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Improvement in the oxidation resistance of liquid-phase-sintered silicon carbide with aluminum oxide additions

Keiichiro Suzuki*, Nobuo Kageyama[1], Takashi Kanno[2]

Research Center, Asahi Glass Co., Ltd., Yokohama 221-8755, Japan

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Abstract

Improvement in oxidation resistance of silicon carbide (SiC) with aluminum oxide (Al_2O_3) additions was investigated using high purity starting materials. Green compacts of SiC powders with impurity of approximately 200 ppm metal mixed with a high purity Al_2O_3 powder were pressureless-sintered followed by hot-isostatic pressing to a density of >99.5%. The sinterability and the strength of the SiC were similar to those from the SiC powder with impurity of 1100 ppm metal. With decreasing Al_2O_3 content and metallic impurity, the oxidation resistance of the SiC increased. SiC with 1.4 mass% Al_2O_3 content had a parabolic oxidation rate constant of 7.8×10^{-12} kg^2 m^{-4} s^{-1} for 400 h oxidation at 1300 °C in dry air, which is lower than those reported for other LPS-SiC and comparable to that of CVD-SiC.

Keywords: A. Sintering; B. Impurities; D. SiC; Oxidation

1. Introduction

Liquid-phase-sintered SiC (LPS-SiC) is an important engineering ceramic material, which has been extensively investigated in recent years. It has high mechanical properties, in particular, excellent fracture toughness due to in-situ toughening during sintering. High oxidation resistance is required for high temperature applications. Chemically-vapor-deposited SiC (CVD-SiC) and solid-state-sintered SiC with boron and carbon have been reported to have a high oxidation resistance [1–4].

Oxidation behavior of LPS-SiC with various additives has been studied [5–12]. The oxidation resistance of LPS-SiC is believed to be lower than that of CVD-SiC or boron-doped SiC, because LPS-SiC contains an oxide grain boundary phase deriving from additives. It is known that cations of additives and impurities of starting materials lower the oxidation resistance of non-oxide ceramics such as Si_3N_4 and SiC. The migration of the cations to the oxidized SiO_2 film decreases the viscosity of the film and increases the diffusion rate of oxygen through the film. Jensen et al. [9] have reported that yttrium aluminum garnet (YAG) in the grain boundary phase of SiC sintered with Al_2O_3 and Y_2O_3 dramatically increase the oxidation rate at 1350 °C due to a possible reaction between SiO_2 and YAG that forms a low viscosity liquid. They have concluded that the SiC, which has a typical additive combination for LPS-SiC, may have the upper-use temperature limit of less than 1345 °C.

The authors have investigated pressureless LPS-SiC with Al_2O_3 additions [13–15]. The SiC had a density of >97% and a favorable fracture toughness of 5–6 MPa m$^{1/2}$ due to a microstructure with elongated plate-like grains resulting in an effective intergranular crack deflection. Its oxidation behavior has been reported to follow a parabolic law from 1200 to 1300 °C in dry air up to 1000 h [7]. An apparent activation energy of 287 kJ/mol was obtained from the oxidation of the SiC at 1100–1400 °C. The mass gain at 1400 °C of the SiC was 1.7 times that at 1300 °C after oxidation for 100 h. The oxidation resistance increased with

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* Corresponding author. Tel.: +81 45 503 7162; fax: +81 45 503 5179.
E-mail address: keiichiro-suzuki@agc.co.jp (K. Suzuki).

[1] Present address: Takasago Factory, Asahi Glass Co., Ltd., Takasago 676-8655, Japan.

[2] Present address: 1-15-7 Kamitammachi, Kanagawa-ku, Yokohama 222-0831, Japan.

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Table 1
Characteristics of SiC starting materials

Denotation	Type	Metallic impurity (ppm)				Oxygen content (mass%)	Specific surface area (m^2/g)	Particle size (μm)
		Al	Ca	Fe	Total			
S1	α	100	100	400	1100	1.05	14	0.48
S2	α	62	12	44	221	1.05	18	0.60
S3	β	19	2	28	158	0.33	16	0.60

S1: A-1, Showa Denko, Japan (commercially available). S2: purified powder of A-1 by acid treatment, Showa Denko. S3: powder synthesized by reaction of Si and C, Showa Denko. Other major metallic impurities of S3: Ni 34 ppm, Mo 22 ppm, Na 1.5 ppm.

decreasing Al_2O_3 content of the SiC, similar to that of hot-pressed SiC with Al_2O_3 [5].

