

Processing and properties of Al₂O₃/SiC nanocomposites by polycarbosilane infiltration

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Abstract Al₂O₃/SiC nanocomposites were made by infiltrating partially sintered alumina bodies with polycarbosilane (PCS) solutions, which is a SiC polymer precursor, with pressureless sintering. The SiC content, densification, phases, strength, and microstructure were investigated with the processing parameters such as PCS solution concentration and heat treatment condition for PCS pyrolysis and sintering. The results were compared with those for pure alumina and nanocomposite samples made by the existing polymer precursor route (i.e. the PCS addition process). The SiC contents of up to 1.5 vol% were obtained by the PCS infiltration. PCS pyrolysis, followed by air heat treatment, was needed before sintering to avoid a cracking problem and to attain a densification as high as 98 % of theoretical. The nanocomposites exhibited significantly higher strength than pure alumina and those prepared by the PCS addition process despite larger grain size. Besides α -Al₂O₃ and β -SiC phases, mullite was present a little in the nanocomposites, which resulted from the reaction of SiO₂ in the pyrolysis product of PCS with the Al₂O₃ matrix during sintering. The nanocomposites had intragranular particles believed to be SiC, which is a typical feature of Al₂O₃/SiC nanocomposites.

Key words Sintering, Nanocomposites, Strength, Al₂O₃, Polycarbosilane, Infiltration

1. Introduction

Alumina is widely used as a wear-resistant material due to its highest hardness among oxide ceramics, relatively high strength, low cost, and ease of densification. Better wear performance of alumina can be obtained by improving the mechanical properties such as hardness, strength, and fracture toughness. 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 Al₂O₃, the strength was increased from 350 to 1520 MPa with some increases in toughness and hardness by the addition of only 5 vol% nano-size SiC particles [1, 2].

Al₂O₃/SiC nanocomposites are mainly fabricated by hot pressing because the densification by pressureless sintering is difficult, like conventional composites reinforced with micro-size particles or whiskers [1-8]. However, it has been also reported that 99 % or higher densification can be achieved by pressureless sintering through the optimization of processing conditions for the compositions of 5~15 vol% SiC [9, 10]. 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 nanometers. Recently a new processing route using SiC polymeric precursors such as polysilazane, polysilastylene, or polycarbosilane has been also attempted [11-13]. 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-size SiC particles in situ. MoSi₂/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 [13].

The present work investigated a new process to improve the strength of alumina easily by modifying such a polymer precursor route. Unlike the existing process, the solution of a SiC polymer precursor was infiltrated into partially sintered (i.e. porous) alumina bodies and pressureless sintering employed to make Al₂O₃/SiC nanocomposites. With polycarbosilane (PCS) as the SiC precursor, it was studied how the processing parameters such as the concentration of precursor solution and the heat treatment condition for pyrolysis and sintering affected the SiC addition, densification, strength, and mi-

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crostructures. The results were compared with those for pure alumina and nanocomposite samples prepared by the existing polymer precursor route (i.e. the PCS addition process).

2. Experimental Procedure

2.1. Fabrication of Al₂O₃/SiC nanocomposites by PCS infiltration

2.1.1. Preparation of alumina bodies

Using an α -Al₂O₃ powder (AES-11, Sumitomo Chemical Co., Japan; Table 1), bar-shaped specimens were compacted by uniaxial pressing (36 MPa, 35×8×5 mm) and then cold isostatic pressing (200 MPa), giving 59 % to the theoretical density (TD; 3.98 g/cm³). Since the forming ability of as-received powder was not good enough, a little amounts of an organic lubricant (Nopco-cera LU-6418, Korea Sanopco Co., Seoul, Korea) and a polyvinyl alcohol binder (M.W. 9000-10000, Aldrich Chemical Co., Milwaukee, WI, USA) were used.

