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Sintered silicon nitride/nano-silicon carbide materials based on preceramic polymers and ceramic powder

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Abstract

A flexible method is presented, which enables the fabrication of porous as well as dense Si_3N_4/nano-SiC components by using Si_3N_4 powder and a preceramic polymer (polycarbosilazane) as alternative ceramic forming binder. The SiCN polymer benefits consolidation as well as shaping of the green body and partially fills the interstices between the Si_3N_4 particles. Cross-linking of the precursor at 300 °C increases the mechanical stability of the green bodies and facilitates near net shape machining. At first, pyrolysis leads to porous ceramic bodies. Finally, subsequent gas pressure sintering results in dense Si_3N_4/nano-SiC ceramics. Due to the high ceramic yield of the polycarbosilazane binder, the shrinkage during sintering is significantly reduced from 20 to 15 lin.%. Investigations of the sintered ceramics reveal, that the microstructure of the Si_3N_4 ceramic contains approx. 6 vol.% nano-scaled SiC segregations, which are located both at the grain boundaries and as inclusions in the Si_3N_4 grains.

Keywords: Si_3N_4; Nano-SiC; Precursors-organic; Nanocomposites; Sintering; Microstructure-final

1. Introduction

Silicon nitride ceramics exhibit high mechanical strength and excellent fracture toughness.[1,2] A further improvement of the mechanical properties at room as well as at high temperatures is anticipated on Si_3N_4 materials with nano-scaled SiC segregations.[3–6] These so-called nanocomposite materials, which Niihara et al. developed two decades ago,[3] are fabricated by hot pressing of amorphous SiCN powders. However, the production of the amorphous SiCN powders by processes like the pyrolysis of preceramic polymers,[7,8] CVD,[3,9] SHS[10] or plasma synthesis[11] is difficult and complex.

The processing of Si_3N_4/SiC nanocomposites with beneficial microstructure and properties can be improved by seeding of a conventional Si_3N_4 powder with a smaller amount of amorphous SiCN powders. During sintering of the Si_3N_4, the SiCN separates into nanocrystalline Si_3N_4 and SiC. Typically, the resulting composites consist of elongated, micro-scaled Si_3N_4 grains and up to 10 vol.% nano-scaled SiC segregations, which are located both within the Si_3N_4 host grains and in the grain boundary glassy phase.[4,5] These SiC segregations can act as a reinforcing phase, which increases the bending strength, the fracture toughness and the creep behaviour at high temperatures.[3,5,11,12]

Another way of fabricating Si_3N_4/SiC nanocomposites is the mixing of crystalline Si_3N_4 and SiC nanopowders. However, the homogeneous dispersion of the submicron powders is difficult, and severe agglomeration problems are observed frequently.[12,13] Furthermore, due to the strong crystal growth during sintering, these nanocomposites show a coarser microstructure in comparison to the Si_3N_4/SiC materials seeded with amorphous SiCN.[12,13] These effects usually decrease the mechanical properties of the composites.[12,13]

The main intent of previous investigations on Si_3N_4/SiC composites was to improve the room as well as high temperature properties of the Si_3N_4 ceramic. However, for both the conventional Si_3N_4 and the Si_3N_4/SiC nanocomposite materials, the debinding effort and the high shrinkage during sintering are

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Table 1
Elemental composition of the pure polycarbosilazane ABSE and the resulting ceramic material after pyrolysis and gas pressure sintering.

Heat treatment	Empirical formula	Crystalline phases	Free carbon content (mol%)	Ceramic yield (wt.%)	Density (g/cm^3)
Polymer state	$SiNC_2H_6$	–	–	–	1.1
1000 °C/0.1 MPa N_2	$SiN_{0.9}C_{1.5}O_{0.25}H_{0.1}$	–	31	72	2.4
1800 °C/1 MPa N_2	$SiN_{0.08}C_{0.95}O_{0.01}$	β-SiC	–	56	3.2

major problems and make the fabrication extensive and difficult, especially for large ceramic components.

