly porous SiOC ceramic, with relative density in the range 0.15 to 0.3 (bulk density ~0.3 to 0.6 g/cc), depending on the amount of microbeads introduced. The compressive strength of the microcellular foams ranged from 0.5 to about 20 MPa. Morphological investigations revealed that the cell size distribution was homogeneous. Foams with a graded cell size or density were produced by varying the PMMA microbeads' size or amount along one axis of the material. These microcellular SiOC foams are currently being tested for various applications, including shields against hypervelocity impacts (for space applications), substrates for zeolites (for sorption and catalysis applications), thermal barriers (for space applications), metal-reinforced composites (for automotive applications).
- Q-IV.3** 10:00 COMPARATIVE FABRICATION OF SiCN CERAMIC PATTERNS FROM CFL AND MIMIC TECHNIQUES  
 Kyoung-Hoon Park(a), In-Kyung Sung(a), Hong H. Lee(b), Dong-Pyo Kim(a), (a)Dept of Fine Chemical Engineering and Chemistry, Chungnam national University, Daejeon, 305-764 Korea, (b)School of Chemical Engineering, Seoul National University, Seoul, 151-742 Korea  
 The polymeric route to nonoxide ceramics offers a unique opportunity for manufacturing ceramic components such as fibers, coatings, and composites by liquid fabrication and subsequent pyrolysis.[1] Siliconcarbide (SiC) and siliconcarbonitride(SiCN) are the promising ceramic materials for microelectromechanical systems(MEMS) application in chemically and mechanically harsh condition.[2-3] In this study, SiCN ceramic patterns on the Si wafer were comparatively fabricated by CFL (Capillary Force Lithography) and MIMIC (Micromolding in Capillaries) processes and a liquid polymeric precursor containing peroxide thermal initiators. The polymeric nanoscale patterns were obtained using PDMS (Polydimethylsiloxane) mold with features in range 200~400nm, followed by thermal curing at low temperature below 90oC and high temperature pyrolysis at 800oC in nitrogen atmosphere to form the ceramic pattern. The morphology and shrinkage behavior were observed by SEM while the high temperature stability was also investigated. As a result, SiCN ceramic patterns from MIMIC were advantageous with no presence of residual layer between patterning and substrate, which does not demand extra process such as reactive ion etching. However, it turned out that the CFL technique was more secure and promising for a large area patterning.  
 1. Narula, C, K., Ceramic precursor technology and its applications, Marcel Dekker, New York, 1995 2. Yiping, L., et. al. Application of microforging to SiCN MEMS fabrication. Sensors and actuators A. 95, 143~151 (2002) 3.Mehran, M. et. al. Silicon Carbide MEMS for harsh environments. Pro. IEEE. 86, 1594 (1998)