The bars were used as infiltration bodies after partial

Table 1
Properties of Al₂O₃ powder (AES-11^a)

Crystalline phase	α -Al ₂ O ₃
Purity (wt%)	99.8
Average particle size (μ m)	0.5
Impurities (wt%)	
Fe ₂ O ₃	0.01
SiO ₂	0.04
MgO	0.1
Na ₂ O	0.03
Sintering condition for 99 % densification	1600°C, 2 h

^aSumitomo Chemical Co., Japan.

Table 2
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
Ceramic yield after pyrolysis at 1000°C in N ₂ (wt%) [14]	62 (80.6 % SiC, 4.7 % SiO ₂ , 12.3 % free C)
Solvent	Hexane, toluene, xylene

^aNippon Carbon Co., Japan.

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 33.8×7.7×4.6 mm, and the densities measured by the Archimedes method were 65 % TD.

2.1.2. Preparation of PCS solution and infiltration

The properties of PCS (NIPUSI Type A, Nippon Carbon Co., Japan) used in this study are given in Table 2. The chemical formula of PCS is [HSiCH₃CH₂]_n. According to the previous report [14], its pyrolysis begins 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 a XRD pattern of PCS pyrolysed at 1200°C, confirming the crystallization of β -SiC.

PCS infiltration solutions of 2, 5, and 20 wt% were prepared using hexane as a solvent. The alumina bars partially sintered were placed in a flask and evacuated for 5 min with a motor-driven aspirator, and then infiltrated with the PCS solutions for 30 min.

2.1.3. Pyrolysis and sintering of infiltrated samples

After drying the infiltrated samples completely at room temperature, pyrolysis and sintering were performed with two conditions, PDS and PBS. In the case of PDS condition, PCS pyrolysis was done during sintering with at 1200°C for 1 h on heating. For the PBS condition, pyrolysis (1200°C, 1 h, N₂), followed by air heat treatment (600°C, 10 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 atmosphere.

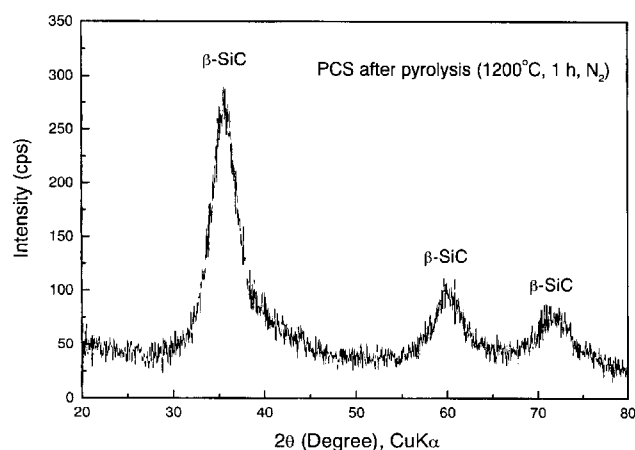


Fig. 1. X-ray diffraction pattern of PCS pyrolysed at 1200°C for 1 h in N₂.

The pyrolysis temperature 1200°C was chosen since the crystallization of β -SiC during heating PCS begins at this temperature as mentioned in Section 2.1.2. The air heat treatment was to remove free carbon formed along with SiC during PCS pyrolysis. The sintering condition, 1600°C and 2 h, was same as the condition for sintering the AES-11 alumina powder to the density of 99 % without any sintering aid, as shown in Table 1. The reason for selecting such a sintering condition was whether to confirm that a dense $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite could be produced by the PCS infiltration process with the same sintering condition for monolithic alumina.

2.2. Fabrication of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites by PCS addition process

Nanocomposites were also prepared by the existing polymer process (i.e. the PCS addition process) to compare with those by the infiltration process. In this process, a necessary amount of PCS was dissolved in hexane and mixed with Al_2O_3 powder (AES-11, Sumitomo Chemical Co., Japan) by wet ball milling for 2 h. The slurry mixture was dried on a hot plate stirrer. The resulting powder was crushed and then sieved through a 100 mesh screen, giving PCS-added alumina powder. The amount of PCS was controlled to make the final composition of nanocomposite be 5 vol% SiC, based on the SiC amount of PCS pyrolysis product being 80.6 wt% (Table 2). This composition was chosen for the following two reasons. First, the $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite system reportedly showed the highest strength improvement with 5 vol% SiC composition [1]. Second, high densification by pressureless sintering was possible for the composition [9, 10].

