

Role of Alumina in the SiC-Y₂O₃-Al₂O₃ Sintering System

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Abstract

Aluminum oxide and an Al element are responsible for the sintering in the SiC-Y₂O₃-Al₂O₃ system. The mixed powders of β -SiC, Y₂O₃ and Al₂O₃ are sintered at various temperatures: at 1925°C for 30 to 40 wt% of SiC, at 1950°C for 45 to 55 wt%, at 2050°C for 60 wt% and at 2150°C for 87.6 wt%. The sintering mechanism can be divided into four groups based on these sintering temperatures.

Introduction

Silicon carbide is stable up to 2200°C, and offers advantageous properties such as considerable strength and good oxidation resistance at high temperatures. That makes silicon carbide a candidate for structural materials used at elevated temperatures, together with Si₃N₄. Pressureless sintered SiC can be formed by the addition of a sintering aid. Several sintering aid systems have been reported: B-C system [1], Al-C system [2,3], Y₂O₃-Al₂O₃ system [4-7] Al-B-C system [8], Al₂O₃-Al₄C₃ system [9] and Al₂O₃ system [10].

Various amounts of SiC can be sintered with yttria and alumina. There are three compounds in the yttria-alumina system. The Y₄Al₂O₉ compound shows a martensitic transformation [11]. Since the high degree of toughness of ZrO₂ ceramics is based on this transformation, toughened ceramics may be prepared from that compound. Oxide products of the sintered specimen vary depending on the amount of SiC [11]. The sintering mechanism must be changed by the product.

This paper presents the role of alumina in the sintering of SiC in the SiC-Y₂O₃-Al₂O₃ system.

Experimental procedure

The preparation of a sintered compact (SiC-88) of 87.6 wt% SiC, 8.1 wt% Y₂O₃ and 4.3 wt% Al₂O₃ has been reported [4]. Yttria (Nippon Yttrium Co. Ltd., 99.9% was dissolved in HCl solution. When ammonia solution was added, Y(OH)₃ was precipitated. This hydroxide was dissolved in HCl solution, and Y-compound was obtained. Aluminum isopropoxide (Wako Chemicals Ind. Co., reagent grade) was dissolved in benzene. HCl solution was added to the benzene solution until white precipitate was not observed. This water solution contained Al-compound β -SiC (Ibiden Co., 0.3 μ m) was added to the water solution of Y- and Al-compounds. After evaporation of water, the mixture of the powder and compounds was molded. The molded powder was fired: 1400 to 2050°C at 6.7°C/min and 2050 to 2150°C at 1.7°C/min.

The specimens of SiC from 30 to 60 wt%, SiC-30, SiC-40, SiC-45, SiC-50, SiC-55 and SiC-60, were prepared using powders of β -SiC, Y₂O₃ and Al₂O₃ (Asahi Chemical Ind., 99.99%). The mixing ratio of Y₂O₃ and Al₂O₃ was 2 mole to 1 mole. The three powders were wet milled with nylon-coated steel balls in a polyethylene container for 24 h. The mixed and dried powder was added to a water solution of 5 wt% of polyethylene glycol. After removing the water, specimens for sintering were obtained in the form of a plate-like shape by cold-pressing at 35 MPa.

followed by cold-isostatic-pressing at 200 MPa. As a standard practice, heat to 500°C at 2°C/min and firing at 500°C for 2 h in air were incorporated in every sintering run to facilitate removal of polyethylene glycol. Sintering was performed in an induction furnace from 1925 to 2050°C at 100°C/min.

The polished surface of a specimen was observed by an optical microscope (Olympus, BH-3). The microstructure of the polished surface was examined by scanning electron microscopy (Hitachi, S-570) with an energy-dispersive X-ray analyser. The crystal structure was determined by an X-ray diffractometer (Rigaku, RAD-B). The thin foil specimens were characterized by transmission electron microscopy (JEOL, 2000EX) and examined by an electron microscope equipped with an energy-dispersive X-ray analyzer (JEOL, 2000FX).

