

Improved durability of Si/B/N/C random inorganic networks

T. Jäschke, M. Jansen*

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany

Available online 15 September 2004

Abstract

The inherent high temperature durability as well as the hardness of random inorganic networks composed of Si, B, N and C, can be raised through the incorporation of rigid structural elements (e.g. borazine rings) as well as through an increase of the carbon content. This has been shown by comparison of the high temperature durabilities and micromechanical properties of newly synthesized Si/B/N/C ceramics derived from different acyclic and cyclic single source precursors. Crosslinking of these specially designed monomers with methylamine provides highly homogeneous preceramic polymers, in which the predetermined structural features of the molecular precursors are embedded. Subsequent pyrolysis and calcination up to 1500 °C converts the polymers into all-inorganic amorphous silicon boron carbonitrides. Depending on the constitution of the precursors, the as-obtained materials exhibit a combination of a high carbon content together with borazine rings embedded into the covalent network. Comparing the high temperature stability, hardness and stiffness of the synthesized ceramics, the best performance is achieved when carbon rich borazine derivatives are employed as single source precursors. Thus, the high temperature durability can be raised up to at least 2000 °C, and, at the same time, the microhardness and elastic modulus is maximized up to 14.5 and 127 GPa, respectively. The new materials have been characterized by IR spectroscopy, elemental analysis, XRD, SEM, DTA/TG, and by nanoindentation. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Single source precursors; Preceramic polymers; Silicon boron carbonitrides; Non-oxide ceramics

1. Introduction

The outstanding thermal, chemical and mechanical properties of random inorganic networks based on the quaternary system Si/B/N/C have caused growing interest in such high performance materials in recent years.¹ Especially the superior high temperature durability even under oxidizing conditions, combined with low densities make these ceramics highly attractive for applications under extreme conditions like in heat engines (in particular turbines), as well as in aviation and aerospace.² In recent years, much work has been done in order to further enhance the advantageous intrinsic properties of Si/B/N/C ceramics, and also to understand the relationships between the structure of the amorphous covalent networks and their material properties.³ Clearly, there exist many open questions concerning this rather young class of materials, stimulating an ongoing development of these multinary non-oxide ceramics. Unlike multinary oxide ceramics, the preparation of silicon boron carbonitrides can-

not proceed via conventional solid-state reactions, or through melting processes, starting from the pure elements or the respective binary compounds. Due to incongruent melting behavior of the nitrides and carbides of silicon and boron, and since these cationic elements exhibit very low self-diffusion coefficients^{4,5} the only feasible approach known so far is the 'polymer route'.^{6–8} Following this reaction path, one or more metalorganic monomers are polymerized (usually by polycondensation reactions) to yield preceramic polymers which are then pyrolyzed at high temperatures until a pure inorganic solid remains.

As a crucial point, the performance of these multinary non-oxide ceramics depends strongly on the homogeneity of the preceramic polymer. Spatial inhomogeneities at the polymer stage have to be avoided, since they induce phase separation and decomposition of the multinary ceramic into its border phases during pyrolysis or thermal load. Thus, cocondensation of different molecular precursors is unfavorable, because different velocities in the substitution reactions of the individual molecular species usually lead to clustering of one cationic species. Instead, highly homogeneous preceramic polymers are obtained using specially designed

* Corresponding author. Tel.: +49 711 689 1501; fax: +49 711 689 1502.
E-mail address: M.Jansen@fkf.mpg.de (M. Jansen).

monomers, so-called ‘single source precursors’, which already contain the electropositive elements in the ratio desired for the final ceramic linked together via a carbon or nitrogen atom.⁹ As both cations are fixed to the bridging group by strong covalent bonds the entire backbone of the precursor survives the crosslinking procedure, leading to a preceramic polymer with a homogeneous distribution of the constituting elements on an atomic scale.¹⁰ As can be seen from the thermal stabilities of Si/B/N/C materials, the incorporation of carbon into the random network increases the thermal durability significantly.^{11,12} It is reasonable that an additional improvement of the high temperature stability can be achieved by further increasing the carbon content of the silicon boron carbonitrides. However, it should also be considered that a higher amount of carbon incorporated affects the good intrinsic oxidation resistance of Si/B/N/C ceramics, thus lowering their potential for applications at elevated temperatures under atmospheric conditions.