The intention of this work was to develop a processing method, which not only allows the fabrication of Si_3N_4/SiC nano-composites, but also offers the potential to improve the manufacturing of ceramic components in an industrial scale. The combination of a Si_3N_4 powder with a polycarbosilazane instead of an organic binder should be a suitable method to realize these aims. The Si_3N_4 powder particles can be coated homogenously with the preceramic polymer by industrial applicable processes like fluidized bed granulation. In comparison to the use of the amorphous SiCN powders prepared from the precursor an extensive processing like separate pyrolysis, milling, sieving, and mixing with the Si_3N_4 powder is not necessary. Additionally, the alternative ceramic forming binder benefits both the consolidation and shaping, which is also an advantage over the conventional powder technologies for the processing of Si_3N_4 ceramics. Subsequent pyrolysis of the polycarbosilazane binder leads to an amorphous SiCN phase, which partially fills the interstices between the Si_3N_4 particles and reduces the porosity in the resulting porous ceramic bodies.[14,15] During sintering, the homogeneously distributed SiCN phase should lead to the formation of nano-scaled SiC segregations within the Si_3N_4 ceramic. To identify and localize these nano-segregations and to characterize the microstructure as well as the chemical composition of the sintered ceramics comprehensive investigations are necessary. The formation of the SiCN ceramic from the polycarbosilazane binder offers also the potential to reduce the sinter shrinkage of the Si_3N_4 ceramic. Therefore, the influence of the SiCN binder on the shrinkage and the porosity after pyrolysis and gas pressure sintering is studied. Investigations of the green bodies, machinability tests and the manufacturing of prototypes should indicate, whether the Si_3N_4 powder/SiCN precursor method is suitable for the industrial fabrication of complex shaped Si_3N_4 components.

2. Experimental

The polycarbosilazane ABSE (ammonolysed bis(dichloromethylsilyl)ethane) is synthesized in toluene as described elsewhere for silazanes.[16,17] The synthesis yield of the colourless, meltable and soluble precursor is approx. 75 wt.%. Table 1 shows that the ceramization of the precursor at 1000 °C (N_2 atmosphere) results in an amorphous SiCN-ceramic (ceramic yield 72 wt.%). At temperatures above 1400 °C, the SiCN at first crystallizes to the thermodynamically stable phases Si_3N_4, SiC and free carbon.[18] At slightly higher temperatures,[19] the decomposition of the Si_3N_4 and the simultaneous reaction with the free carbon phase according to equation 1 occurs, leading to SiC. After sintering at 1800 °C, mainly crystalline β-SiC has been formed with a ceramic yield of 56 wt.%.

$$Si_3N_4(s) + 3C(s) \rightarrow 3SiC(s) + 2N_2(g) \quad (1)$$

As powder component, Si_3N_4 with a mean particles size (d_{50}) of 650 nm and a specific surface area of 7 m^2/g was used, which already contains 10 wt.% of rare earth and transition metal oxide additives necessary for the liquid phase sintering.

The processing of the ceramic components started with the fabrication of the Si_3N_4 powder/polycarbosilazane precursor mixture by a granulation process described elsewhere.[20,21] The precursor forms an homogeneous coating on the Si_3N_4 powder as well as connects the powder particles with each other. The resulting pourable and non-dusting granulate exhibit a mean granule particle size (d_{50}) of approx. 70 μm and a composition of 80 wt.% Si_3N_4 powder with 20 wt.% polycarbosilazane (42.2 vol.%).

Subsequently, the Si_3N_4/polycarbosilazane granulates were consolidated by uniaxial pressing at 140 MPa to discoidal specimens with 30 mm in diameter and a thickness from 12 to 14 mm. The specimens were thermally crosslinked in a tube furnace at 300 °C (RO 10/100, Heraeus, Hanau, Germany) under continuous nitrogen gas flow (200 cm^3/min). After ceramization of the precursor binder at 1000 °C (N_2 atm.), subsequent liquid phase sintering was accomplished in a gas pressure sinter furnace (FPW 7038, FCT Systeme GmbH, Rauenstein, Germany). To inhibit the thermal decomposition of silicon nitride and to facilitate densification, between 1700 and 1800 °C the nitrogen pressure is raised from 0.2 to 1 MPa.

Dimensional changes and mass losses of the specimens were measured after pyrolysis and gas pressure sintering. From this data, bulk density and shrinkage of the samples were calculated. Specimens powdered with a vibration cup mill (pulverisette 9, Fritzsch GmbH, Idar-Oberstein, Germany) were used for the determination of the skeletal density by Helium pycnometry (Accu Pyc II 1340, Micromeritics Instrument Corp., Norcross, GA, USA). From the difference between the skeletal and the bulk density data, the porosity of the specimens after pressing, pyrolysis and gas pressure sintering was calculated.

The elemental composition of the powdered samples was analyzed at the Pascher Microanalytical Laboratory (Remagen, Germany). The phase composition was investigated with a Philips Xpert X-ray diffractometer (Co anode). Raman spectroscopy measurements were performed with a BX 41 spectrometer (Olympus GmbH, Hamburg, Germany), operating with a HeNe laser (wavelength 632.8 nm) and a beam of 150 μm in diameter.