The PCS-added alumina powder was compacted by uniaxial pressing (36 MPa, 35×8×5 mm) and then cold-isostatically pressed at 200 MPa, producing bar specimens with green density 56 % TD. The bar compacts were pyrolysed and sintered with the two conditions, PDS and PBS, as in the infiltration process to make $\text{Al}_2\text{O}_3/5$ vol% SiC nanocomposites.

2.3. Density measurement and phase analysis

Sintered density was measured by the Archimedes method to find the densification degree of nanocomposite samples. The conversion of measured to relative densities was done based on the theoretical density of pure Al_2O_3 (3.98 g/cm³) in the case of samples by the infiltration process. This is because their SiC contents were 1.5

vol% or less so that the theoretical densities calculated using the rule of mixture were 3.97 g/cm³ at the smallest, being of little difference from that of Al_2O_3 . In the case of samples by the PCS addition process (i.e. 5 vol% SiC composition), relative densities were calculated based on the theoretical density from the rule of mixture, 3.94 g/cm³.

Using an X-ray diffractometer (D/MAX-2000, Rigaku, Japan), crystalline phases of pyrolysis product of PCS only as well as the nanocomposite samples were analyzed.

2.4. Strength measurement and microstructure analysis

Three point bend tests were performed to measure the strengths of nanocomposites, using a universal testing machine (H10K-S, Hounsfield, UK). Pure alumina samples prepared with the PDS and PBS conditions were also tested for comparison. The span and the cross head speed used were 20 mm and 5 mm/min, respectively. The tensile surfaces of the bar specimens were finished using diamond grinding wheels to 1200 grit with a slight beveling.

Microstructures of the fracture surfaces of bend-tested specimens were observed with a scanning electron microscope (SEM) (JSM 6300, JEOL, Japan). SEM observation of thermally etched surfaces was also performed to investigate the matrix grain size and the distribution of SiC particles. Thermal etching was performed at 1450°C for 1 h in Ar.

3. Results and Discussion

3.1. Infiltration properties of alumina bodies

Table 3 shows the infiltration results of partially sintered alumina bodies with the concentration of PCS solution. For the concentrations of 2, 5, and 20 wt%, the average infiltrated amounts of PCS were 0.26, 0.66, and 2.39 %, respectively, increasing proportionally to the concentration. The corresponding SiC contents predicted were 0.16, 0.4, and 1.5 vol%, respectively, which were calculated from the SiC yield data of PCS pyrolysis in Table 2. These results illustrate that the SiC amount added by the infiltration process can be controlled by the adjustment of PCS solution concentration.

3.2. Pyrolysis and densification properties of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites

The sintered densities and phases of the nanocompos-

Table 3
Infiltration results of alumina bodies with PCS solution concentration

PCS solution concentration (wt%)	Weight before infiltration, W (g)	Weight gain by infiltration, ΔW (g)	ΔW/W (%)	Predicted SiC content (vol%)
2	2.8801	0.0073	0.25	0.16
	2.8539	0.0073	0.26	
5	2.8476	0.019	0.67	0.4
	2.8226	0.0184	0.65	
20	2.8039	0.0671	2.39	1.5
	2.8499	0.068	2.39	

Table 4
Densities and phases of samples prepared with PDS condition

Sample	SiC content (vol%)	Sintered density (% TD ^a)	Phases	Remark
Pure alumina	0	99	α-Al ₂ O ₃	
Infiltrated with 2 wt% PCS solution	0.16	99	-	Internal cracks
Infiltrated with 5 wt% PCS solution	0.4	98	α-Al ₂ O ₃ , β-SiC ^b , 15R sialon ^c	Internal cracks
Infiltrated with 20 wt% PCS solution	1.5	95	α-Al ₂ O ₃ , β-SiC ^b , 15R sialon ^c	Internal cracks
PCS added	5	79	α-Al ₂ O ₃ , β-SiC ^b , 15R sialon ^c	-

^aTheoretical density of Al₂O₃ (3.98 g/cm³).

