

Densification and phase formation behavior of alumina infiltrated with polycarbosilane

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Conventional powder processing is commonly used to fabricate $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites, in which SiC is added in a powder form with sizes of tens to hundreds nanometres. Recently a new processing route using a SiC polymeric precursor such as polysilazane, polysilastyrene, or polycarbosilane has been also attempted, where a polymeric precursor solution is mixed with alumina powder. The resulting powder is dried and heat-treated or sintered to form nano-sized SiC particles *in situ* by the pyrolysis of the polymeric precursor. In this study, porous alumina bodies were infiltrated with the hexane solution of polycarbosilane and sintered at 1600°C for 2 h in Ar or N_2 . The densification and phase formation behavior was studied as was the effect of SiO_2 addition.

Key words: $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites, Polycarbosilane, Infiltration, Sintering.

Introduction

It is now well established that the mechanical properties of ceramic materials can be significantly improved by the nanocomposite approach, proposed first by Niihara as a new design concept of structural ceramics [1]. For Al_2O_3 , the strength was increased from 350 to 1520 MPa with some increase in toughness and hardness by the addition of only 5 vol% nano-sized SiC particles [1, 2]. Conventional powder processing is commonly used to fabricate the nanocomposites, in which SiC is added in a powder form with sizes of tens to hundreds nanometres. Recently a new processing route using SiC polymeric precursors such as polysilazane, polysilastyrene, or polycarbosilane has been also attempted [3-5]. In this processing, a polymeric precursor solution, prepared with an organic solvent such as toluene or hexane, is mixed with alumina powder. The resulting powder is dried, and then pyrolysis of the added precursor is induced during sintering or separate heat treatment before sintering to form nano-sized SiC particles *in situ*. MoSi_2/SiC nanocomposites prepared using polycarbosilane by hot pressing were reported to exhibit dramatically improved strength both at room and high temperatures in comparison to those prepared by the conventional powder processing [5].

In the present work, porous alumina bodies were

infiltrated with the hexane solution of polycarbosilane (PCS) and sintered at 1600°C for 2 h at normal pressure. The densification and phase formation behavior were studied with varying sintering conditions such as atmosphere type (N_2 or Ar) and heating schedule. The effect of SiO_2 additions was also investigated.

Experimental Procedure

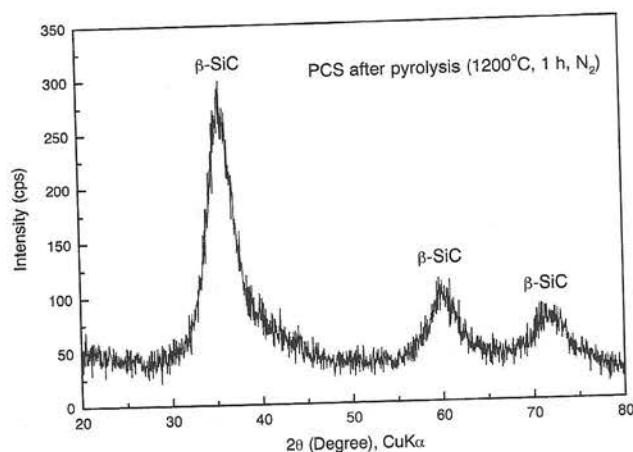
Using an $\alpha\text{-Al}_2\text{O}_3$ powder (AES-11, Sumitomo Chemical Co., Japan), bar-shaped specimens were compacted by uniaxial pressing (36 MPa, $35 \times 8 \times 5$ mm) and then cold isostatic pressing (200 MPa). For the samples with SiO_2 additions, a SiO_2 sol (Ludox LS, Dupont, Wilmington, DE, USA; 30 wt% SiO_2 , 12 nm) was added into an alumina slurry and well dispersed to give 2.82 wt% SiO_2 . After drying, bar samples were also compacted. The composition of 2.82 wt% SiO_2 was chosen to give 10 wt% mullite after final sintering. The samples without and with SiO_2 are denoted as AO and AS, respectively, from now on. The green densities for both cases were 59% theoretical density (TD). The bars were used as infiltration bodies after partial sintering at 1200°C for 1 h in air to burn out the organic additives and provide a proper stiffness for the infiltration process. The sizes of bars partially sintered were about $33.8 \times 7.7 \times 4.6$ mm, and the densities measured by the Archimedes method were 65% TD.

