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Institutions: Max Planck Society

Published on: 01 Nov 1993 - Journal De Physique Iv (EDP Sciences)

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H. SchÖnfelder, F. Aldinger, R. Riedel. Silicon carbonitrides - A novel class of materials. Journal de Physique IV Proceedings, EDP Sciences, 1993, 03 (C7), pp.C7-1293-C7-1298. 10.1051/jp4:19937199 . jpa-00251832

HAL Id: jpa-00251832

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Submitted on 1 Jan 1993

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Silicon carbonitrides - A novel class of materials

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Abstract

Silicon carbonitride monoliths derived from polymer powder compacts via polymer pyrolysis represent a new class of structural ceramic materials due to the complete coalescence of the powder particles during polymer decomposition and the formation of a uniform ceramic matrix free from any grain boundaries or secondary phases. The submicron pore channel system penetrating the material can be minimized in volume by infiltration of liquid polysilazane solution or by post-HIPing so that relative densities of 96 % can be reached. The monoliths are oxidation resistant up to 1600 °C in air due to the formation of a highly pure silica oxidation layer and they exhibit a creep rate of $1 \cdot 10^{-6} \text{ s}^{-1}$ at 1650°C and 30 MPa load. Initially x-ray amorphous silicon carbonitride can be crystallized in nitrogen or in air to form $\text{Si}_3\text{N}_4/\text{SiC}$ or $\text{Si}_3\text{N}_4/\text{SiC/C}$ nanocomposites.

Experimental (fig. 1)

Fusible polyhydridomethylsilazane $[\text{CH}_3\text{SiH}_2\text{NH}]_m[(\text{CH}_3)_2\text{SiNH}]_n$ with a molecular weight distribution of 900 - 1100 is thermally crosslinked at 400 °C for 2 h under argon atmosphere and for 1 h under vacuum ($5 \cdot 10^{-3}$ mbar). The resulting infusible foam is ball milled and sieved to the desired particle size distribution and then cold isostatically pressed (640 MPa) to form a polymer powder compact. Subsequent heating to 1000°C in a quartz glass tube under argon atmosphere induces the decomposition of the polymer and the formation of monolithic silicon carbonitride [1]. In order to increase the density of the monoliths a solution of 70 % polysilazane in THF can be infiltrated into the open pore channel system and pyrolysed to deposit additional matrix material. In this technique, the samples are evacuated for 30 min ($1 \cdot 10^{-2}$ mbar) while the solution is cooled to - 73°C in order to reduce the vapour pressure. Then the samples are put on top of the viscous

solution and start submerging while the solution is heated to room temperature. After 1 h of infiltration the samples are taken out of the solution and pyrolysed as before. Alternatively, silicon carbonitride pyrolysed to 800 °C only is encapsulated in glass under vacuum ($1 \cdot 10^{-2}$ mbar) and hot isostatically pressed at 200 MPa and 1100°C for 1 h.

