Liquid Phase Sintering and Mechanical Properties of SiC with Rare-Earth Oxide

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Key-words: Silicon carbide, Rare-earth oxide, Hot-pressing, Microstructure, Strength, Fracture toughness

A SiC powder of median size 0.8 μm was mixed with polyacrylic acid (PAA, dispersant) in a 0.3 mol/l-R(NO₃)₃ solution (R=Yb, Y, Gd, Sm, Nd and La) at pH 5 to adsorb uniformly the sintering additive (R³⁺ ion) on the SiC surface. The aqueous 30 vol% SiC suspension with 0.52 mass% PAA and 1.50 mass% R₂O₃ (as R(NO₃)₃), relative to SiC, was consolidated by filtration through a gypsum mold to form green compacts of 50–52% theoretical density. The consolidated green compacts were densified with grain growth to 76–99% relative density by hot-pressing under a pressure of 39 MPa at 1950°C for 2 h in an Ar flow. The addition of R₂O₃ of smaller R³⁺ ion was effective to enhance the sinterability of SiC and also to achieve smaller grain size of SiC. This result was discussed based on the additional experiment result on the chemical interaction between SiC compact and the SiO₂–R₂O₃ liquid. The average flexural strength and Weibull modulus of dense SiC were 612 MPa and 5.1, 719 MPa and 9.8 for Gd₂O₃, Y₂O₃ and Yb₂O₃ addition, respectively.

[Received November 14, 2005; Accepted December 20, 2005]

1. Introduction

Silicon carbide (SiC) is potentially useful as a high temperature structural material because of its high strength, high hardness, high creep resistance, and high oxidation resistance. For the fabrication of dense SiC, sintering additives of metal compounds, or boron and carbon, are needed because of the high covalency of SiC. The microstructure and density of fired SiC, which affect the resultant mechanical properties, depend on the characteristics of the starting powder, reactivity of sintering additives, packing density of the green compact, and sintering temperature. Recently chemical methods for the addition of sintering additives such as Al₂O₃ plus Y₂O₃ to SiC powder have been studied to control the liquid phase sintering and the resultant microstructures of SiC ceramics. The sinterability of the SiC–Al₂O₃–Y₂O₃ system depends on the amount and ratio of Al₂O₃–Y₂O₃. The densification of SiC progresses through the dissolution-reprecipitation mechanism of SiC in the liquid phase of the SiO₂–Al₂O₃–Y₂O₃ system. An amorphous SiO₂ film forms on the surface of as-received SiC powder. Addition of the sintering additives to SiC by chemical method are expected to provide the following advantages: (1) a uniform distribution of the additives around SiC particles, (2) increased densification rate by the well-distributed liquid and (3) decrease of the amount of additives. In previous papers, we investigated the interactions of the silicon carbide-yttrium nitrate-polyacrylic acid (PAA) system in an aqueous suspension to disperse uniform the sintering additive around SiC particles. The derived conclusions are as follows: (1) The amount of Y³⁺ ion adsorbed on SiC particles of isoelectric point pH 2.5 increased with an increase of pH because of the electrostatic attraction between negatively charged SiC surface and Y³⁺ ion. (2) The amount of PAA adsorbed on SiC particles decreased with increasing pH because of the electrostatic repulsion between negatively charged SiC surface and dissociated PAA. (3) The addition of PAA to the SiC suspensions with Y³⁺ ion increased the amount of Y³⁺ ion fixed to SiC particles. This result was explained by the two types of fixation mechanisms of Y³⁺ ion through adsorbed PAA: accumulation effect by neutral PAA and electrostatic attraction effect by negatively charged PAA. The Y(NO₃)₃ fixed to SiC particles is pyrolyzed in an Ar atmosphere at 1000°C to form nanometer-size Y₂O₃ on the surface of SiC particles. In this paper, we report on the sinterability, microstructures and mechanical properties of the SiC–R₂O₃ compacts (R=Yb, Y, Gd, Sm, Nd and La) hot-pressed at 1950°C. The liquid formation temperature of the SiO₂ surface layer of SiC–Y₂O₃ systems is reported to be 1775°C. This temperature is 300°C higher than the liquid formation temperature of the SiO₂–Al₂O₃–Y₂O₃ system. Once the SiC–R₂O₃ system is highly densified, the thermal resistance of SiC is greatly enhanced. However, few papers report the systematical sintering study of the SiC with rare-earth oxides. The purpose of this study is to investigate the sinterability, microstructural and mechanical properties of SiC–R₂O₃ system.

