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Gas pressure sintering of SiC sintered with rare-earth-(III)-oxides and their mechanical properties

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Abstract

The sintering behaviour of LPS-SiC and the influence of the size of the rare-earth cations on the secondary phase characteristics were investigated with different rare-earth oxide additions. In all cases, the most important sintering mechanism was found to be the solution-reprecipitation process. This fact was corroborated by TEM and EDS analyses. Post-sintering annealing resulted in devitrification of the secondary phases coupled with anisotropic grain growth due to the phase transformation from β-SiC to α-SiC. Improved fracture toughness of the annealed materials was attributed to crack deflection by the elongated grains. SEM microstructural analyses were performed in order to elucidate structure–property relationships. A comparative study in reference to the additive system Y_2O_3–AlN demonstrates significantly improved high-temperature properties of the Lu_2O_3-containing SiC ceramics.

Keywords: A. Sintering; C. Strength; D. SiC; Rare-earth oxides; Fracture toughness

1. Introduction

Silicon carbide is a potentially important material for high-temperature structural components because of its unique combination of properties, such as excellent oxidation resistance, high-temperature strength retention, high wear resistance, good thermal conductivity and thermal shock resistance. However, it is difficult to densify without additives because of the covalent nature of Si–C bond and the low self diffusion coefficients [1]. Prochazka [2], in his pioneering work, developed a pressureless sintering method leading to good sinterability of silicon carbide powder with additions of boron and carbon. Later on, combined additions of boron, aluminium, carbon or their compounds were successfully used as sintering aids to fabricate SiC ceramics [3–9].

An innovative approach of using liquid-phase sintering for the densification of SiC was introduced by Omori and Takei [10–12] in the 1980s. They investigated several oxide systems and showed that oxide additives do promote the densification of SiC via a liquid phase. During last decade, additive systems such as Al_2O_3–Y_2O_3 and AlN–Y_2O_3 were extensively used to obtain dense LPS-SiC ceramics [13–20]. However, it was established that the densification aids invariably form ‘‘weak’’ grain-boundary phases [13,14] affecting the final high-temperature properties.

In order to improve the thermo-mechanical properites, several rare-earth oxides were introduced in recent years as densification additives for Si_3N_4 and SiAlON ceramics [21–26]. These new rare-earth oxide additive systems were introduced for the modification of the grain boundaries by highly refractory crystalline rare-earth disilicates ($R_2Si_2O_7$) leading to improved high-temperature properties. Moreover, it has been observed that the solubility of N in oxynitride glasses containing rare-earth oxides can reach higher levels as compared to conventional additive systems [27].

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The glass transition temperatures and softening points of oxynitride glasses are significantly higher than those of silicate glasses [28], contributing to superior high-temperature properties of the sintered ceramics.

The present sintering study is a contribution towards the understanding of the sintering behaviour of LPS-SiC with different combinations of rare-earth oxides. In this case, the melting point depression in the R_2O_3–R'_2O_3 systems at intermediate composition is exploited for the formation of a liquid phase. Out of large number of additive systems investigated (R = Nd, Gd, Dy, Y, Ho and R = Ho, Er, Lu) [29], the combinations of R = Gd, Dy and R′ = Ho were selected for the present study based on the sinterability of 50:50 (molar ratio) compositions to near theoretical density by means of gas pressure sintering at 2000 °C. The prevailing sintering mechanism in this study was found to be classical liquid phase sintering with solution-reprecipitation of SiC which was corroborated by the TEM and EDS investigations. Microstructural development and phase evolution after sintering and annealing were investigated with the help of SEM and XRD. Anisotropic grain growth behaviour coupled with the β-SiC → α-SiC transformation was correlated with the fracture mechanical properties. In a separate study, LPS-SiC with conventional Y_2O_3–AlN and new rare-earth additive system Lu_2O_3–AlN were compared in terms of mechanical behaviour at room and high temperatures.