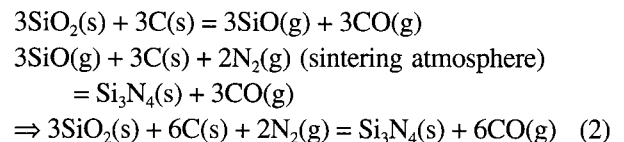
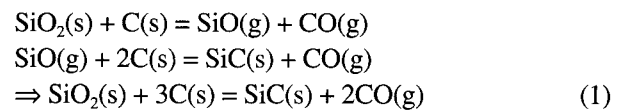
^bNot detected by XRD due to its small content but believed to be present.

^cMinor phase.

ite samples by the PCS infiltration and addition processes are given in Table 4 with the data for pure alumina sample, which were prepared with PDS condition. The same data for the samples prepared with PBS condition are given in Table 5.

In the case of PDS condition (Table 4), the nanocomposite samples by the infiltration process showed 99, 98, and 95 % densities for the PCS solution concentrations 2, 5, and 20 wt%, respectively, whereas the pure alumina showed 99 % density. The densification tended to decrease a little with increasing the concentration. On

the other hand, the nanocomposite samples by the addition process was 79 %, indicating very low densification. The X-ray diffractometry (XRD) of the samples by both the infiltration and addition processes revealed 15R sialon phase besides α-Al₂O₃ and β-SiC (Table 4 and Fig. 2). It should be noted that the peaks for β-SiC are not shown in the XRD patterns (Fig. 2) because the amounts of SiC in the nanocomposite samples were too small to detect. The reason for the presence of 15R sialon can be inferred as follows. The pyrolysis products of PCS include SiO₂ (4.7 wt%) and free C (12.3 wt%) besides SiC (80.6 wt%), as described in Table 2. Therefore the following reactions can occur between SiO₂ and free C above 1400°C when samples are prepared under PDS condition [15, 16]:



In reactions (1) and (2), the reaction ratios between SiO₂ and C are 1.7 : 1 and 2.5 : 1 in weight, respectively, so that the SiO₂ of the PCS pyrolysis products are removed by these reactions. However, most of the carbon remains and at higher temperatures can induce the following

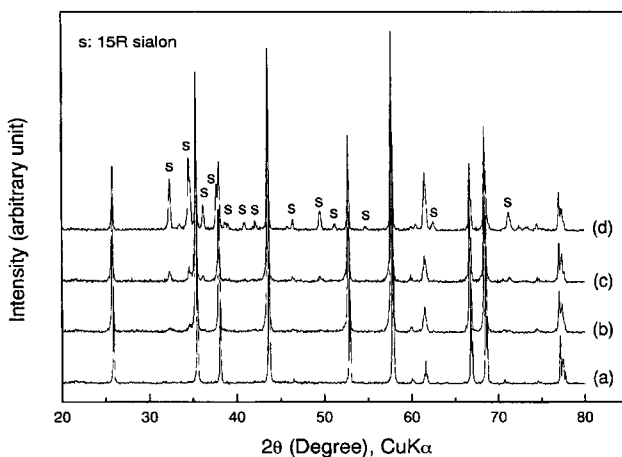


Fig. 2. X-ray diffraction patterns of samples prepared with PDS condition: (a) pure alumina; (b) and (c) nanocomposites by 5 and 20 wt% PCS solution infiltration, respectively; (d) nanocomposite by PCS addition.