The purpose of this study is to improve the oxidation resistance of LPS-SiC with Al_2O_3 additions. High purity SiC powders with low amounts of Al_2O_3 additive were pressureless-sintered (PLS) and subsequently hot-isostatic pressed (HIP) to obtain dense sintered bodies. The sinterability and the flexural strength of SiC with different purities and crystal types have been compared. Subsequently, the effect of the Al_2O_3 content and metallic impurity on oxidation resistance of the SiC has been investigated.

2. Experimental procedure

A standard purity α-SiC powder and high purity α- and β-SiC powders were used as the starting materials. The characteristics of the powders are listed in Table 1. High purity low soda α-Al_2O_3 powders (A1: AKP-50, Sumitomo Chemicals, Japan, A2: RA-30, Iwatani Chemicals Industry, Japan) were used as sintering additives. The purities of the powders A1 and A2 were >99.99 mass% (Na < 10 ppm) and >99.9 mass% (Na 30 ppm), respectively. The mean particle sizes of the powders A1 and A2 were 0.23 and 0.83 μm, respectively. The powder A2 was used only for the samples of SiC from the powder S1 for the oxidation tests. SiC and Al_2O_3 powders with various addition amounts were mixed using a ball-mill in ethanol with a plastic jar and steel-ball-implanted plastic balls. The dried powder mixtures were uniaxially pressed in a steel die under 20 MPa followed by isostatic pressing under 200 MPa.

The green compacts were sintered pressurelessly in a graphite resistance furnace. The samples were embedded in a powder bed composed of graphite grits (size < 0.5 mm, purity 99.99 mass%, Toyo Carbon, Japan) and the Al_2O_3 powder A2, which was placed in a graphite case with a lid. The mass ratio of graphite grits and Al_2O_3 was 98:2 in most cases. The temperature of the furnace was raised at 400 °C/h in vacuum from room temperature to 1000 °C and in an argon atmosphere above 1000 °C, and it was held at 1975 °C for 2.5–5 h. Then the pressureless-sintered bodies were HIPped at 1950 °C for 2 h in argon of 190 MPa. The dimensions of the sintered samples were approximately 80 mm × 40 mm × 10 mm.

Densities of the sintered bodies without the as-sintered surface were determined by the Archimedes method. Theoretical densities were determined by the rule of mixtures with the starting compositions to calculate the relative densities. For flexural strength and oxidation resistance tests, the samples were cut into specimens of 3 mm × 4 mm × 40 mm and the cut surfaces were mirror-polished. Three point flexural strength measurements were performed under a crosshead speed of 0.5 mm/min at room temperature (RT) and at 1300 °C. For the oxidation test the specimens were placed on high purity Al_2O_3 setters with fairly good point contacts between the specimen and the setter. In a box-type furnace with $MoSi_2$ heating elements, the stacked setters with the specimens were put in an Al_2O_3 muffle through which dried air was passed at a speed of 0.15 L/min. The oxidation tests were performed at 1300 °C for 300–400 h. The specimens were weighed at the beginning of the test and at intervals throughout the exposure period.

3. Results and discussion

Table 2 shows the relative densities and flexural strengths of the SiC samples at RT and at 1300 °C with a 2 mass% addition of Al_2O_3 after PLS (before HIP) and after HIP. The obtained densities of the PLS-SiC were in the range of 98–99%. The densities of PLS-SiC from the α-SiC powder S1 and S2 indicate that the difference in the purity of the starting powder does not affect the sinterability. The SiC from the β-SiC powder S3 with 2 mass% Al_2O_3 had a favorably comparable sinterability to those of the α-SiC powders. For reference SiC from a commercially available β-SiC powder (UF grade, Betarundum, Ibiden, Japan) had a

Table 2
Relative densities and flexural strengths of SiC after PLS and HIP with 2 mass% Al_2O_3 using three SiC powders

SiC powder	Relative density (%)		Flexural strength (MPa)			
	PLS	HIP	RT		1300 °C	
			PLS	HIP	PLS	HIP
S1	98.7	99.9	539 (205)	654 (61)	404 (110)	525 (26)
S2	99.0	99.9	669 (31)	685 (51)	468 (33)	448 (62)
S3	98.4	99.9	559 (48)	704 (65)	411 (28)	518 (67)

$n = 5$, values in parenthesis are standard deviation.