The properties of PCS (NIPUSI Type A, Nippon Carbon Co., Japan) used in this study are given in Table 1. The chemical formula of PCS is $[\text{HSiCH}_2\text{CH}_2]_n$. According to a previous report [6], its pyrolysis begins

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Table 1. Properties of polycarbosilane (NIPUSI Type A^a)

Appearance	white powder
Density (g/cm ³)	1.1 (at room temperature)
Average molecular weight (g/mole)	1400
Melting point (°C)	230
Chemical composition (wt%)	
Si	50
C	40
H	8.1
O	0.5
N	0.7
	62
Ceramic yield after pyrolysis at 1000°C in Ar (wt%) [6]	(80.6% SiC, 4.7% SiO ₂ , 12.3% free C)
Solvent	Hexane, toluene, xylene

^a Nippon Carbon Co., Japan.**Fig. 1.** X-ray diffraction pattern of PCS pyrolysed at 1200°C for 1 h in N₂.

at 300°C and ends at 800°C, resulting in ceramic materials (62 wt% for the PCS weight) composed of 80.6 wt% SiC, 4.7 wt% SiO₂, and 12.3 wt% free carbon. At 1000°C, it is amorphous, and crystallization to β -SiC begins above 1200°C. Figure 1 shows the XRD pattern of PCS pyrolysed at 1200°C, confirming the crystallization of β -SiC. PCS infiltration solution (20 wt% concentration) was prepared using hexane as a solvent. The partially sintered alumina bars were placed in a flask and evacuated for 5 minutes with a motor-driven aspirator, and then infiltrated with the PCS solution for 30 minutes.

After drying the infiltrated samples completely at room temperature, pyrolysis and sintering were performed with two conditions, PDS and PBS. In the case of the PDS condition, PCS pyrolysis was done during sintering with a hold at 1400°C for 1 h on heating. For the PBS condition, pyrolysis (1400°C, 1 h, N₂ or Ar), followed by an air heat treatment (600°C, 1 h), was done separately prior to sintering. For both the conditions, pressureless sintering was performed in a graphite furnace at 1600°C for 2 h in N₂ or Ar atmosphere.

The air heat treatment was to remove free carbon formed along with SiC during the PCS pyrolysis. The sintering condition, 1600°C and 2 h, was such that the alumina powder (AES 11) can be sintered to 99% TD with no sintering aid. The reason for selecting this condition was to know whether a dense Al₂O₃/SiC nanocomposite can be produced by the PCS infiltration process with the same sintering conditions for monolithic alumina.

Sintered densities were measured by the Archimedes method to find the densification degree of infiltrated samples. The conversion of measured to relative densities was done based on the theoretical densities of the matrices (*i.e.*, 3.98 and 3.88 g/cm³ for AO and AS samples, respectively). This is because their SiC contents were 1.5 vol% so that the theoretical densities calculated using the rule of mixture were of little difference from those of the matrices. In the case of the AS samples, the theoretical density was calculated from the rule of mixtures by assuming the amounts of Al₂O₃ and mullite were 90 and 10 wt%, respectively. Crystalline phase analysis was performed using an X-ray diffractometer (XRD) (D/MAX-2000, Rigaku, Japan). Microstructures of the fracture surfaces were observed with a scanning electron microscope (SEM) (JSM 6300, JEOL, Japan).

Results and Discussion

The average amounts of PCS infiltrated in the partially sintered AO and AS bodies were 2.4 wt% after complete drying. The corresponding SiC contents were 1.5 vol% which were calculated from the SiC yield data of PCS pyrolysis in Table 1. The results of sintering and phase analyses of the samples after sintering are summarized in Table 2. The corresponding XRD patterns are given in Figs. 2 and 3. The sintered densities were higher for samples treated in a N₂ atmosphere than for those treated in an Ar atmosphere. The

Table 2. Densities and phases of infiltrated samples after sintering

Sintering condition		Sintered density (%TD ^a)		Crystalline phases besides Al ₂ O ₃	
		AO	AS	AO	AS
N ₂ atmosphere	PDS	92	96	β -SiC	β -SiC
				2H-SiC	2H-SiC
	PBS	96	96	β -SiC	β -SiC
				2H-SiC	2H-SiC
Ar atmosphere	PDS	74	85	β -SiC	β -SiC
				2H-SiC	2H-SiC
	PBS	89	89	β -SiC	β -SiC
				2H-SiC	2H-SiC

^aTheoretical density: 3.98 and 3.88 g/cm³ for AO and AS, respectively.

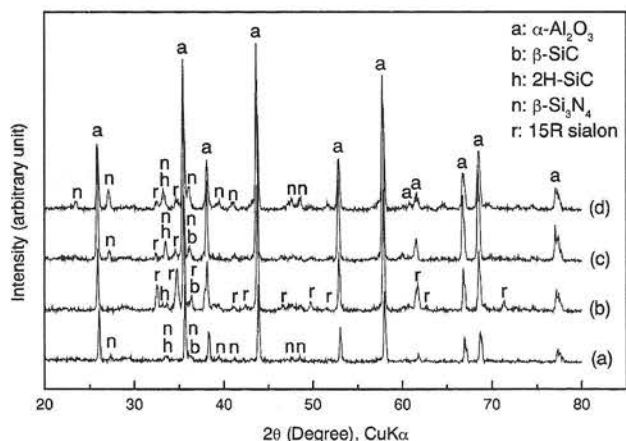


Fig. 2. X-ray diffraction patterns of the PCS infiltrated samples sintered in N_2 atmosphere: (a) AO sample in PDS condition, (b) AO sample in PBS condition, (c) AS sample in PDS condition, and (d) AS sample in PBS condition.