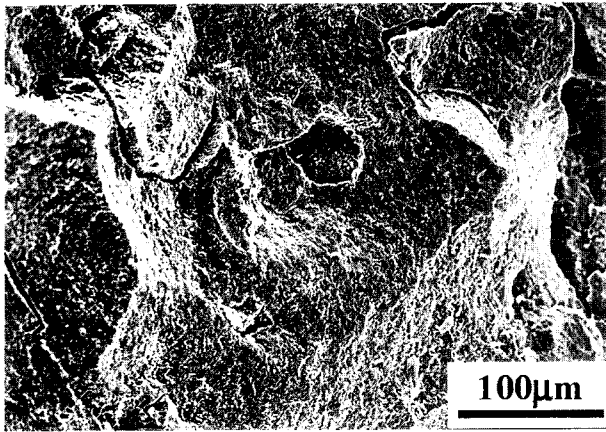
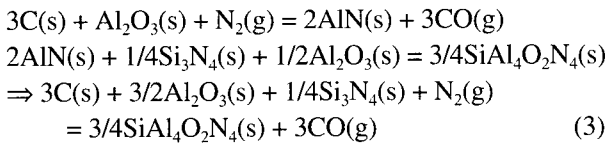


Fig. 3. Scanning electron micrograph of the fracture surface of sample by the infiltration process prepared with PDS condition, showing internal cracking.

reactions under N_2 atmosphere, finally forming 15R sialon ($SiAl_4O_2N_4$):



It can be seen that reactions (1), (2), and (3) all produce CO gas. Hence, in Table 4, the internal cracks observed in the samples by the infiltration process and the low densification of the samples by the PCS addition process are attributed to the CO gas evolution. Figure 3 illustrates internal cracks typically observed in the samples prepared by the infiltration process.

In the case of PBS condition (Table 5), the samples by the infiltration process showed a densification as high as 98 % TD even for the PCS solution concentration 20 wt% and showed no internal cracking differently from PDS condition. The sample prepared by the PCS addition process also showed quite an enhanced densification, 94 % TD, compared to the densification for PDS condition, 79 % TD. These results indicate that in the fabrication of Al_2O_3/SiC nanocomposites both by the

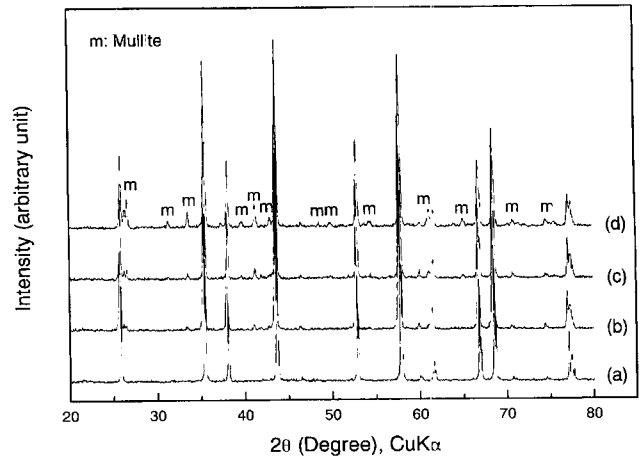


Fig. 4. X-ray diffraction patterns of samples prepared with PBS condition: (a) pure alumina; (b) and (c) nanocomposites by 5 and 20 wt% PCS solution infiltration, respectively; (d) nanocomposite by PCS addition.

PCS infiltration and addition processes, heat treatment condition is very important. Besides $\alpha-Al_2O_3$ and $\beta-SiC$ phases, mullite ($3Al_2O_3 \cdot 2SiO_2$) was detected by XRD for the nanocomposite samples prepared with PBS condition (Table 5 and Fig. 4). In the case of PBS condition, the air heat treatment ($600^\circ C$, 10 h) probably removed the free C of the pyrolysis products of PCS, leaving SiC and SiO_2 . Hence it can be inferred that the SiO_2 reacted with the Al_2O_3 matrix and thereby mullite formed during sintering. In addition, the SiO_2 presumably contributed to the promotion of densification by forming a liquid phase of $MgO-Al_2O_3-SiO_2$ system, where the MgO was an impurity component in the alumina powder used (Table 1).