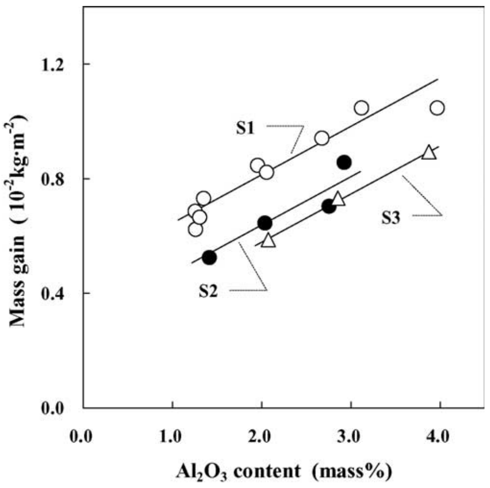

Fig. 1. Mass gain of oxidation at 1300 °C after 1000 h as a function of Al_2O_3 content for the sintered SiC fabricated from three SiC powders S1, S2 and S3.

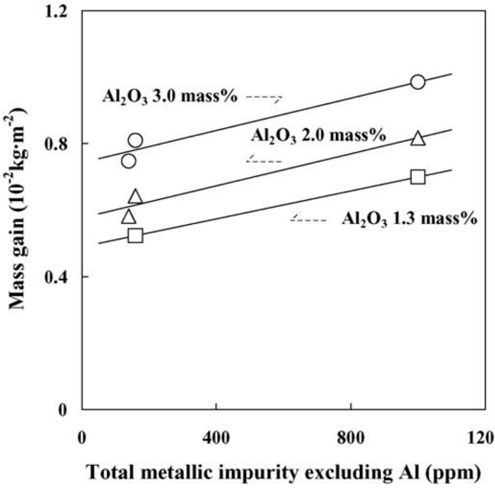

Fig. 2. Mass gain of oxidation at 1300 °C after 1000 h as a function of total metallic impurity excluding Al of the sintered SiC for Al_2O_3 content of 1.3, 2.0, and 3.0 mass%.

relatively lower density of 97.1% after PLS in the same fabricating process. The HIP treatment increased the density in each case to 99.9%. The flexural strengths of the SiC of the powders S1 and S3 at RT and at 1300 °C increased in the range of 21–30% with HIP, whereas that of the SiC of the powder S2 did not have a considerable change with HIP, the reason of which has not been understood.

When decreasing the Al_2O_3 addition to less than 2 mass%, the density of the sintered SiC decreased. The least amount of Al_2O_3 content required to increase the density of the SiC beyond 99.5% was 1.3–1.4 mass% for the SiC of the powders S1 and S2, and 2 mass% for that of the powder S3 in this study.

Fig. 1 shows the mass gain versus Al_2O_3 content for the SiC fabricated from three starting SiC powders after oxidation at 1300 °C for 1000 h. The mass gains after 1000 h were determined by extrapolating the data up to 300–400 h. The extrapolation is considered to be correct, because each mass gain curve as a function of the square root of oxidation time was linear from the origin according to the parabolic law. The Al_2O_3 content was the analyzed value of the specimen. The higher the purity of the starting SiC powder, the higher the oxidation resistance of the SiC. The slopes of the three linear lines were almost similar, 1.7×10^{-3} kg m^{-2} (Al_2O_3 %)$^{-1}$. Each mass gain decreased with the decreasing Al_2O_3 content in the SiC. It is noted that the relation between the mass gain and the Al_2O_3 content showed the same tendency irrespective of the differences in crystal type (α, β) and the purity of the starting SiC powder.