Results

The sintering temperature, holding time and oxide products of sintered specimens are shown in Table 1. The sintering temperature varied depending on

Table 1. Sintered specimens

Name	SiC (wt%)	Y ₂ O ₃ (wt%)	Al ₂ O ₃ (wt%)	Sintering Temp.(°C)	Sintering Time(min.)	Oxide product
SiC-30	30	57.1	12.9	1925	1	Y ₄ Al ₂ O ₉
SiC-40	40	48.9	11.1	1925	1	Y ₄ Al ₂ O ₉
SiC-45	45	44.9	10.1	1950	5	Y ₄ Al ₂ O ₉ , Y ₂ O ₃ , Al ₂ O ₃
SiC-50	50	40.8	9.2	1950	5	Y ₄ Al ₂ O ₉ , Y ₂ O ₃ , Al ₂ O ₃
SiC-55	55	36.7	8.3	1950	5	Y ₄ Al ₂ O ₉ , Y ₂ O ₃ , Al ₂ O ₃
SiC-60	60	32.6	7.4	2050	1	Y ₄ Al ₂ O ₉ , Y ₂ O ₃
SiC-88	87.6	8.1	4.3	2150	0	Y ₄ Al ₂ O ₉ *, Y ₃ Al ₅ O ₁₂ *

*Product between 1800 and 1900°C.

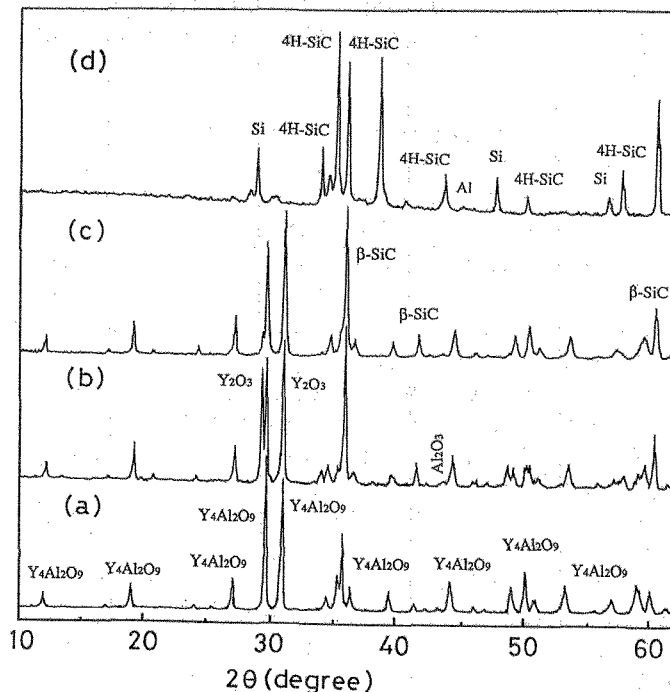


Fig. 1. X-ray diffraction pattern: (a) SiC-40, (b) SiC-50, (c) SiC-60 and SiC-88.

amount of SiC. The oxide of SiC-88 was not products contained in the final product, but in the product fired at 1800-1900°C. The specimens were divided into four groups according to the sintering temperature, namely, SiC-30 and SiC-40, from SiC-45 to SiC-55, SiC-60, and SiC-88.

Figure 1 shows the X-ray diffraction pattern of SiC-40, SiC-50, SiC-60 and SiC-88. The pattern of SiC-30 is similar to that of SiC-40. The presence of Al_2O_3 and β -SiC was clear in SiC-30 and SiC-40, but there were not Y_2O_3 and ZrO_2 . The X-ray pattern from SiC-45 to SiC-55 was almost same. The pattern of SiC-88 indicates the disappearance of β -SiC and the formation of 4H-SiC, Al and oxide compounds existed, but have not been identified in SiC-88. The product fired between 1800 and 1900°C contained the oxide products of $\text{Y}_4\text{Al}_2\text{O}_9$ and Al_5O_{12} [5]. These two compounds are decomposed above 1900°C [5].

