

Effect of High-Yield Polycarbosilane Addition on Microstructure and Mechanical Properties of Alumina

Yuichi SAWAI and Yoshiyuki YASUTOMI*

Department of Energy Devices, Hitachi Research Laboratory, Hitachi, Ltd., 7-1-1, Omika-cho, Hitachi-shi 319-1292

*Japan Fine Ceramics Center, 2-4-1, Mutsumo, Atsuta-ku, Nagoya-shi 456-8587

高収率ポリカルボシランを添加したアルミナ焼結体の機械特性及び微構造

沢井裕一・安富義幸*

(株)日立製作所日立研究所エネルギー素子研究部無機材料グループ, 319-1292 日立市大みか町 7-1-1

*(財)ファインセラミックスセンター, 456-8587 名古屋市熱田区六野 2-4-1

Effect of polycarbosilane (PC), with high ceramic yield of 85%, added to Al_2O_3 was investigated. Green density of the Al_2O_3 powder compact increases by the PC coating. Al_2O_3 ceramics containing 5 to 10 vol% SiC derived from PC were fabricated by the hot-press sintering at temperatures between 1600°C and 1800°C. After hot-pressing at 1600°C, almost all PC-derived SiC-phase exists at grain boundaries as fine crystalline grains, which results in a significant decrease in Al_2O_3 grain-growth rate and in a low fraction of porosity as well. Some of the PC-derived SiC-phase may be drawn inside the Al_2O_3 grains during grain growth at 1800°C to form intragranular SiC nanoparticles. Four-point bending strength of Al_2O_3 was increased, and the scatter in bending strength values significantly decreased by the PC coating. Intragranular fracture mode was observed in the PC-coated Al_2O_3 composite, while Al_2O_3 +SiC powder composite exhibited intergranular fracture.

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1. Introduction

Al_2O_3 is well known for its high thermal and chemical stability, high strength, hardness, oxidation resistance and thermal conductivity. A number of researches have been carried out to improve the strength and reliability of Al_2O_3 ceramics. Yasuoka et al. improved the mechanical strength of Al_2O_3 and suppressed the decrease in strength at high temperature by dispersing nanoparticles of YAG into Al_2O_3 matrix.¹⁾ Wang et al. established the in-situ dispersion technique of MgAl_2O_4 nanoparticles in the Al_2O_3 matrix and improved the mechanical strength.²⁾ Superplasticity in fine grained Al_2O_3 was brought out by spinel or ZrO_2 dispersion.^{3)–6)} Four-point bending strength of 5 vol% SiC nanoparticle dispersed Al_2O_3 increases up to 760 MPa while the strength of monolithic Al_2O_3 is about 400 to 500 MPa.⁷⁾ The addition of nano SiC particles also reduces the tensile creep rate of Al_2O_3 , i.e., the creep life time of the Al_2O_3 /SiC nanocomposite becomes longer.^{8)–10)} Nanocomposite of Al_2O_3 and the second phase dispersion exhibits improvement in mechanical properties.

The majority of the dispersed SiC particles are located at grain boundary triple points. SiC particles also exist on the Al_2O_3 grain boundaries as well as in the grains.^{7),11),12)} Such a nanoparticle dispersion suppresses the grain growth of Al_2O_3 matrix,^{12)–14)} and that is one reason of the functions of Al_2O_3 , such as superplasticity or creep resistance, brought out by the second phase dispersion.^{3)–6),8)–10)} Sternitzke et al. have synthesized Al_2O_3 /SiC_{PC} nanocomposites from polycarbosilane coated Al_2O_3 powder, and improved the bending strength.¹⁵⁾ Where polycarbosilane (PC) is the most typical polymeric precursor for SiC based ceramics, and the SiC phase derived from PC is denoted as SiC_{PC}. The ceramic yield of the polycarbosilane they used was low and some pores may be introduced in the pyrolysed one. Thus the intermediate crashing and forming process are necessary after the pyrolysis process of the PC-coated on Al_2O_3 particles to obtain highly dense Al_2O_3 /SiC_{PC} composites.