10:20

**BREAK**

- Q-IV.4** 10:40 -Invited- **NANODEVICES THAT EXPLORE THE SYNERGIES BETWEEN PDCs AND CARBON NANOTUBES**  
**Rishi Raj** and Sandeep R. Shah, Department of Mechanical Engineering, University of Colorado at Boulder, Boulder CO 80309-0427, USA  
 It is increasingly evident that carbon-based polymer derived ceramics, e.g. silicon carbonitride, embody functional properties which are apparently equivalent to carbon nanotubes. In this work we compare the electrochemical supercapacitor behavior, and the accompanying electrochemico-mechanical actuation properties of three kinds of structures: (i) simple carbon nanotube structures, (ii) carbon nanotube structures coated with ultrathin coatings of silicon carbonitride, and (iii) silicon carbonitride by itself. These comparisons suggest the presence of monolayer graphene sheets in silicon carbonitride. If true, and it does appear to be the case, then these findings open up new scientific questions, for example how do such structures evolve from the chemical state, and how can the graphene structures be manipulated to obtain novel multifunctional properties in the PDCs?
- Q-IV.5** 11:20 **PREPARATION OF HIGH-TEMPERATURE STABLE Si-B-C-N FIBERS FROM TAILORED SINGLE SOURCE POLYBOROSILAZANES**  
 S. Bernard(a), M. Weinmann(b), D. Cornu(a), P. Miele(a), F. Aldinger(b). (a)Laboratoire des Multimateriaux et Interfaces, UMR CNRS 5615-Université Claude Bernard Lyon 1, 69622 Villeurbanne Cedex, France. (b)Max-Planck-Institut für Metallforschung, Pulvermetallurgisches Laboratorium, Heisenbergstrasse 5, 70569 Stuttgart, Germany  
 Novel ceramic materials play a major role for the development of new technical applications. Ceramic materials in the quaternary Si-B-C-N system are of great interest because of their covalent bonding providing mechanical reliability and high temperature stability in inert or oxidative atmosphere. In recent years, the polymer pyrolysis route became of increasing interest for the preparation of such ceramics. In particular, 'single source' polyborosilazanes such as  $\{B[C_2H_4SiRNH]_3\}_n$  (R = H, CH<sub>3</sub>) have been shown to be convenient preceramic polymers for the elaboration of Si-B-C-N bulk ceramics of homogeneous composition.  
 The structure of such Polymer-Derived Ceramics (PDCs) can remain amorphous above 1800°C leading to a high thermal and a high oxidation resistance. Si-B-C-N fibers are accordingly deemed to be usable at high temperature and under oxidizing conditions without a noticeable decrease of their mechanical properties. The synthesis of novel 'single source' polyborosilazanes which have rheology and thermal stability for melt-spinning process are reported in this paper. The curing process of the green fibers in non-oxidative environment and their pyrolytic conversion into high temperature-stable Si-B-C-N ceramic fibers will also be discussed.
- Q-IV.6** 11:40 **SYNTHESIS AND PROPERTIES OF POLYMER DERIVED METAL / SiCN CERAMIC MICRO- AND NANO-COMPOSITES** Adel Francis(a), Ralf Hauser(b), and Ralf Riedel(b), (a)Central Metallurgical Research and Development Institute (CMRDI), P.O.box 87 Helwan –Cairo, Egypt, (b)Darmstadt University of Technology, Institute of Materials Science, Petersenstraße 23, 64287 Darmstadt, Germany  
 Ceramics are used in engineering technologies because of their diverse structural, chemical, and functional properties. The innovative precursor based processing can lead to low-cost and flexible approaches of manufacturing of advanced ceramics. Owing to their high temperature and oxidation resistance, non-oxide polymer-derived ceramics are suitable for applications in hot and corrosive environments. Using the concept of "Active Filler Controlled Pyrolysis"[1, 2] opens up the possibility to synthesise ceramics with tailored mechanical, electrical and magnetic properties. Here we will introduce two different pathways to embed metal particles in a SiCN matrix, derived from the commercially available polysilazane Ceraset® (Kion Inc. USA):  
 1. Mixing and milling of metal powders with pre crosslinked polysilazane and subsequent pyrolysis.  
 2. Chemical reaction between low valent metal compounds such as metal carbonyl compounds with pure polysilazane followed by polymer-to-ceramic-transformation. The final products are denoted as M-SiCN with M = Fe, Co, Mn, Cr, Ti. The elemental composition, microstructure, and property relations of the M-SiCN ceramics will be discussed.  
 [1] P. Greil, "Active-Filler-Controlled Pyrolysis of Preceramic Polymers" J. Am. Ceram. Soc. 78 (1995) 835  
 [2] A. M. Tsirlin, G. I. Shcherbakova, E. K. Florina, N. A. Popova S. P. Gubin, E. M. Moroz, R. Riedel, E. Kroke, M. Steen, "Nano-structured metal-containing polymer precursors for high temperature non-oxide ceramics and ceramic fibres – syntheses, pyrolysis and properties", J. Eur. Ceram. Soc. 22 (2002)2577
- Q-IV.7** 12:00 **LUNCH**