The SEM image of SiC-30, SiC-40, SiC-45, SiC-50, SiC-55 and SiC-60 are shown in Fig. 2. The SiC particle sizes of SiC-30 and SiC-40 were nearly same as that of the starting SiC. The SiC particles were not dispersed uniformly. The crystal of

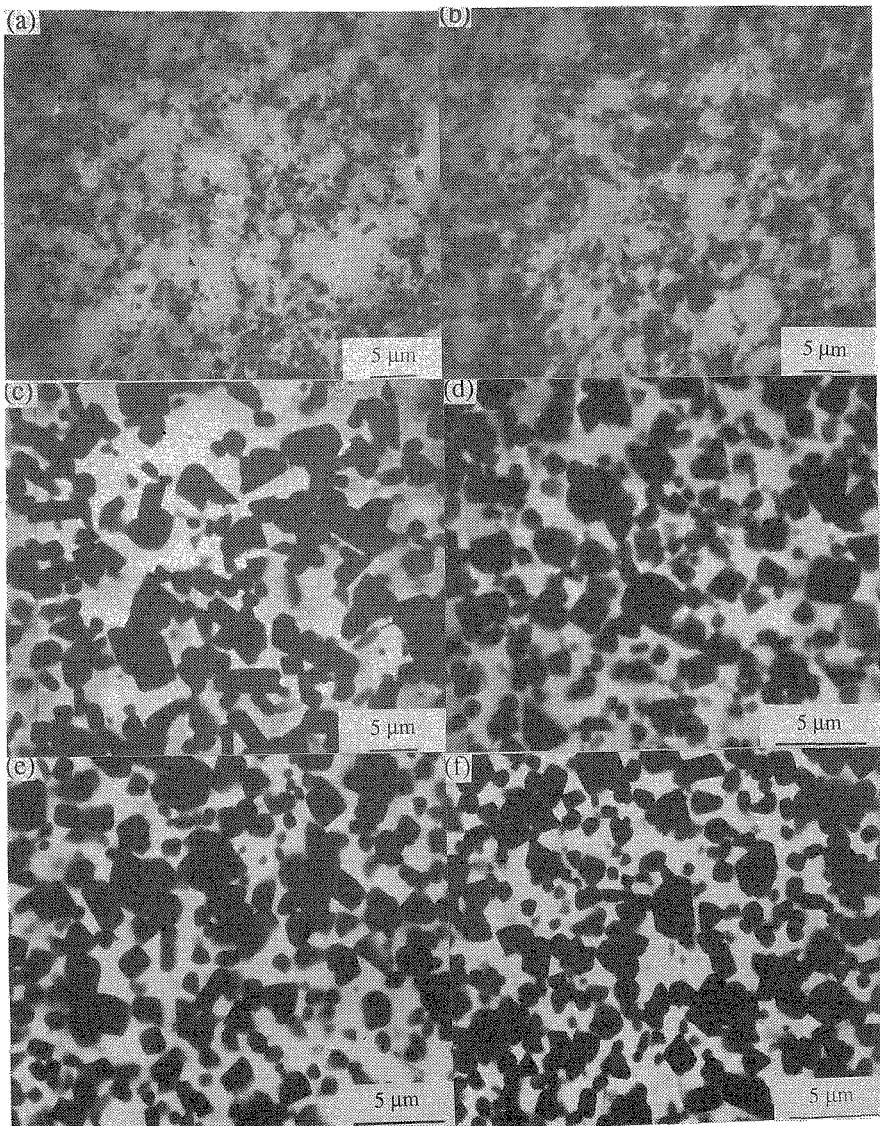


Fig. 2. SEM image: (a) SiC30, (b) SiC-40, (c) SiC-45, (d) SiC-50, (e) SiC-55 and (f) SiC-60.

SiC grew in SiC-45 to SiC-60. Firing at 1950°C from SiC-45 to SiC-60, which were prepared by the same method as that used with SiC-30 and SiC-40, produced a uniform dispersion of SiC crystals.

Figure 3 shows the optical micrograph of SiC-88. White oxide particles were dispersed in the SiC matrix. Black particles, identified by the following elemental analysis, were an Al metal. The SEM image and elemental analyses of SiC-88 are shown in Figs. 4 and 5. The particles having Si and C elements referred to the SiC matrix that did not contain the Al and Y elements. The Al element was detected from the particle with the largest amount of the Si element, but the C and Y were not.