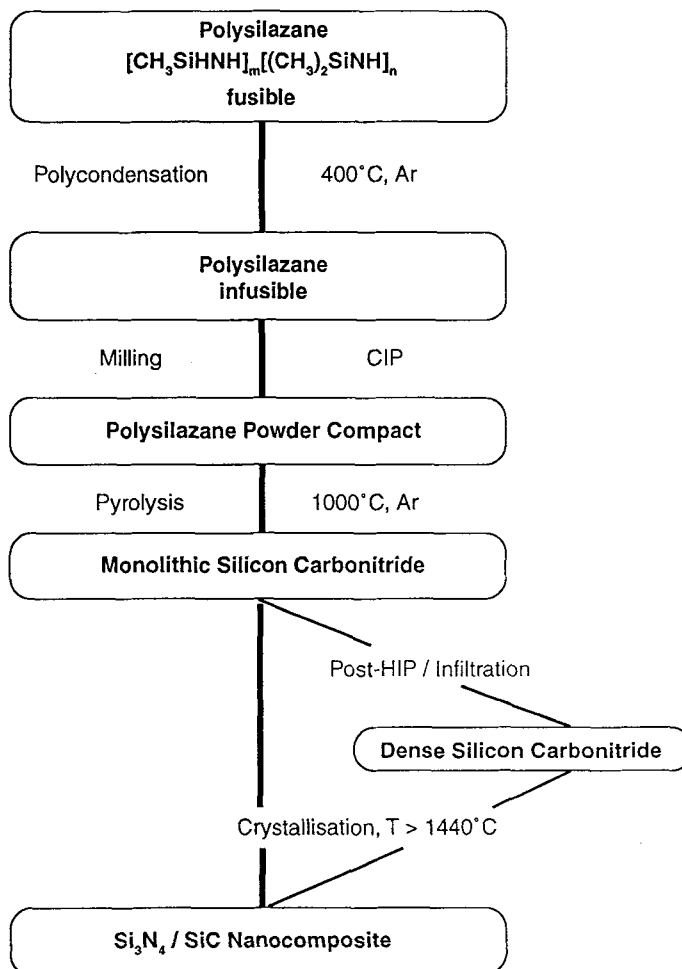


Fig.1 : Schematic experimental procedure for the preparation of silicon-based nonoxide ceramics derived from polysilazane.

Results and Discussion

Densification of the novel material starts at the polymer powder stage. Analogously to ceramic powder, polysilazane powder can be cold isostatically pressed to tough greenbodies. However, extremely high green densities of 84 % can be reached due to plastic deformation of the powder particles and no binders are necessary. During pyrolysis the polysilazane is decomposed to form x-ray amorphous, non-stoichiometric silicon carbonitride of the formal composition $\text{Si}_{3+x}\text{N}_4\text{C}_{x+y}$ ($x, y \geq 0$). This ceramization process is caused by the release of methane and hydrogen between 600 and 800°C and by simultaneous particle coalescence forming a uniform ceramic matrix which is penetrated by a continuous submicron pore channel system (fig. 2). Relative sample densities increase up to 93 % and also larger parts stand the linear shrinkage of 27 % without crack formation (fig. 3).

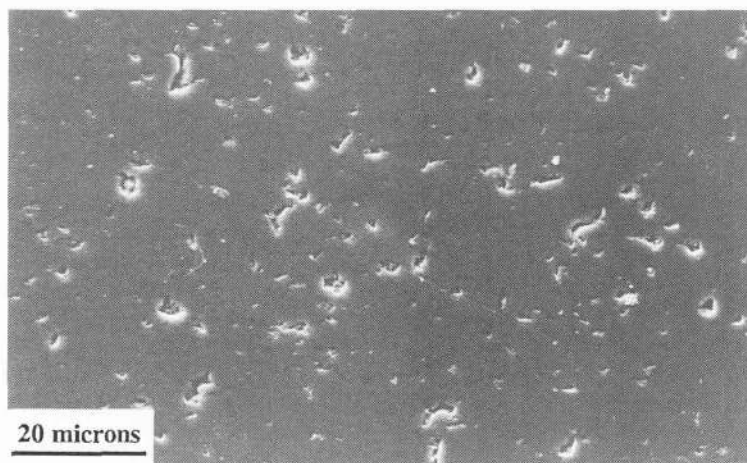


Fig. 2 : SEM micrograph of the uniform Si-C-N matrix and isolated pores interconnected by a continuous submicron pore channel system.

The coarseness of the open pore channel system can be adjusted by means of the polymer particle size distribution. A coarse powder yields a pore radius distribution maximum near 1 micron while a fine powder yields a distribution maximum at 75 nm (fig. 4). Densities between 88 and 93 % are attainable this way. In order to further reduce the porosity the open pore channel system can effectively be infiltrated by liquid polysilazane solution which deposits additional matrix material upon pyrolysis. After three infiltrations an initial relative density of 90 % can be increased to 96 %.