Recently, Nippon Carbon Co., Ltd. have manufactured

the high molecular weight PC (type-UH, $M_w=10000$ –11000). Ceramic yield of PC type UH (denoted PC(UH)) is more than 75%, and PC(UH) does not melt at high temperature without oxidation curing. Thus it can be expected to fabricate highly dense Al_2O_3 /SiC_{PC} composites without the intermediate forming process by using PC(UH) as a compaction binder. The objective of the present work is to obtain the Al_2O_3 /SiC_{PC} composites with high reliability and to investigate the effects of PC(UH) addition on the microstructure and the mechanical properties of Al_2O_3 ceramics.

2. Experimental procedure

Figure 1 shows a synthetic route for the Al_2O_3 /SiC_{PC} com-

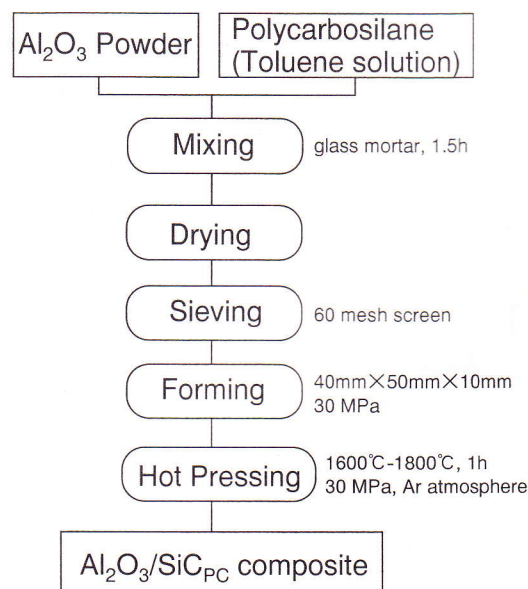


Fig. 1. Synthetic route for preparing Al_2O_3 /SiC_{PC} composites.

posite. Calculated amount of toluene solutions of PC(UH) was mixed with Al_2O_3 powder (Taimei Chemical Co., Ltd., TM-DAR, $0.21\ \mu\text{m}$) by a glass mortar for 1.5 h. The mixed slurry was then dried and sieved through a 60 mesh screen. Amount of PC(UH) addition was calculated with considering its ceramic yield as the total amount of SiC_{PC} comes to 5 vol% or 10 vol%. In this way, two samples of 5.75 mass% and 11.5 mass% PC(UH) coated Al_2O_3 powders were prepared. The powder mixtures of Al_2O_3 and 5 vol% or 10 vol% SiC powder (Showa-Denko Co., DU-A1, $0.45\ \mu\text{m}$) were also prepared by ball milling with SiC ball in ethanol for 24 h. Thermogravimetric analysis (TGA; Model TG-DTA2000, Mac Science, Tokyo, Japan) was performed on PC(UH) and the other kind of polycarbosilane (Nippon Carbon Co., Ltd., type-S) up to 1000°C at a heating rate of $5^\circ\text{C}/\text{min}$ under argon flow.

Green compacts (15 mm in diameter, 3 mm in thickness) of the PC(UH) coated Al_2O_3 powder, Al_2O_3 and SiC powder mixture and as-received Al_2O_3 powder were prepared by uniaxial pressing under 30 MPa of pressure. The green densities of as formed compacts were calculated by measuring the volume and the weight of the green compacts. The compacts were then heated up to 1000°C at the rate of $100^\circ\text{C}/\text{h}$ in Ar atmosphere, kept for 1 h, and the green densities were measured again. Relative density was calculated using the theoretical density of Al_2O_3 ($3.98\ \text{g}\cdot\text{cm}^{-3}$) and that of PC(UH) ($1.1\ \text{g}\cdot\text{cm}^{-3}$).