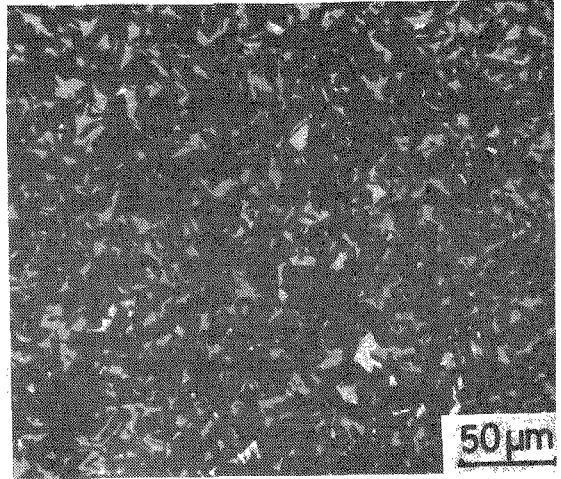
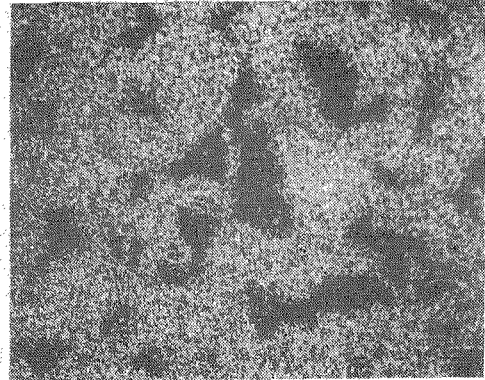


Fig. 3. Optical micrograph of SiC-88.

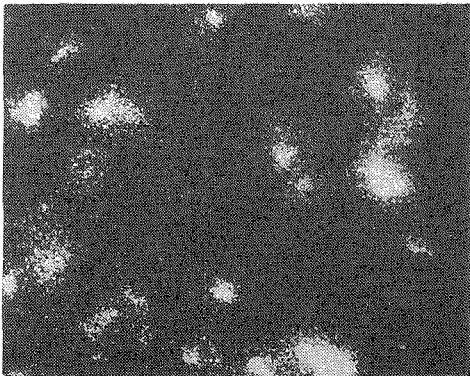
This particle must be a Si semiconductor. The black particle shown in Figs. 4 and 5 contained much Al and a small amount of Si, but did not contain the C element.



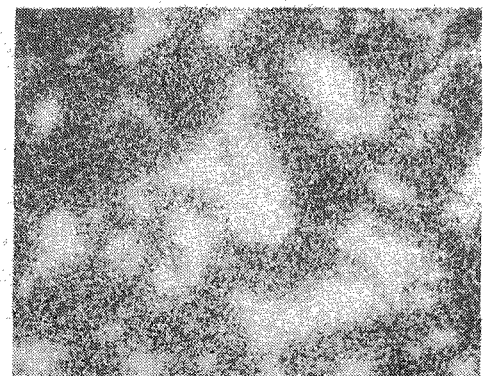
(a)



(b)



(c)



(d)

Fig. 4. SEM image and elemental analysis of SiC-88: (a) SEM image, (b) C, (c) Al and (d) Si.

