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Journal of the European Ceramic Society 30 (2010) 759–767

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Processing and mechanical properties of Si_3N_4 composites employing polymer-derived SiAlOC as sintering aid

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Received 14 March 2009; received in revised form 6 August 2009; accepted 13 August 2009
Available online 1 October 2009

Abstract

Silicon nitride ceramics have been densified with polymer-derived SiAlOC sintering aid. Dense samples were prepared at relatively mild temperatures (1600 °C) from blends with 30 wt.% of pyrolysed SiAlOC additives. Decreasing the SiAlOC aid content to 15 wt.% resulted in porous Si_3N_4 samples (∼85% rel. density). The properties of dense samples were influenced by the remaining SiAlOC glass ($HV = 15.5$ GPa, $K_{IC} = 4$ MPa m$^{1/2}$). Increasing the sintering temperature to 1780 °C for 5 min significantly changed the phase composition and properties of the composites. The major phase was O′-sialon in the sintered samples. Additional annealing of the samples at 1530 °C for 16 h further decreased the amount of the residual glassy phase and consequently affected the mechanical properties. The Vickers hardness of dense samples was 18.5 GPa and the fracture resistance ranged between 4.0 and 4.5 MPa m$^{1/2}$. The compressive creep test (1400 °C/100 MPa/24 h) of the SNA30-A sample sintered at 1600 °C for 30 min without an additional crystallisation step showed a promising low creep rate of 8.6×10^{-8} s^{-1}. Further improvement of creep resistance is expected for the crystallised samples.

Keywords: Precursor-organic; Composites; Creep; Spectroscopy; Oxynitrides

1. Introduction

Conversion of polysilazanes, polycarbosilazanes and polysiloxanes to dense ceramic fibres and foams has been intensively studied in the last decades.[1–4] However, the preparation of dense bulk ceramics from polymer-derived precursors is still a matter of research owing to the attractive shaping properties and low fabrication temperatures.[5] Amorphous bulk polymer-derived ceramics (PDCs) with interesting mechanical properties were prepared by warm pressing.[6,7] Preparation of a bulk crystalline body from polymer precursor, even with high ceramic yield of 85%, is still a problem because the polymer-to-ceramic conversion and the crystallisation of amorphous PDCs is accompanied by intrinsic shrinkage, serious cracking and pore formation. For that reason, crystalline reactive fillers were often used for the preparation of bulk PDCs.[4,8]

Among organosilicon polymers recently the polysiloxanes have been more intensively studied from the wide range of silicon-based polymer ceramic precursors because they can be handled in air, contrary to the oxygen and humidity sensitive polysilazanes.[9–12] Silicon oxycarbide (SiOC) is produced from polysiloxanes by crosslinking and pyrolysis. The incorporation of carbon into silicate glasses strengthens the molecular structure of the glass network, and thereby, improves the thermal and mechanical properties of SiOC glass.[3] By further heat-treatment, complex nanostructures are formed by phase separation in SiOC glass, in which nanocrystalline SiC, free carbon and remaining amorphous SiOC coexist.[14–17] These materials have exceptional properties, such as low creep rate and high thermal stability. Especially the excess free carbon phase plays an important role in the stability of amorphous and nanocrystalline phases.[13,18–20]

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doi:10.1016/j.jeurceramsoc.2009.08.014

Table 1
Starting composition of samples and used sintering conditions.

Sample	Composition			Sintering conditions				
	Si_3N_4 (wt.%)	SiAlOC (wt.%)	Heating rate (°C/min)	Dwell at				Cooling rate (°C/min)
				1400 °C (min)	1600 °C (min)	1780 °C (min)	1530 °C (min)	
SNA30-A	70	30	20	30	30	–	–	30
SNA30-C	70	30	20	30	30	5	–	30
SNA30-D	70	30	20	30	30	5	960	30
SNA15	85	15	20	30	30	5	–	30

The basic silicon oxycarbide matrix can be doped by different elements, e.g. Al, Zr or Hf, having high affinity to oxygen or carbon, and improve the properties of SiOC.[3,21–23] Depending on the dopant composition and its volume fraction, the properties of SiOC can be varied in a rather wide range.