The green compacts for hot pressing ($40\ \text{mm}\times 50\ \text{mm}\times 10\ \text{mm}$) of 5.75 mass% and 11.5 mass% PC(UH) coated Al_2O_3 powders, and 5 vol% and 10 vol% SiC mixed Al_2O_3 powders were prepared under the same compaction conditions described above. The green compacts were placed in a graphite die and heat-treated in a graphite resistance heating furnace (Model High Multi 10000, Fujidempa Kogyo, Osaka, Japan). At the initial heating stage, R.T. to 700°C , the samples were heated at the rate of $100^\circ\text{C}/\text{h}$ for degassing and pyrolysis of PC(UH). Then the heating was continued at the rate of $600^\circ\text{C}/\text{h}$ to the treating temperature of 1600, 1700 or 1800°C and kept for 1 h under a hot pressing pressure of 30 MPa. Heat treatment was carried out in an ambient argon atmosphere.

To investigate the crystallization behavior of PC(UH) and the PC(UH) in the Al_2O_3 matrix up to 1000°C , X-ray diffraction (XRD; Model RINT 2500, Rigaku, Tokyo, Japan) measurements were performed on the heat-treated PC(UH) and the $\text{Al}_2\text{O}_3/\text{SiC}_{\text{PC}}$ composites with $\text{Cu K}\alpha$ radiation using an automated powder diffractometer equipped with a monochromator.

Apparent density of hot press sintered compacts was measured by the Archimedes immersion technique in water. Porosity of each sample was obtained by a mercury porosimetry (Auto Pore 3, Shimadzu Corp., Tokyo, Japan), under a pressure up to 413 MPa (60000 psi).

The surfaces of the sintered compacts were polished with diamond powder ($0.5\ \mu\text{m}$). Then the polished compacts were thermally etched at 1350°C for 1 h in air. Microstructure of the etched surfaces and the fracture surfaces were observed by scanning electron microscopy (SEM; Model S-800, Hitachi, Tokyo, Japan). Particle size distribution was determined by the line intercept method after the polished surface was thermally etched.

Four-point bending strengths were determined using a four-point rupture test on $3\ \text{mm}\times 4\ \text{mm}\times 40\ \text{mm}$ bar samples of which surfaces and edges were polished with diamond powder ($0.5\ \mu\text{m}$). The fracture surfaces were observed by SEM. Young's modulus was measured for each sample (Panametrics Model 5900 PR, 200 MHz, 60 dB). The distribution of the PC-derived SiC phase have been investigated by transmission electron microscopy (TEM);

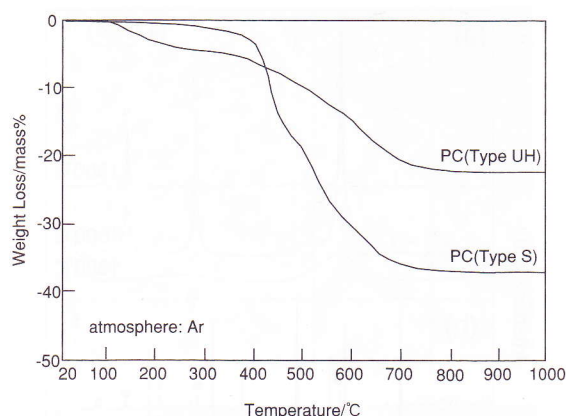


Fig. 2. TGA curves of polycarbosilane type-UH and type-S under flowing argon (heating rate: $5^\circ\text{C}/\text{min}$).

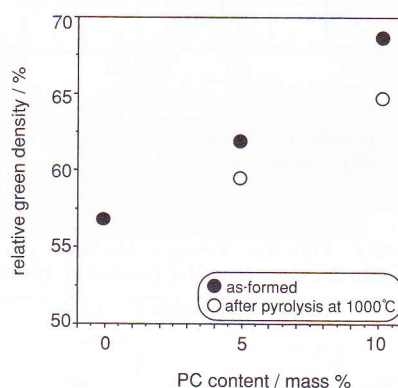


Fig. 3. Relative green density of Al_2O_3 powder compact as a function of PC(UH) content.

Model JEM-100CX II, JEOL Ltd., Tokyo, Japan).