Mass gains as a function of total metallic impurity excluding Al of the sintered SiC are shown in Fig. 2 for three levels of Al_2O_3 content read from the lines in Fig. 1. The impurity was calculated as a mass amount of SiC in the sintered body using impurity data shown in Table 1. The slope of the line for 2 mass% of Al_2O_3 was 2.4×10^{-6} kg m^{-2} ppm^{-1}. This value is eight times that of the Al content, indicating that the metallic impurity excluding Al has a larger effect on oxidation than Al. However, in this study, the metal cation that plays a major role has not been identified. Impurity elements such as Fe and K have been known to lower the viscosity of SiO_2 glass resulting in an increase of the oxidation rate [6]. In our other

Table 3

A comparison of parabolic oxidation rate constants at 1300 °C for SiC in this study and those from relevant literatures

	SiC	Parabolic rate constant (kg^2 m^{-4} s^{-1})	Oxidation atmosphere	Oxidation time (h)[a]	Reference
A	LPS-SiC	7.8×10^{-12}	Dry air	0–400	This study
B	LPS-SiC	8.4×10^{-11}	Room air	0–600	Jensen et al. [9]
C	LPS-SiC	5.0×10^{-10}	Room air	0–50	Baxter et al. [10]
D	LPS-SiC	5.1×10^{-11}	Dry air	30–200	Guo et al. [12]
E	LPS-SiC	2.3×10^{-10}	Dry oxygen (0.1 MPa)	0–12	Singhal [6]
F	CVD-SiC	6.5×10^{-12}	Dry oxygen (0.1 MPa)	0–100	Ogbuji et al. [1]
G	CVD-SiC	1.3×10^{-11}	Dry oxygen (0.1 MPa)	0–100	Fox [2]
H	Sintered SiC	2.2×10^{-12}[b]	Room air	0–12	Costello and Tressler [3]

A: SiC with 1.4 mass% Al_2O_3 content fabricated from powder S2. B: SiC with YAG content. C: hot-pressed SiC with Al_2O_3 and Y_2O_3. D: SiC with AlN and Er_2O_3. E: hot-pressed SiC with Al_2O_3 (Al: 1.0 mass%, Fe: 0.1 mass%). H: boron-doped SiC.

[a] Time range used for calculation of parabolic rate constant.

[b] The parabolic rate constant expressed in terms of thickness has been converted to that in terms of mass gain [17].

study [16], in which a Ca or Fe source added to SiC powder with Al_2O_3, Ca was found to have a stronger effect on increasing the mass gain by oxidation than Fe. Therefore, in this case, Ca and Fe, certain amounts of which are contained in SiC, are supposed be the main cations that affect the oxidation resistance.

Table 3 shows the parabolic oxidation rate constants (K_P) at 1300 °C for various SiC in this study and those from relevant literatures.

$\Delta m^2 = K_P t$, where Δm is mass gain per unit area during time, t.

The SiC with the highest oxidation resistance in this study had a K_P of 7.8×10^{-12} kg^2 m^{-4} s^{-1} at 1300 °C. We can demonstrate that this K_P value is lower than those of other LPS-SiC ceramics and comparable to those of CVD-SiC. The data of CVD-SiC in Table 3 are results of oxidation in dry oxygen. Incidentally the mass gain of the SiC sintered with Al_2O_3 after oxidation in dry oxygen was approximately 10% higher than that after oxidation in dry air at 1300 °C, which is not described in detail in this paper. The high oxidation resistance of the SiC in this study would be attributed to only Al_2O_3 addition with a small amount in case the SiC starting powder has very high purity.

4. Conclusion

Oxidation resistance of LPS-SiC was significantly improved using high purity SiC powder with a minimal addition of Al_2O_3, pressureless-sintered and subsequently HIPped to obtain a density of >99.5%. The lowest mass gain obtained after oxidation of 1000 h in dry air at 1300 °C and the lowest parabolic rate constant K_P at 1300 °C were 5.3×10^{-3} kg m^{-2} and 7.8×10^{-12} kg^2 m^{-4} s^{-1}, respectively, for SiC with 1.4 mass% Al_2O_3 content from the α-SiC powder with a metallic impurity of 221 ppm. The K_P value of the SiC is comparable to that of the CVD-SiC. The LPS-SiC with only Al_2O_3 additive and low metallic impurity can be a useful engineering ceramic with excellent oxidation resistance for high temperature applications.

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