3.3. Strength and microstructure of Al_2O_3/SiC nanocomposites

The strengths and matrix grain sizes of the nanocomposite samples by the PCS infiltration and addition processes are also given in Table 5 with the data for pure

Table 5
Densities, phases, strengths and grain sizes of samples prepared with PBS condition

Sample	SiC content (vol%)	Sintered density (% TD ^a)	Phases	Strength (MPa)	Average grain size of Al_2O_3 (μm)
Pure alumina	0	99	$\alpha-Al_2O_3$	294	2~3
Infiltrated with 5 wt% PCS solution	0.4	99	$\alpha-Al_2O_3$, $\beta-SiC^b$, mullite ^c	357	5~10
Infiltrated with 20 wt% PCS solution	1.5	98	$\alpha-Al_2O_3$, $\beta-SiC^b$, mullite ^c	419	5~10
PCS added	5	94	$\alpha-Al_2O_3$, $\beta-SiC^b$, mullite ^c	255	1~3

^aTheoretical density of Al_2O_3 ($3.98 g/cm^3$).

^bNot detected by XRD due to its small content but believed to be present.

^cMinor phase.

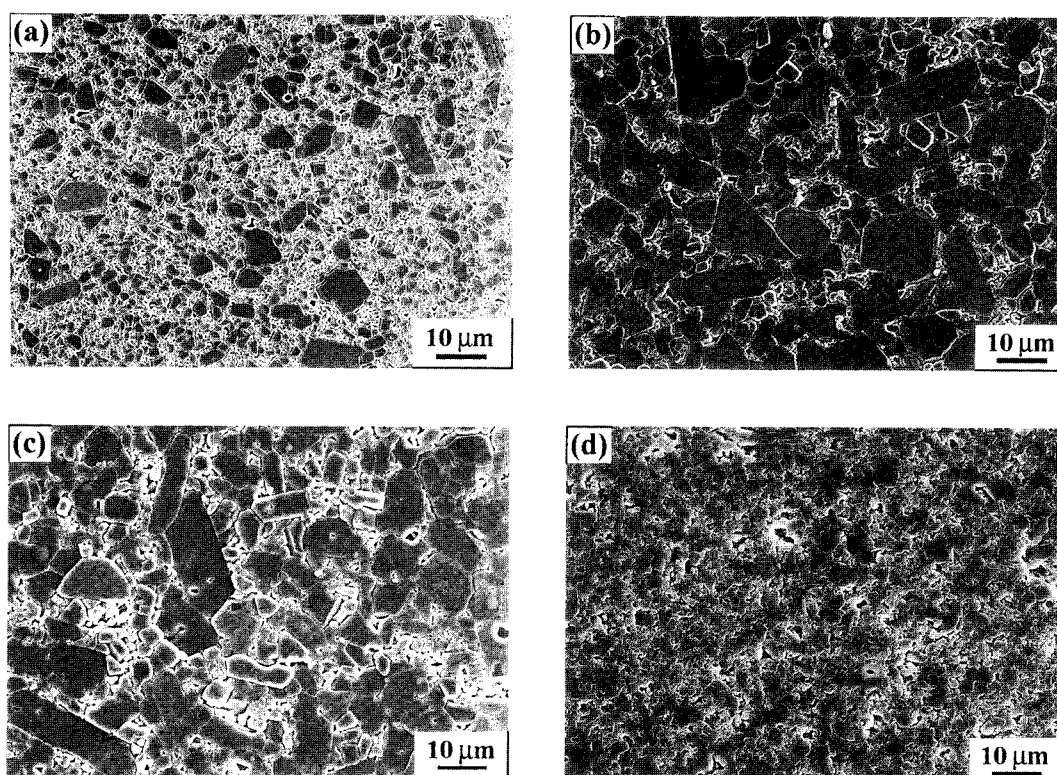


Fig. 5. Scanning electron micrographs of thermally etched surfaces of the samples prepared with PBS condition: (a) pure alumina; (b) and (c) nanocomposites by 5 and 20 wt% PCS solution infiltration, respectively; (d) nanocomposite by PCS addition.