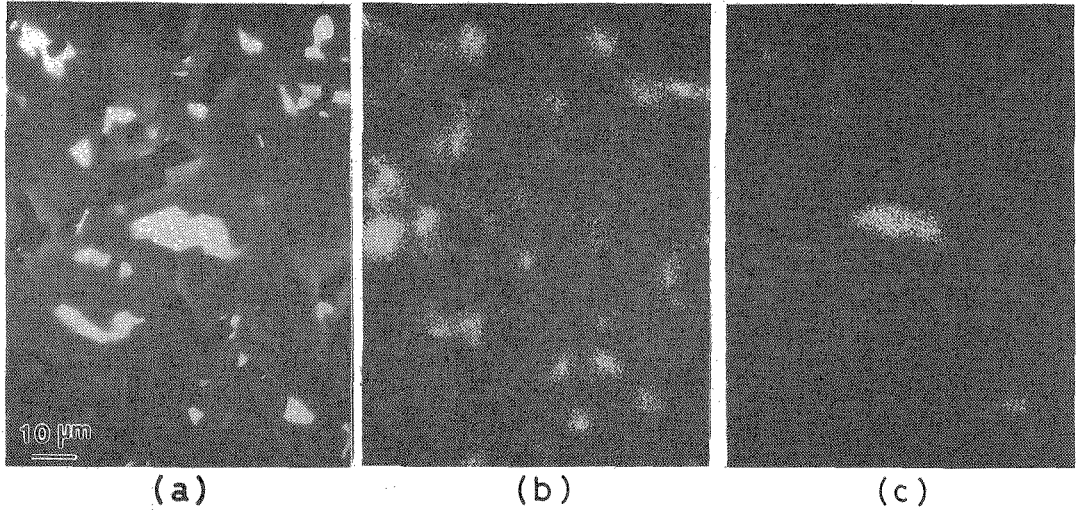


Fig. 5. SEM image and elemental analysis of SiC-88: (a) SEM image, (b) Al and (c) Y.

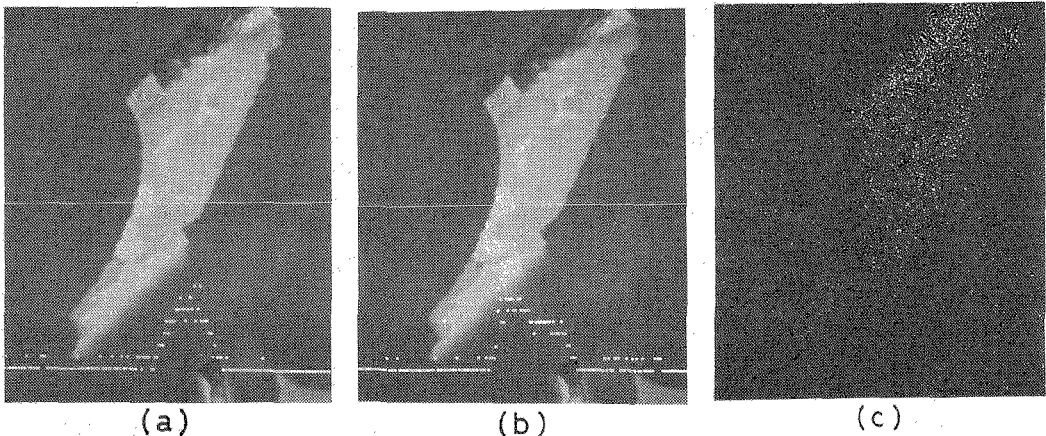


Fig. 6. SEM image and elemental analysis of a particle in SiC-88: (a) Al, (b) Y and (c) Al.

This evidence identified the black particle as being an Al metal with Si. The white oxide particle suggested that the Si element was one of the constituent elements. The C element was not detected in the oxide. The oxide particles were divided into two groups, one with the Al element and the other without it. Figure 6 shows the SEM image of an area of a particle where the amount of Al was different. The edge of the particle, consisting of a large amount of the yttrium element, came in contact with the black Al metal adjacent to the SiC matrix. In this oxide particle, an Al-O compound was eliminated from an Y-Al-O compound and reacted with SiC. Both compounds could not be crystallographically identified by X-ray diffraction pattern.

Discussion

SiC-30 and SiC-40, fired at the same temperature and with the same SiC dispersion, can be sintered in the same manner. The oxide part of the two specimens is composed of $Y_4Al_2O_9$. The $Y_4Al_2O_9$ compound prepared from Al_2O_3 and Y_2O_3 is responsible for sintering of specimens. A mixture of $2Y_2O_3$ and Al_2O_3 was fired at 1920°C to form an $Y_4Al_2O_9$ polycrystal with the particle size of

several hundred μm [12]. So the $\text{Y}_4\text{Al}_2\text{O}_9$ oxide of SiC-30 and SiC-40 is exclusively sintered, and then excludes the SiC particle, as shown in Fig. 2. The excluded particle does not take part in sintering and does not grow larger than the starting size. Silica on the SiC surface can react with $\text{Y}_4\text{Al}_2\text{O}_9$. The addition of several percent of silica lowers the melting temperature of $\text{Y}_4\text{Al}_2\text{O}_9$ near 1925°C [13]. It is possible that silica on β -SiC may reduce the melting temperature of the oxide part in SiC-30 and SiC-40 near 1925°C . The Si element was not detected in the oxide part by EDAX. The sintering temperature of $\text{Y}_4\text{Al}_2\text{O}_9$ with 3 wt% SiO_2 was ca. 1700°C where the liquid phase didn't appear [12]. This evidence indicates that the melt of $\text{Y}_4\text{Al}_2\text{O}_9$ with SiO_2 is not related to sintering of SiC.