3. Results and discussion

When PC(type-S) is fired in Ar atmosphere, it starts to decompose at about 400°C as shown in Fig. 2. At about 800°C , it completely melts and transforms into a black amorphous inorganic polymer with loss of organic groups and subsequently changes into a SiC ceramics. PC(UH) also starts to decompose at about 400°C , partially melts, and finally changes into a SiC ceramics as well. PC(UH) has high molecular weight fraction extracted from PC(type-S), and the weight loss of PC(UH) is lower than that of PC(type-S). The ceramic yield of PC(UH) is about 80% and it may be excellent as a use of the compaction binder for ceramic powders.

Figure 3 shows the relationship between the PC(UH) content and the green densities of the Al_2O_3 powder compacts. The solid circles and the open circles indicate the green density of as-formed samples and the samples after pyrolysis, respectively. Green density of the Al_2O_3 powder compact increases with increasing the PC(UH) content, and reasonably high green density of 65% was achieved at 11.5 mass% of PC(UH) after pyrolysis, while relative densities of the green compacts of as-received Al_2O_3 is about 57%. Nearly the closest packing of Al_2O_3 particles tends to occur when they are coated with PC(UH). It may due to the improvement of powder fluidity by the PC(UH) coating, leading to the highly dense accumulation in comparison with as-received Al_2O_3 powder. One of the advantages of the PC(UH) coating is the improvement of the densification of powder compacts.

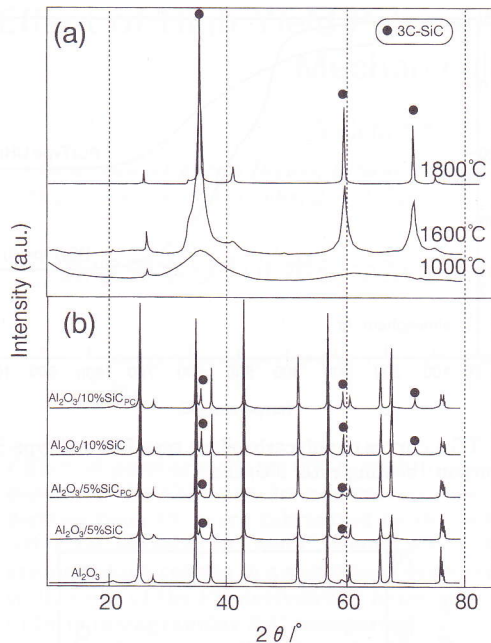


Fig. 4. XRD spectra of (a) heat-treated PC(UH) under argon, and (b) Al₂O₃/SiC_{PC} composites.

Table 1. Density, Porosity, Young's Modulus and Poisson's Ratio of the Al₂O₃/SiC Compacts Hot Pressed at 1600°C

	Density /g·cm ⁻³	Porosity/%	Young's modulus / GPa	Poisson's ratio
Al ₂ O ₃ +5vol%SiC _{PC}	4.01	0.49	388.8	0.23
Al ₂ O ₃ +10vol%SiC _{PC}	3.91	0.43	380.2	0.23
Al ₂ O ₃ +5vol%SiC	4.00	0.89	407.7	0.23
Al ₂ O ₃ +10vol%SiC	3.84	1.65	392.2	0.23

The powder X-ray diffraction patterns of PC(UH) heat-treated at 1000, 1600 and 1800°C are shown in Fig. 4(a). The pyrolysed PC(UH) exhibits an amorphous Si-C phase at 1000°C, well crystallized 3C-SiC at 1600°C and completely crystallized 3C-SiC at 1800°C. The XRD patterns of the Al₂O₃/SiC_{PC} compacts given in Fig. 4(b) shows that the components of the Al₂O₃/SiC_{PC} heat-treated at 1600°C was only α -Al₂O₃ and 3C-SiC without any reacting phases. Almost all the heat-treated PC converted to 3C-SiC crystalline phase even it is surrounded by the Al₂O₃ matrix. No significant effects on phase transition of Al₂O₃ can be observed by PC(UH) addition.

Density, porosity, Young's modulus and Poisson's ratio of the sintered body at 1600°C are summarized in Table 1. Young's modulus and Poisson's ratio of Al₂O₃/SiC_{PC} are quite similar to those of Al₂O₃/SiC. However, porosity of Al₂O₃/SiC_{PC} is smaller than that of Al₂O₃/SiC. The PC coating improves the powder fluidity and packing, and its high ceramic yield results the fully densified sintered body.