As an option, one could try to reinforce and stabilize the amorphous network additionally through the incorporation of rigid structural elements, which could act as inhibitors suppressing conformational changes inside the random network. As a crucible precondition, such building units have to be thermally durable, because they must not decompose at elevated temperatures for which the material is designed. An atom group which fulfills these requirements of rigidity and stability nearly perfectly is the six-membered planar borazine ring, being extremely inflexible and stiff due to strong p_{π} – p_{π} interactions between boron and nitrogen. By polymerizing suitably functionalized borazine derivatives to serving as single source precursors, it should be possible to incorporate such units into the preceramic polymer, and thus into the final ceramic.

In this contribution we present the synthesis and characterization of new amorphous ceramics in the quaternary system Si/B/N/C. Starting from acyclic and cyclic single source precursors, random inorganic networks are prepared with combinations of different carbon contents and borazine rings incorporated.

2. Experimental

2.1. General procedures

All reactions were carried out under inert atmosphere (argon) in rigorously dried reaction apparatus and solvents. Hexane was distilled from CaH_2 (Merck). Commercially available methylamine (Messer Griesheim) was used without further purification.

2.2. Characterization techniques

IR spectra were recorded between 400 and 4000 cm^{-1} on a Bruker IFS 113v FT-IR spectrometer, using KBr pellets.

Scanning Electron Microscopy. SEM pictures of the ceramics were obtained from a Philips XL30 TMP scanning electron microscope.

Thermal degradation of the preceramic polymers has been studied by means of simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in a Netzsch STA 409 (heating rate 10 K min^{-1} , argon flow) equipped with a Balzers QMS421 quadrupole mass spectrometer. The oxidation behavior of the synthesized ceramics was checked by heating the samples in a flow of pure oxygen up to $1300\text{ }^{\circ}\text{C}$ at a rate of 10 K min^{-1} .

Quantitative analyses of nitrogen and oxygen have been carried out simultaneously in a Leco TC-436 hot gas extraction analyzer, whereas carbon was measured in a Leco C-200 hot gas extraction analyzer. Silicon and boron were quantified by means of ICP-OES in an Arl 3580B spectrometer after digestion of the ceramic samples using a mixture of $\text{HF}/\text{HNO}_3/\text{HCl}$.

The macroscopic density of the as-obtained ceramic material was measured using an automatic Micromeritics AccuPyc 1330 helium pycnometer.

Powder X-ray diffraction patterns were recorded on a STOE Stadi-P diffractometer in transmission mode with Debye-Scherrer geometry, with germanium-monochromated $\text{Cu K}\alpha$ radiation. The ceramic powder samples were placed in a glass capillary ($\varnothing 0.5\text{ mm}$) and diffraction patterns were collected between 4° and 76° in 2θ using a position sensitive detector (PSD).

The microhardness and elastic modulus of the ceramic powders were measured using the MTS Nano Indenter XP with a Berkovich triangular pyramid diamond indenter tip. Eleven to twelve indentations per sample were carried out, distributed on several grains, depending on the grain size. At a constant deformation rate of 0.05 s^{-1} and a penetration depth of up to 500 nm the load applied to the sample was recorded as a function of displacement. The powder samples were embedded in epoxy resin and then polished using fine diamond paste. The as-obtained data was statistically analyzed using the computer program ‘Analyst’.

2.3. Synthesis of the precursor molecules

The acyclic single source precursors $\text{Cl}_3\text{Si-CH}_2\text{-BCl}_2$ (TSDM) and $\text{Cl}_2(\text{CH}_3)\text{Si-CH}_2\text{-BCl}_2$ (DSDM) were synthesized according to a recently published procedure.¹³ By reacting these two molecules with hexamethyldisilazane, the new precursors $[\text{B}\{\text{CH}_2(\text{SiCl}_3)\}\text{NH}]_3$ (TSMB) and $[\text{B}\{\text{CH}_2(\text{SiCl}_2\text{CH}_3)\}\text{NH}]_3$ (DSMB) were obtained, respectively.¹⁴

2.4. Preparation of the preceramic polymers

A solution of 13.9 g (61 mmol) TSDM or 11.7 g (56 mmol) DSDM or 15.9 g (30 mmol) TSMB or 16.3 g (35 mmol) DSMB in 150 ml hexane is added dropwise to a solution of 100 ml methylamine (69.4 g , 2.234 mol) in 150 ml hex-

Download English Version:

<https://daneshyari.com/en/article/9777954>

Download Persian Version:

<https://daneshyari.com/article/9777954>

[Daneshyari.com](https://daneshyari.com)