The sintering temperature and the crystal size of SiC were the same from SiC-45 to SiC-55, indicating that three specimens are produced by the same sintering mechanism. There is insufficient oxide for obtaining the dense specimen. After the $\text{Y}_4\text{Al}_2\text{O}_9$ polycrystal becomes dense in the middle stage of the sintering process, the $\text{Y}_4\text{Al}_2\text{O}_9$ compound is partially decomposed to form Al_2O_3 and Y_2O_3 . Ytria doesn't cause sintering of SiC [4]. Since alumina is effective on sintering of SiC above 1900°C [10], the SiC powder is sintered at the final stage by alumina. So the SiC crystal becomes as large as $5\ \mu\text{m}$ in diameter. The final sintering is not associated with the liquid phase of oxide, as shown by the fact that the Si element was not detected by EDAX.

The crystal size and constitution of SiC-60 were not different from those of SiC-45, SiC-50 and SiC-55. The higher sintering temperature of SiC-60 is explained by the decrease of the oxide content. Above 2000°C , SiC and Al_2O_3 react to form Al and Si [5,14]. The Al element in SiC-60 was not detected by the measurement of transmission electron microscopy and EDAX. The sintering process of SiC-60 was not affected by an Al liquid. The melt of $\text{Y}_4\text{Al}_2\text{O}_9$ brought about the final densification.

The sintering of SiC-88 can be completed after the formation of Al and Si [5]. The original β -SiC crystal is transformed into 4H-SiC by the Al element [15]. The solubility limit of Al in SiC is 1 wt% at 2200°C [16]. An Al content of SiC-88 of more than 1 wt% is necessary for the formation of the Al metal. The oxide additive considerably promotes the shrinkage of SiC-88 at 2000°C [4,5]. The sintering at the final stage is made possibly by the Al metal or SiC doped with Al. The density of the specimen, prepared from the SiC powder doped with 1 wt% of Al, is ca. 94% [2]. An Al liquid, rather than SiC doped with Al, brings about the dense specimen of SiC-88. The liquid of Al_2O_3 - SiO_2 and Al_2O_3 - Al_2O_3 in the SiC- Al_2O_3 system effects on the final densification near 2000°C [14]. Even if the unidentified oxide of SiC-88 has these compounds, their concentration might be too low to affect the densification.

Summary

The Al element and Al-compounds are responsible for the densification of β -SiC, Y_2O_3 and Al_2O_3 powders. The sintering mechanism can be classified into four groups based on the firing temperatures.

1. The densification of SiC-30 and SiC-40, which prepared from the β -SiC (30 and 40 wt%) and oxide (70 and 60 wt% of $\text{Y}_4\text{Al}_2\text{O}_9$) powders, is achieved at 1925°C exclusively by the sintering of $\text{Y}_4\text{Al}_2\text{O}_9$.
2. As the ratio of oxide ($\text{Y}_4\text{Al}_2\text{O}_9$) is changed from 45 to 55 wt%, the sintering temperature rises to 1950°C . After the densification of $\text{Y}_4\text{Al}_2\text{O}_9$ at the middle stage, the SiC powder is sintered by alumina at the final stage to form the dense specimen.

3. The liquid phase of $Y_4Al_2O_9$ participates at the final stage the sintering of SiC-60 which is synthesized from 60 wt% of β -SiC and 40 wt% of $Y_4Al_2O_9$ at 2050°C.
4. The mixture of 87.6 wt% β -SiC, 8.1 wt% Y_2O_3 and 4.3 wt% Al_2O_3 is finally sintered at 2150°C by the Al liquid.

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