The comparison of the microstructures of all the samples are shown in Fig. 5. The Al₂O₃/5%SiC_{PC} and Al₂O₃/10%SiC_{PC} sintered at 1600°C consist mainly of uniform fine grains less than 1 μ m. Constituent grains in the Al₂O₃/5%SiC and Al₂O₃/10%SiC sintered at 1600°C are larger than those of the sintered Al₂O₃/SiC_{PC}, which indicates the PC-derived thin SiC layer prevents contact between the Al₂O₃ particles and deteriorate the grain growth of Al₂O₃.

The average particle size was determined from Fig. 5 by the line intercept method as shown in Fig. 6. Data points of

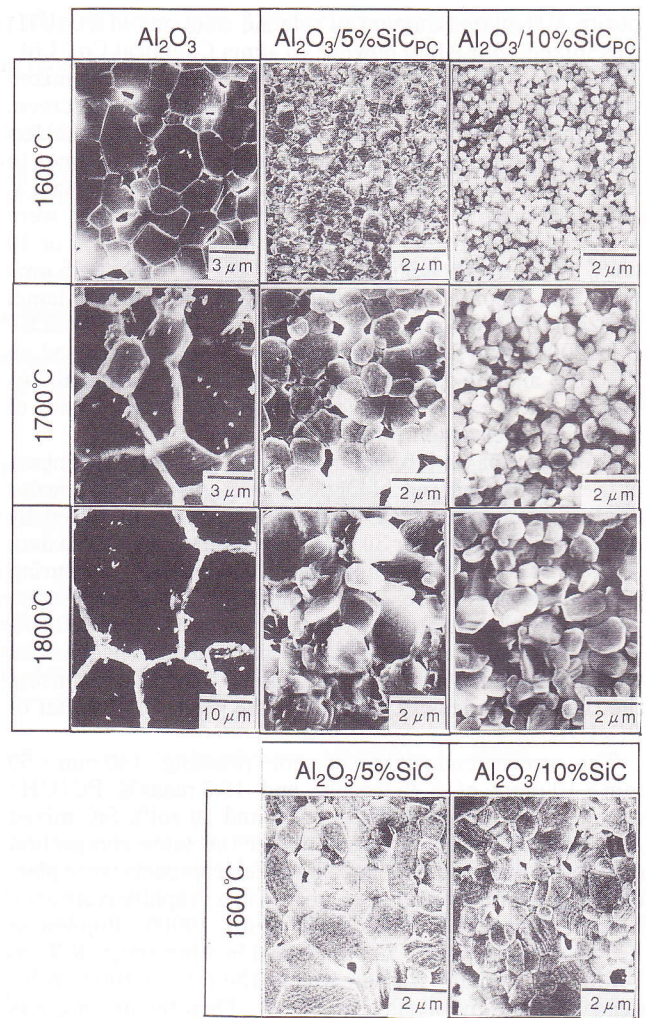


Fig. 5. SEM images of polished and etched surfaces of Al₂O₃, Al₂O₃/SiC_{PC} and Al₂O₃/SiC composites.

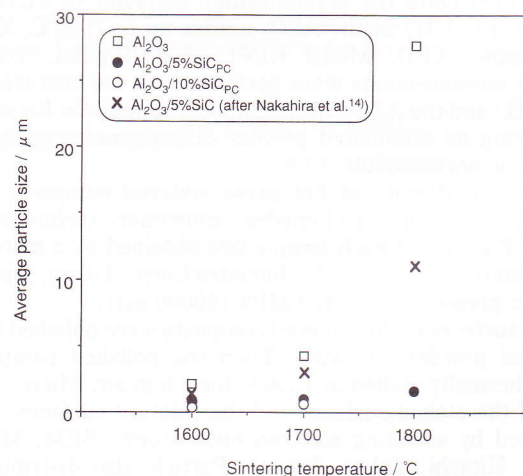


Fig. 6. Mean particle size of Al₂O₃, Al₂O₃/SiC_{PC} and Al₂O₃/SiC composites as a function of sintering temperature.