Thursday, May 27, 2004

Afternoon

Session V : Products II

Chairpersons : R. Raj & M. Weinmann

Q-V.1 14:00 -Invited-

PRECURSORS DERIVED CERAMIC MEMBRANES

**Yuji Iwamoto**, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta-ku, Nagoya 456-8587, Japan

Microporous ceramic membranes for gas separation have increasing attention because of their promising applications at higher temperatures and in chemically severer environments compared to polymer membranes. Chemical processing via a solution route using metallorganic precursors is suitable for synthesizing microporous ceramic membranes, giving a thin layer with desired chemical composition on a porous support. In this study, novel composite membranes, nanoparticle-dispersed amorphous silica membranes have been designed and synthesized. Some metals with an affinity for hydrogen have been selected for the nanoparticles. This is expected to be essential to enhance the hydrogen permselectivity of the amorphous silica-based membranes. As our initial study, Ni nanoparticle-dispersed amorphous silica membranes were synthesized by an in-situ compositing method composed of the three main processes: 1) Preparation of a homogeneous solution precursor for the Si-Ni-O system, 2) Dip-coating of the solution precursor onto an anodic alumina support with the minimum pore diameter of 3 nm, and 3) Heat treatment at 600 °C in air followed by heat treatment at 500 °C in hydrogen flow. TEM observation revealed that a crack-free layer with a thickness of about 400 nm was homogeneously deposited on the porous support surface, and Ni-nanoparticles with a diameter of about 10 nm were found to be located mainly at the membrane surface layer with a region thickness of about 200 nm. The composite membrane exhibited H<sub>2</sub> permeance of 1.4x10<sup>7</sup> mol/m<sup>2</sup>•sec•Pa at 500 °C, and the permeability ratios of H<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>/He were measured to be 84 and 5, respectively. One possible reason for the unique hydrogen permselectivity observed in this study was thought to be explained by a synergistic effect of the plural functionalities, Ni nanoparticle-derived hydrogen affinity and molecular sieving function of amorphous silica network. At the presentation, the effects of the nanoparticle-dispersion as well as the chemical processing conditions on the hydrogen permselectivity will be discussed from a view point of a novel nanostructure design concept for developing hydrogen permselective ceramic membranes.

This work has been supported by NEDO as a part of the R&D Project on Highly Efficient Ceramic Membranes for High-Temperature Separation of Hydrogen promoted by METI, Japan.

Q-V.2 14:40

PERIODIC MESOPOROUS SiCO GLASSES FROM SOL-GEL TEMPLATING APPROACH

Bérangère Toury, Florence Babonneau, Chimie de la Matière Condensée, UPMC-CNRS, 4 place Jussieu, 75005 Paris, France

The use of bis(silylated) precursors, (RO)<sub>3</sub>Si-X-Si(OR)<sub>3</sub>, in conjunction with surfactants allows the preparation of periodic mesoporous organosilicas (PMOs). A large variety of PMOs has already been investigated. The presence of Si-O and Si-C bonds in the framework makes them very suitable as precursors for porous oxycarbide glasses. Previous studies on sol-gel derived SiCO glasses have demonstrated the unique high temperature properties of these materials in terms of mechanical strength and chemical durability. Additionally, if these materials can exhibit a periodic porous network, then they can find applications as filters, catalysts or membranes for severe operating conditions. The challenge will thus be to convert PMOs in SiCO glasses without a total collapse of the porous network during the pyrolysis treatment under inert atmosphere.

PMOs with various geometries (2D-hexagonal and also cubic Pm3n structures) have been prepared from bis(silylated) precursors and cationic surfactants as well as block-copolymers. The samples have been pyrolyzed under Argon at T=880-1000°C, and the pyrolysis intermediates analyzed by X-ray diffraction, multinuclear solid state NMR (<sup>29</sup>Si, <sup>13</sup>C and <sup>1</sup>H) and N<sub>2</sub> adsorption-desorption experiments. The mechanism for the organosilica-to-glass transformation will be discussed as well as the high temperature behavior of these porous glasses.

Q-V.3 15:00

EVALUATION OF STRUCTURE AND POROSITY CHANGES IN CARBON AEROGELS

Young-Jae Lee, R&D Center, Samsung Fine Chemicals, Co., Ltd., 103-1 Moonji-dong, Yoosung-gu, Daejeon 305-380 Korea

Organic aerogels were synthesized by sol-gel process and heated at 1000 °C in inert atmosphere, resulting in nano-structured carbon aerogels. The carbon aerogels were heated at different temperature in the absence/presence of B. Boron is known to be a unique element, which can be located in carbon structure as a substitutional element. The objectives here are to understand the effects of heat treatment and the presence of B on structure and porosity changes in carbon aerogels. This study will present the changes of crystallinity and porosity of the aerogels by heat treatment temperature (HTT) and the presence of B, and compare the results with those of typical carbon materials.