2. Experimental procedure

Commercially available α-SiC, β-SiC and R_2O_3 (R = Gd, Ho, Dy, Y, Lu) and AlN powders were used as starting materials. The characteristics of these powders are summarized in Table 1. Powder mixtures were prepared by attrition milling for 4 h in isopropanol with Si_3N_4 milling media using a polyamide container and keeping a ball-to-charge weight ratio of 6:1. After drying and granulation by sieving with a mesh width of 160 μm, the processed powders were cold isostatically pressed at 240 MPa. The compositions of the powder premixes are given in Table 2.

Sintering was performed in a graphite-heated gas pressure furnace (FCT, Germany) at 2000 °C for 1 h. The first stage of sintering was carried out under a slight N_2 overpressure of 0.2 MPa for 30 min, followed by a pressure sintering cycle of 30 min at the same temperature under 10 MPa N_2 to achieve complete densification. Annealing schedules were performed in the same graphite furnace at 1950 °C for different times to effect the β → α-SiC phase transformation. The heating and cooling rates were kept fixed at 10 °C/min.

Table 2
Compositions of powder premixes

Designation	β-SiC:α-SiC (mol%)	Additive A:B (mol%)
1Gd–1Ho	90:10	$50Gd_2O_3:50Ho_2O_3$
1Dy–1Ho	90:10	$50Dy_2O_3:50Ho_2O_3$
Y–AlN	90:10	$40Y_2O_3:60AlN$[a]
Lu–AlN	90:10	$50Lu_2O_3:50AlN$

[a] Optimized composition in Y_2O_3–AlN system.

X-ray powder diffractometry (XRD) was performed with a Siemens D5000 X-ray diffractometer using filtered Cu Kα radiation with a wavelength of $\lambda = 1.5406$ Å. The X-ray diffraction patterns were analysed by using Siemens DIFFRAC-AT software for identifying the phases present and for quantifying the extent of β → α-SiC conversion. The percentage of α-SiC formed upon annealing is calculated from the ratio of the relative intensities of the (1 0 1) reflection of the α-SiC polytype 6H (F) and the SiC reflection with maximum intensity ($F_{\max}$), followed by comparison of that ratio with a calibration curve established by Nader [30].

For scanning electron microscopy (SEM) observations, the specimens were ground and polished to 1 μm surface finish. After polishing, the samples were plasma etched using a RF Plasma Barrel Etcher (Biorad PT7150) for 3–3.5 min in a mixture of CF_4 and O_2 at 1:1 ratio. Microstructures of the sintered and annealed specimens were examined with scanning electron microscopes of types S200, Cambridge Instruments, and DSM 982 GEMINI, Leo. Grain sizes and aspect ratios were calculated using an image analysis software (Imtronic, Germany). The sintered samples were cut, thinned and investigated using energy filtered transmision electron microscope (EFTEM) having a maximum accelerating voltage of 120 keV (Zeiss EM 912 Omega). This instrument was also used for energy dispersive microanalysis (EDS).

Table 1
Characteristics of the starting powders

Powder	Designation manufacturer	Chemical analysis (wt.%)	Particle size distribution			Specific area (m^2/g)	Density (g/cm^3)
			d_{10} (μm)	d_{50} (μm)	d_{90} (μm)		
α-SiC	A-10 H.C. Starck, Germany	C-30.0, O-0.9, Al-0.03, Ca-0.01, Fe-0.05	0.18	0.51	1.43	11.1	3.22
β-SiC	BF-12 H.C. Starck, Germany	C-30.0, O-1.2, Al-0.05, Ca-0.005, Fe-0.03	0.25	0.89	3.50	17.8	3.22
AlN	Grade C, H.C. Starck	N-30.0, C-0.1, O-2.5, Fe-0.005	0.34	0.92	3.07	5.0	3.26
Y_2O_3	Grade C, H.C. Starck	Al-0.005, Ca-0.003, Fe-0.005	1.21	4.48	8.08	12.9	5.02
Gd_2O_3	STREM CHEMICALS USA	99.99% Gd		~1 to 2 μm		–	7.41
Dy_2O_3	STREM CHEMICALS USA	99.90% Dy		<65 μm		–	7.81
Ho_2O_3	Alfa Aesar, Germany	99.99% Ho		4–5 μm		–	8.36
Lu_2O_3	STREM CHEMICALS USA	99.90% Lu	–			–	9.45