Al₂O₃+5 vol% SiC in Fig. 6 are quoted from the reference.¹⁴⁾ The SiC particle dispersion suppresses the grain growth of Al₂O₃. In this study, Al₂O₃+PC(UH) showed more significant decrease in grain growth rate, and the mean particle size decreases with increasing the amount of

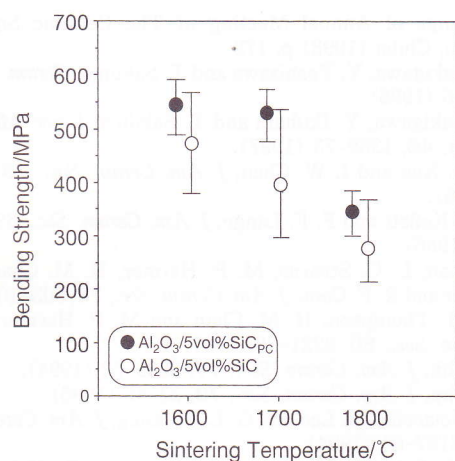


Fig. 7. Four-point bending strength of $\text{Al}_2\text{O}_3/\text{SiC}_{\text{PC}}$ and $\text{Al}_2\text{O}_3/\text{SiC}$ composites as a function of sintering temperature.

PC(UH). Thus dense and fine grain Al_2O_3 composites can be obtained by PC(UH) coating.

The bending strength of Al_2O_3 at each temperature slightly increased, and the scatter in strength values significantly decreased by PC(UH) coating as shown in Fig. 7. The maximum values of bending strength of the $\text{Al}_2\text{O}_3/\text{SiC}_{\text{PC}}$ and the $\text{Al}_2\text{O}_3/\text{SiC}$ composites are almost same, however, the minimum value increases by PC(UH) coating, which results the increase in the mean value, and the decrease in the scatter of the bending strength. It may due to decrease in the mean particle size and the number of defects in the $\text{Al}_2\text{O}_3/\text{SiC}_{\text{PC}}$ composites. It indicates the PC(UH) coating results the increase in reliability of the Al_2O_3 sintered body.

Figure 8 shows the thermally etched fracture surfaces of

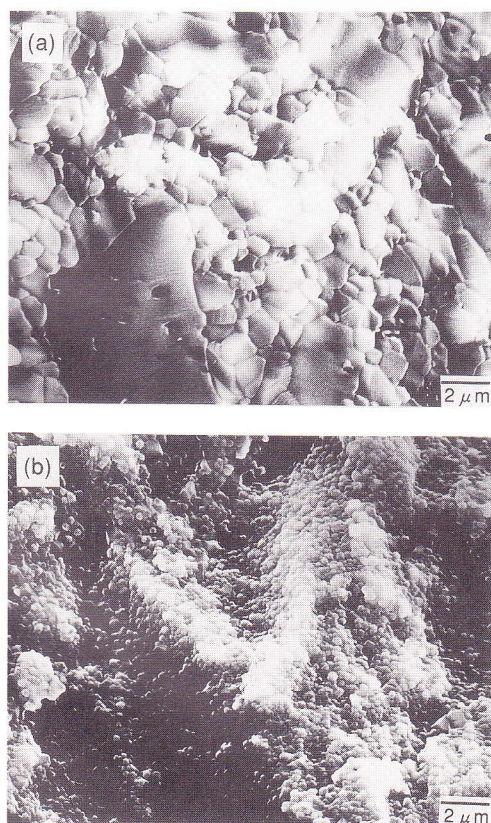


Fig. 8. Fracture surfaces of (a) $\text{Al}_2\text{O}_3/\text{SiC}$ and (b) $\text{Al}_2\text{O}_3/\text{SiC}_{\text{PC}}$ composites.