- Q-V.4** 15:20 CERAMERS – FUNCTIONAL MATERIALS FOR ADSORPTION TECHNIQUES  
Michaela Wilhelm, Christian Soltmann, Dietmar Koch, Georg Grathwohl, Keramische Werkstoffe und Bauteile, University of Bremen, Am Biologischen Garten 2/IW3, 28359 Bremen, Germany  
 Pyrolysis of preceramic polymers can be applied to prepare thermally and chemically stable materials which are to be characterized by a high porosity and large specific surface area. These properties can be properly adjusted via composition of the precursor and via thermal treatment. The resulting components are used as catalyst supports, as media for sensor applications, as membranes with selective permeability or as adsorbents. The ceramer adsorbents which are presented here are designed to operate under severe conditions when aggressive media are present and high adsorption capacities are demanded.  
 The preceramic silicon organic precursors are synthesized via hydrolysis and condensation reactions using several silanes (e.g.  $\text{RSi(OR)3}$ ) or siloxanes with different functionalities (polar or nonpolar). Additionally, filler particles as e.g. prepyrolyzed precursors are added to the polymers. During processing the pyrolysis is stopped when a hybrid state is reached and the polymer is partly converted to ceramic. The resulting material is therefore called ceramer. In this case the maximum temperature applied during pyrolysis is  $800^\circ\text{C}$  in inert atmosphere. [...] It turns out that the new ceramer adsorbents can be designed for high adsorption capacities as alternative material for activated carbon. Moreover they show a significant advantage against activated carbon as the adsorbed species (polar or nonpolar) can be easily released e.g. by heating. Therefore the ceramers are especially suitable for cyclic ad- and desorption processes as it is necessary for storage or purification applications.
- 15:40 **BREAK**
- Q-V.5** 16:00 SYNTHESIS AND CHARACTERIZATION OF BULK LUMINESCENT Si/SiO<sub>2</sub> NANOCOMPOSITES THROUGH GEL PYROLYSIS  
 P. Bettotti(a), G. Das(a), S. Modena(b), L. Pavesi(a), G. Mariotto(a), G.D. Soraru(b), (a)Dipartimento di Fisica, Università di Trento, Via Sommarive 14, 38050 Trento, Italy, (b)Dipartimento di Ingegneria dei Materiali e Tecnologie Industriali, Università di Trento, Via Mesiano 77, I-38050 Trento, Italy  
 This work describes the synthesis and characterization of bulk silica glasses containing silicon nanocrystals (Si-nc). The bulk samples were fabricated from sol-gel-derived precursors followed by pyrolysis in inert atmosphere at temperature in the range  $1000\text{--}1200^\circ\text{C}$ . The starting silicon alkoxide was triethoxysilane, which bears an Si-H functionality. Er was incorporated in the solution by using  $\text{ErCl}_3$ . Synthesis conditions ( $\text{H}_2\text{O}/\text{OEt}$  ratio) and pyrolysis parameters (maximum temperature and dwelling time) were optimized to increase the luminescence intensity.  
 The formation of Si-nc in the glass matrix was clearly indicated by the structural analysis performed using x-ray diffraction and Raman spectroscopy. From an optical point of view, the samples were transparent in the visible even though they were more than 1 mm thick. Photoluminescence experiments confirm the presence of Si-nc showing a wide emission band between 700 and 900 nm (the maximum of the emission depends on synthesis conditions). In those samples where also Er was incorporated, typical emission lines at 1.535 nm were observed whose excitation spectrum does not show any Er related resonance. This demonstrates a coupling between Er and Si-nc. Time decay measurements show Er lifetimes of several milliseconds.
- Q-V.6** 16:20 SELF ORGANISATION OF NANOCRYSTALS IN AN AMORPHOUS MATRIX THROUGH PHASE SEPARATION MECHANISM IN SOL-GEL DERIVED MATERIALS  
A. Gaudon, A. Lecomte, B. Soulestin, R. Guinebretière, A. Daurer. Science des Procédés Céramiques et de Traitements de Surface, UMR 6638. ENSCI, 47 Av. A. Thomas 87065 Limoges, France.  
 Sol-gel processing is a well-known route to control the homogeneity of oxide materials at the molecular level. This approach has been frequently used to elaborate mixed oxides at low temperature. But the sol-gel way is also known to promote the formation of non-equilibrium phases. For example in the  $\text{ZrO}_2\text{-SiO}_2$  system the existence of an amorphous phase separation prevents obtaining zircon ( $\text{ZrSiO}_4$ ) at low temperature. In this communication we will show that the phase separation occurring in the  $\text{ZrO}_2\text{-SiO}_2$  system results in the formation of nanostructured materials. The samples were prepared by mixing zirconium n-propoxide and tetraethylorthosilicate in various proportions. After gelation, a slow drying at  $60^\circ\text{C}$  allows to produce bulk xerogels. Thermal treatments at  $1000^\circ\text{C}$  induce the appearance of zirconia nanocrystals dispersed into the silica glass matrix. The appearance and growth of those particles were followed using Small Angle X-ray Scattering (SAXS). Corresponding SAXS curves present a well-defined peak related to a correlation length between zirconia nanocrystals. The relative amounts of zirconia and silica precursors and the thermal treatment parameters allow controlling the microstructure. Microstructural parameters were also characterized through transmission electron microscopy and x-ray diffraction line profile analysis.
- Q-V.7** 16:40 SiBCO CERAMICS FROM POLYBOROSILOXANES  
Verena Liebau, Ralf Hauser and Ralf Riedel, University of Technology Darmstadt, Institute of Materials Science, Petersenstr. 23, 64287 Darmstadt, Germany  
 While boron-free SiCO ceramics tend to decompose in the temperature range between  $1100$  and  $1300^\circ\text{C}$ , it has been found that the presence of boron influences the thermal stability and the crystallization behavior of these ceramics [1-4]. Polymer-to-ceramic transformation studies showed that in amorphous boron-free SiCO ceramics crystallization of cristobalite occurs at temperatures of about  $1300^\circ\text{C}$  [5]. In our study we found that boron containing SiBCO ceramics reveal no formation of cristobalite up to  $1500^\circ\text{C}$ .  
 Here we present the synthesized high temperature resistant ceramics in the SiBCO system from novel polyborosiloxanes. The synthesis and the thermal decomposition of the boron containing precursors, as well as the thermal stability of the solid phases derived therefrom are reported. The oxidation resistance, crystallization, and thermal behavior of the SiBCO ceramics are of particular interest in this study.