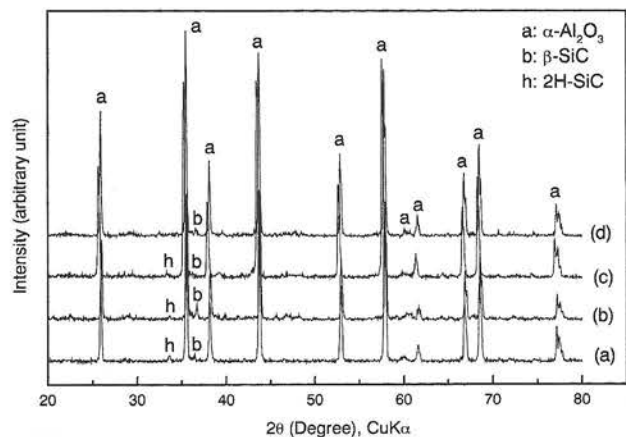
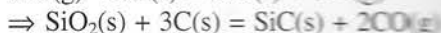
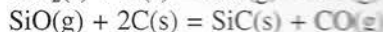
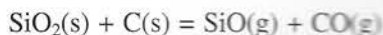


Fig. 3. X-ray diffraction patterns of the PCS infiltrated samples sintered in Ar atmosphere: (a) AO sample in PDS condition, (b) AO sample in PBS condition, (c) AS sample in PDS condition, and (d) AS sample in PBS condition.

PBS condition resulted in higher densification than the PDS condition especially in an Ar atmosphere. Although higher densification was obtained for samples treated in a N_2 atmosphere, β - Si_3N_4 and 15R-sialon ($SiAl_4O_2N_4$) phases were formed besides the SiC phase (Fig. 2). This indicates that some part of the infiltrated PCS reacted with the N_2 atmosphere instead of forming SiC phase, which was not intended. Therefore the higher densification for samples treated in a N_2 is attributed to this decreased content of SiC. In ceramic nanocomposites, the SiC particles are known to reduce the sintering rate by inhibiting grain boundary diffusion and grain boundary migration. In the case of samples treated in an Ar atmosphere, only β - and 2H-SiC phases were formed as the secondary phases (Fig. 3). The PBS condition resulted in much higher densification than the PDS condition especially for the AO samples. For the AS samples, the densification in the PDS condition increased significantly to 85%TD,

approaching that in the PBS condition (89%TD). It is speculated that the low densification of the AO samples in the PDS condition was due to the presence of free carbon, which is one of the pyrolysis products of PCS. The pyrolysis products of PCS include SiO_2 (4.7 wt%) and free C (12.3 wt%) besides SiC (81.6 wt%), as shown in Table 1. The free carbon can react with SiO_2 to form SiC above $1400^\circ C$ [7, 8] as follows:



In reaction (1), the reaction ratio between SiO_2 and C is 1.7:1 by weight, so that the SiO_2 in the PCS pyrolysis products can be removed by this reaction. However, most of the carbon remains and can inhibit sintering by reacting with Al_2O_3 matrix at higher temperatures. In contrast in the PBS condition, the free carbon could be removed by the air heat treatment, resulting in a higher densification. The increased densification of the AO samples in the PDS condition supports the above speculation, where the amount of SiO_2 added was enough to react with all the free carbon. It is evident that the densification of the PCS infiltrated samples can be improved by the SiO_2 addition or the air heat treatment. However, the densities obtained are still low probably for the following reasons. In the case of the SiO_2 addition, reaction (1) should be completed before reaching temperatures where significant sintering occurs and pores are closed. Otherwise sintering is inhibited by CO gas evolution. In addition, SiC whiskers can form by this reaction [8-10], which are detrimental to sintering. In the case of the air heat treatment, the condition used ($600^\circ C$, 1 h, air) might not be sufficient to oxidize the free carbon completely. It is expected that such problems can be solved with more rigorous control of the heating conditions.

Conclusions

The SiC contents of the PCS infiltrated samples were 1.5 vol%. A higher densification was obtained for samples treated in a N_2 atmosphere, but β - Si_3N_4 and 15R-sialon ($SiAl_4O_2N_4$) phases were formed besides SiC phase. In the case of samples treated in an Ar atmosphere, only β - and 2H-SiC phases were formed as the secondary phases as was intended. The densification of the PCS infiltrated samples was promoted by the SiO_2 addition or by employing an air heat treatment step prior to sintering. However, the densities obtained (85 or 89%TD) were still low probably because the reactions to remove the free carbon by carbothermal reduction of SiO_2 and oxidation of carbon (one of the PCS pyrolysis products) were not precisely controlled. The densification problem will be overcome with more rigorous control of the heating conditions.

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