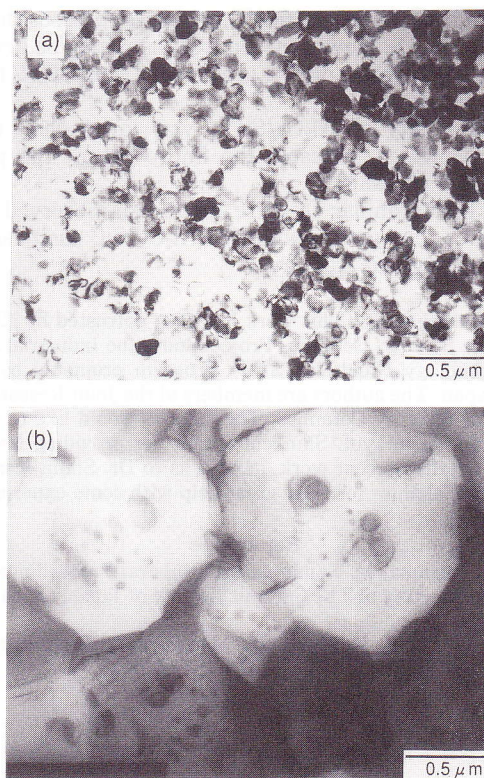


Fig. 9. Distribution of the PC(UH)-derived SiC-phase in Al_2O_3 matrix sintered at (a) 1600°C and (b) 1800°C observed by TEM method.

(a) the $\text{Al}_2\text{O}_3/\text{SiC}$ and (b) the $\text{Al}_2\text{O}_3/\text{SiC}_{\text{PC}}$ composites sintered at 1600°C. Al_2O_3 and $\text{Al}_2\text{O}_3/\text{SiC}$ composite exhibit intergranular fracture,¹⁴⁾ and the $\text{Al}_2\text{O}_3/\text{SiC}$ composite in this study also displays intergranular fracture as shown in Fig. 8(a). The fracture mode of the $\text{Al}_2\text{O}_3/\text{SiC}_{\text{PC}}$, however, is intragranular as shown in Fig. 8(b).

Distribution of the PC-derived SiC-phase was analyzed by TEM method as shown in Fig. 9. No significant change in grain size can be observed in the $\text{Al}_2\text{O}_3/\text{SiC}_{\text{PC}}$ composite heat-treated at 1600°C. Almost all SiC phase derived from polycarbosilane at 1600°C exists at the grain boundary as the fine crystalline grains, and separate each Al_2O_3 grain. It means the PC coating prevents contact between the Al_2O_3 particles and suppresses the grain growth. The Al_2O_3 grains of the sample heat-treated at 1800°C are larger than those of 1600°C, which contain some SiC nanoparticles inside the grain. Some PC-derived SiC layer also exists at the grain boundary. The PC-derived SiC layers suppress the grain growth, however, some of them may be drawn inside the grain during the grain growth.

4. Conclusion

In this study, the effects of polycarbosilane (Nippon Carbon Co., Ltd., type-UH) addition on the microstructure and the mechanical properties of Al_2O_3 ceramics were investigated and the following was concluded.

(1) Four-point bending strength of Al_2O_3 was increased, and the scatter in bending strength values significantly decreased by the polycarbosilane coating in comparison with the $\text{Al}_2\text{O}_3/\text{SiC}$ (particle) composite.

(2) Polycarbosilane addition results in a significant decrease in the grain growth rate of Al_2O_3 , and the mean particle size decreases with increasing the polycarbosilane content.

(3) The polycarbosilane derived SiC phase is present at

the grain boundaries at 1600°C, which suppresses the grain growth of Al_2O_3 . However, some of them may be drawn inside the Al_2O_3 grains during grain growth at 1800°C to form SiC nanoparticles.

(4) Porosity of $\text{Al}_2\text{O}_3/\text{SiC}_{\text{PC}}$ was lower than that of $\text{Al}_2\text{O}_3/\text{SiC}$ which indicates the improving of the powder fluidity and packing.

(5) Intragranular fracture mode was observed in the $\text{Al}_2\text{O}_3/\text{SiC}_{\text{PC}}$ composites while the $\text{Al}_2\text{O}_3/\text{SiC}$ composites exhibit intergranular fracture.

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