## LOW TEMPERATURE SYNTHETIC ROUTE FOR BORON CARBIDE

Shampa Mondal and Ajit K. Banthia, Materials Science Centre, Indian Institute of Technology, Kharagpur-721302, India

Boron carbide is a highly refractory material that is of great interest for both its structural and electronic properties. Of particular importance are its high-temperature stability, high hardness, high cross section for neutron capture, and excellent high-temperature thermoelectric properties. This combination of properties gives rise to numerous applications, including uses as an abrasive wear-resistant material, ceramic armor, a neutron moderator in nuclear reactors, and, potentially, for power generation in deep-space flight applications. Boron carbide powders can easily be made by carbothermal reduction of boric oxides at high temperatures, but the formation of pure boron carbide in processed forms, such as films and fibers, is difficult. As an alternative to high-temperature powder techniques, there has recently been great interest in the development of polymer precursors to ceramic materials. The aim of the present work is to develop a cost effective and low temperature manufacturing process for boron carbide from cheap and easily available raw materials. The initial objective of our research is the preparation and evaluation polymers, which would serve as precursors for boron carbide. The polymeric precursor is synthesized by the reaction of boric acid and polyvinyl alcohol that on pyrolysis at 4000C and 8000C gives boron carbide. The polymeric precursor and its pyrolyzed products are characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). X-ray diffraction shows that boron carbide (B<sub>4</sub>C) obtained from this method has orthorhombic crystal structure. It is a unique low temperature (~ 400°C) synthetic route for boron carbide.