alumina sample, which were prepared with PBS condition. The pure alumina had strength of 294 MPa and its average grain size was 2~3 μm . The nanocomposite samples by the infiltration process had strengths of 357 and 419 MPa for PCS solution concentrations 5 and 20 wt%, respectively. That is, they showed higher strength than pure alumina despite larger matrix grain sizes of 5~10 μm . For the sample infiltrated with 20 wt% PCS solution, the strength was enhanced by 43%. SEM micrographs showing the grain sizes of these samples are given in Fig. 5. It is speculated that the larger grain sizes of the nanocomposite samples by the infiltration process resulted from the liquid phase formed by SiO₂ as mentioned before, which can increase grain growth rate. On the other hand, the strength of the sample by the PCS addition process was 255 MPa, which was even lower than that of pure alumina. Such a low strength is attributed to its relatively low densification of 94%. In contrast to those by the infiltration process, this sample had a uniform and fine grain size [Fig. 5(d)], indicating that its SiC content (5 vol%) was high enough to inhibit grain growth by grain boundary pinning.

In the nanocomposite samples by the infiltration process, intragranular particles believed to be SiC were observed as shown in Fig. 6. Such a microstructure,

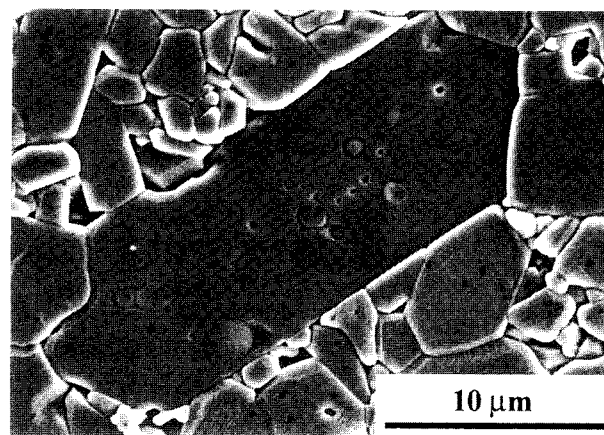


Fig. 6. Scanning electron micrograph of nanocomposite sample by the infiltration process (20 wt% PCS solution) prepared with PBS condition, showing intragranular particles.

known to be a typical feature of Al₂O₃/SiC nanocomposites, is thought to be responsible for their enhanced strengths.

4. Conclusions

The PCS infiltration process using pressureless sintering could fabricate Al₂O₃/SiC nanocomposites with SiC

contents of up to 1.5 vol%. PCS pyrolysis, followed by air heat treatment, was needed before sintering to avoid a cracking problem and to attain a densification as high as 98 % TD. The cracking problem is inferred to have resulted from free carbon in the pyrolysis product of PCS, which can produce CO gas. The nanocomposites exhibited significantly higher strength than pure alumina and those prepared by the PCS addition process despite larger grain size. Besides α -Al₂O₃ and β -SiC phases, mullite was present a little in the nanocomposites, which resulted from the reaction of SiO₂ in the pyrolysis product of PCS with the Al₂O₃ matrix during sintering. The SiO₂ presumably contributed to densification and grain growth by forming a liquid phase. The nanocomposites had intragranular particles believed to be SiC, which is a typical feature of Al₂O₃/SiC nanocomposites. The newly developed PCS infiltration process seems to be simple and efficiently produce Al₂O₃/SiC nanocomposites with a small SiC content.

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