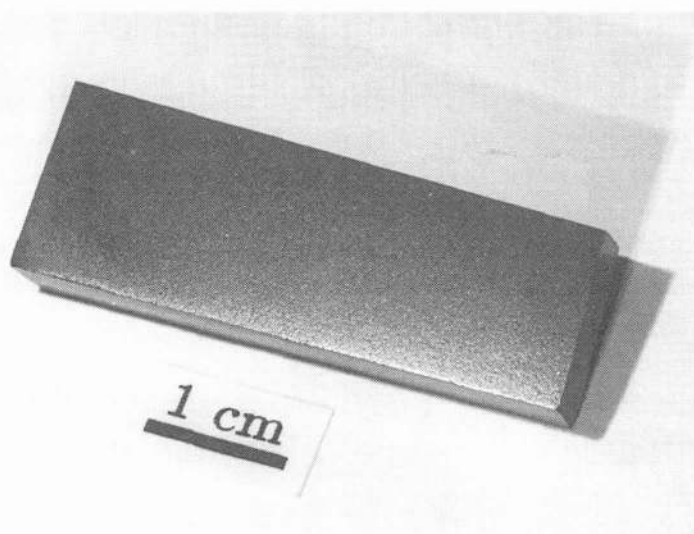


Fig. 3 : Monolithic silicon carbonitride part.

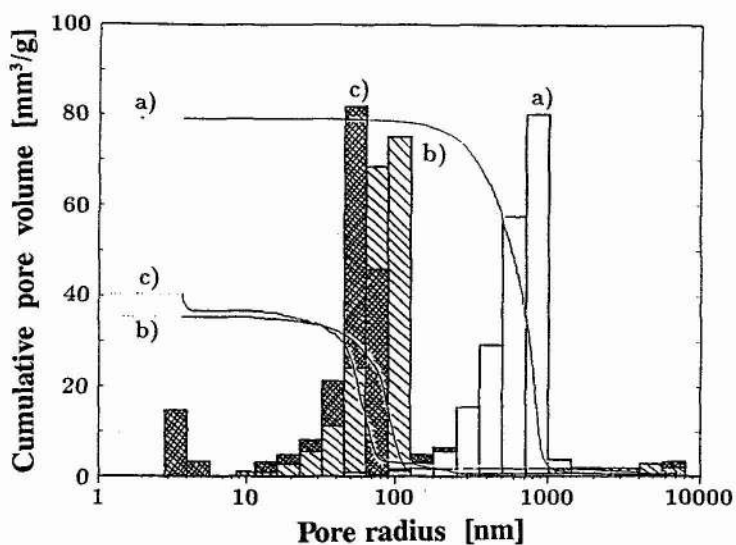


Fig. 4 : Pore radius distributions of silicon carbonitride pyrolysed from polysilazane powder with (a) coarse, (b) medium-size, and (c) fine particle size maximum.

First data on the mechanical and thermal properties show that silicon carbonitride reaches a Vickers hardness of 12 GPa and a 4-point bending strength of 175 MPa with maximum values of 245 and 375 MPa. Due to the absence of grain boundaries and oxidic sintering aids the creep rate is as low as $1 \cdot 10^{-6} \text{ s}^{-1}$ at 1650°C and 30 MPa load [2]. For the same reasons the material is highly

oxidation resistant. Weight gains after 24 h of isothermal oxidation at 1000 - 1400 °C are below 1% and the oxidation rates are asymptotically approaching zero (fig. 5). Due to the small pore channel radii of 75 - 100 nm Knudsen flow of the air inside the pore channels becomes effective [3]. In this gas flow regime the diffusivity D_K of oxygen increases with the square root of the temperature T :

$$D_K = \frac{4}{3} r \left(\frac{2RT}{\pi M} \right)^{\frac{1}{2}}$$

r : pore channel radius

R : gas constant

M : mass of transported species

As the rate of the initial oxidation reaction between oxygen and silicon carbonitride to form silica increases exponentially with temperature, oxygen consumption at the pore channel walls is faster than oxygen gas diffusion to the interior of the sample. Thus the pore channel mouths are preferentially thickened until they completely seal the pore channels resulting in a strong reduction of the total surface area being oxidized. Most important, however, the low diffusion coefficient of oxygen in pure silica of 10^{-6} - 10^{-11} cm^2s^{-1} [4] leads to a sharp decrease of the oxidation rate especially at higher temperatures (fig. 5). At lower temperatures the transition from reaction controlled to diffusion controlled oxidation is less pronounced as it takes more than 24 h to be complete.