There are several reports on application of PDCs as a binder for crystalline ceramic powders.[24–27] However, this work is focused on the preparation of dense Si_3N_4/SiAlOC composites, where polymer-derived SiAlOC serves as a sintering aid. In comparison to Si_3N_4 materials densified with common crystalline oxide additives (Al_2O_3, MgO, CaO, RE_2O_3, etc.) at temperatures 1750–1800 °C for 1–2 h, the expected advantage of applying amorphous PDCs as sintering aid is the lower sintering temperature ($t_s < 1650\,°C$) and shorter holding time ($\tau < 40$ min). For that reason the main goal of this work is to fabricate Si_3N_4/SiAlOC-based ceramics with high density at temperatures below 1650 °C and with mechanical properties comparable to conventionally prepared alumina containing Si_3N_4 ceramics at higher temperatures. Due to the expected partial decomposition and/or crystallisation of the SiAlOC phase above 1500 °C, thermodynamic analysis of the studied system was carried out together with dilatometric measurements prior to the sintering experiments. The microstructure, phase composition and some room temperature mechanical properties (HV, K_{IC}) of dense Si_3N_4/SiAlOC samples were evaluated. First results on the compressive creep resistance of the ceramic composite sintered at 1600 °C under 100 MPa load are also reported.

2. Experimental procedure

A commercial α-Si_3N_4 (SN-E10, Ube Industries, Japan) and in-lab prepared polymer-derived SiAlOC precursors (TU Darmstadt, Germany) have been used for the preparation of the starting mixtures. The SiAlOC precursor was synthesized by sol–gel method from poly-methylsilsesquioxane (MK polymer, Wacker-Bensil GmbH; Burghausen, Germany) with 23.6 wt.% of alumatrane (ABCR GmbH, Germany) in isopropanol solvent. The mixture was crosslinked and pyrolysed in a quartz tube up to 1100 °C in argon atmosphere for 2 h. The detailed process for the preparation of amorphous SiAlOC used in this work is described by Harshe et al.[28] The final composition of the pyrolysed polymer-derived sintering aid was $Si_{1.00}Al_{0.11}O_{1.90}C_{0.49}$. According to this composition, the crystalline product composed of SiC, SiO_2 and Al_2O_3 should contain 6.4 wt.% free carbon.

The Si_3N_4 matrix powder and pyrolysed SiAlOC additives were mixed in weight ratios 85:15 (samples SNA15) and 70:30 (samples SNA30). The mixtures were mechanically activated by high energy milling (Pulverisette 6, Fritsch, Germany) for 90 min in argon atmosphere. The starting powder mixtures passed through a 42 μm sieve were pressed into disks of 12 mm diameter with a uniaxial pressure of 100 MPa. The samples were densified by hot-pressing under a load of 30 MPa in static $N_2 + CO$ atmosphere. BN powder bed was used to minimize the possible reaction with the graphite die at elevated temperatures. The sample compositions and applied sintering conditions are listed in Table 1.

Densities of sintered samples were measured by the Archimedes method in mercury. Samples were cut, polished and etched in $CF_4 + O_2$ gas mixture (Plasma barrel etcher, Polaron PT7150). The microstructures of etched cross-sections of the hot-pressed samples were examined by SEM (Zeiss EVO 40 HV). Phase composition was identified by X-ray diffraction analysis (Bruker D8-Discover, Cu Kα radiation). Precise powder XRD measurements were conducted also in Debye-Scherrer transmission geometry (STOE Stadi-P, Germany) using Co Kα radiation ($\lambda = 0.178892$ nm); data acquisition was performed with a position-sensitive detector. The Vickers hardness (HV) was measured on polished cross-sections of pellets with a load of 9.8 N (LECO Vickers Hardness Tester, LV100). The indentation fracture resistance (K_{IC}) was measured on the same equipment with a load of 98 N and calculated according to Shetty's equation.[29] The presence and form of free carbon was investigated by Raman spectroscopy (Raman Spectrometer LabRam HR 800) using Ar-ion laser with $\lambda = 514.5$ nm. The compressive creep tests were carried out at 1400 °C in air under a load of 100 MPa for 24 h. Preliminary transmission electron microscopy (TEM) results were obtained with a FEI CM20 microscope operating at 200 keV.

3. Results and discussion

3.1. Thermodynamic analysis

The preliminary sintering curves recorded up to 1800 °C in nitrogen atmosphere showed that the softening of pyrolysed SiAlOC in Si_3N_4 matrix starts at ~1250 °C in SNA30 samples, followed by densification above 1320 °C. However, the densification rate was slow. A simple increase of sintering tem-