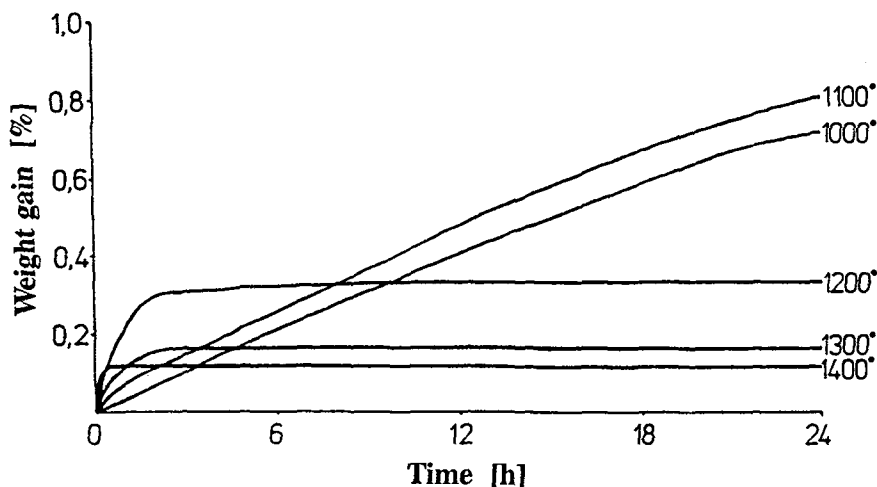


Fig. 5 : Weight gain versus time during isothermal oxidation in air.

Within the nonstoichiometric system $\text{Si}_{3+x}\text{N}_4\text{C}_{x+y}$ ($x, y \geq 0$) the thermodynamically stable phases at 1 bar nitrogen pressure and $T \leq 1440^\circ\text{C}$ are Si_3N_4 , SiC and graphite. However, after heat treatment of 50 h at 1400°C the amorphous state is still retained metastable. Electron spectroscopic imaging (ESI) based on EELS shows no phase separations within a resolution of 20 angstrom and confirms the completely amorphous structure of silicon carbonitride. Above 1440°C , some of the silicon bonded to nitrogen within the amorphous network reacts with carbon to form silicon carbide and nitrogen gas. This reaction is accompanied by a weight loss of 17 % in the solid phase and a significant increase of porosity to 30 %. Simultaneously, the crystallisation of β -SiC and α - Si_3N_4 is induced. A totally different process takes place when amorphous silicon carbonitride is crystallized in air. Due to the formation of the highly pure silica layer by surface oxidation of the monoliths, nitrogen diffusion is inhibited. Thus no decomposition reaction and no porosity increase occurs. In contrast, sealing of the pore channel mouths by SiO_2 eliminates the open porosity. Whereas at 1500°C the material is still largely amorphous, α - Si_3N_4 and α -SiC start to crystallize at 1600°C . Hence, a monolithic $\text{Si}_3\text{N}_4/\text{SiC}/\text{C}$ nanocomposite material has been created that is oxidation resistant up to 1600°C in air.

Conclusion

The results exhibit that two types of materials can be processed by means of the technique described above:

1. Amorphous silicon carbonitride produced at temperatures as low as 1000°C , and
2. $\text{Si}_3\text{N}_4/\text{SiC}/\text{C}$ nanocomposites with an oxidation resistance of up to 1600°C in air.

The relative densities of up to 93 % of the synthesized silicon carbonitride can be increased by liquid infiltration or post-HIPing to 96 %.

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