2. Experimental procedure

2.1 Forming and hot-pressing of SiC

A SiC powder with the following characteristics, supplied by Yakushima Electric Industry Co., Ltd., Kagoshima, was used in this experiment: chemical composition (mass%), SiC 98.90, SiO₂ 0.66, C 0.37, Al 0.004, Fe 0.013, median size 0.8 μm, specific surface area 13.4 m²/g. As-received α-SiC powder was dispersed at 30 vol% solid in a 0.3 mol/l-R(NO₃)₃ aqueous solution at pH 5 and then PAA (average molecular weight 10000, Daiichi Kogyo Co., Kyoto) of 0.40 mg/m²-SiC surface (saturated amount) was added to be adsorbed on the SiC...
to observe the microstructures by scanning electron microscope (SM300, Topcon Technologies, Inc., Tokyo). The hot-pressed SiC was cut into the specimens with sizes of 3 mm height, 4 mm width and 38 mm length. The specimens were polished with SiC paper of Nos. 600 and 2000 and diamond paste of 6 and 1 μm. The flexural strength of SiC–R₂O₃ system was measured at room temperature by four-point flexural method over spans of 30 mm (lower span) and 10 mm (upper span) at a crosshead speed of 0.5 mm/min. The fracture toughness was evaluated by single-edge V-notch beam (SEVNB) method. A thin diamond blade 1 mm thick, where the tip of V-notch had a curvature radius of 20 μm, was used to introduce V-notch of \(a/W=0.1–0.6\) (\(a\) : notch length, \(W\) : width of the beam). The strength of the notched specimen was measured by three-point loading over a span 30 mm at a crosshead speed of 0.5 mm/min. Equation (1) provides the fracture toughness and equation (2) indicates the shape factor \(Y\) of crack at \(S/W=7.5\). \(P\), \(P_l\), and \(B\) in Eqs. (1) and (2) are the span width, applied load and the thickness of beam, respectively.

\[
K_{IC} = \frac{3PS}{2BW^2}Ya^{1/2} \quad (1)
\]

\[
Y = 1.964 - 2.837\lambda + 13.711\lambda^2 - 23.250\lambda^3 + 24.129\lambda^4
\]

\[
(\lambda = a/W) \quad (2)
\]

2.2 Interaction of SiC–SiO₂–R₂O₃ system

The interaction between SiC and the sintering additive was investigated using the following samples. A high purity SiO₂ powder with a specific surface area of 200 m²/g was immersed in a 0.3 mol/l–R(NO₃)₃ solution at a volume ratio of SiO₂/\(R₂O₃\) = 0.85/1.0. This volume ratio is same to the ratio of SiO₂ layers on the SiC surface to the amount of \(R(NO₃)₃\) fixed to the SiC surface in the suspension. The SiO₂-containing \(R(NO₃)₃\) suspension at pH 5 was freeze-dried. This powder was calcined at 800°C for 2 h to change to Si₂O₃–R₂O₃ system. The calcined powder was formed to the sizes of 5 mm length, 5 mm width and 2 mm height by cold isostatic pressing at 24 MPa. On the other hand, 30 vol% SiC powder without sintering additive in an aqueous solution containing PAA of 0.4 mg/ml at pH 5 was consolidated to the size of 10 mm length, 10 mm width and 3.5 mm height. The SiC powder was hot-pressed under a pressure of 39 MPa at 1950°C for 2 h in an Ar flow. The SiO₂–R₂O₃ compact was put on the porous SiC compact (71.2% relative density). These two compacts were heated at 1950°C for 10 min in an Ar atmosphere. The interface of both the compacts and the depth of the infiltration of the SiO₂–R₂O₃ liquid into the SiC compact were observed to understand the chemical interaction between SiC and SiO₂–R₂O₃ liquid.

3. Results and discussion

3.1 Hot-pressing of SiC with \(R₂O₃\)

The SiC–R(NO₃)₃–PAA suspension at pH 5.0 was filtered through a gypsum mold and the consolidated powder compacts were calcined at 1000°C in an Ar atmosphere. The packing density of the SiC with \(R₂O₃\) was about 50% of theoretical density. Figure 1 shows the relative density of the SiC with \(R₂O₃\) after the hot-pressing at 1950°C. The added \(R₂O₃\) reacts with SiO₂ on the surface of SiC and forms a liquid phase. The relative density of the SiC was 96.5±2.1% for Yb₂O₃ addition, 96.2±1.8% for Y₂O₃ addition, 95.1±1.6% for Gd₂O₃ addition, 82.2±0.6% for Sm₂O₃ addition, 84.6±1.4% for Nd₂O₃ addition and 78.8±2.4% for La₂O₃ addition, respectively.\(^{15}\) Apparently, the \(R₂O₃\) with a smaller R³⁺ ion was effective for the densification of SiC. The sintering mechanism was investigated to analyze the difference in the bulk density. Figure 2 shows the slope in the log \((∆L/L₀)–log t\) plot, where \(∆L/L₀\) is the shrinkage of SiC compact heated at 1950°C for t minutes. In the initial stage of the heating, the slope was in the range of 0.52–0.59 for Yb₂O₃, Y₂O₃ and Gd₂O₃ addition, and 0.66–0.70 for Sm₂O₃, Nd₂O₃ and La₂O₃
Experimental result suggests that Y0.50–0.61 for Sm fracture probability of 50 hot-pressed with Yb the grain growth of SiC. The final stage of heating, the slope was in the range of 0.27–0.36 for Yb, Y2O3 and Gd2O3 addition, and 0.50–0.61 for Sm2O3, Nd2O3 and La2O3 addition. The slopes of 0.33, 0.5 and 1.0 in the early stage of sintering represent the liquid phase sintering dominated by diffusion of SiC in the SiO2–R2O3 liquid, dissolution-reprecipitation mechanism and viscous deformation mechanism, respectively. The experimental result suggests that (1) the densification of the SiC compacts with Yb2O3, Y2O3 and Gd2O3 in the initial stage proceeded by dissolution-reprecipitation of SiC in the oxide liquid, and (2) the SiC with Sm2O3, Nd2O3 and La2O3 was densified by the mixed mass transport mechanisms of dissolution-reprecipitation of SiC and viscous deformation by the liquid. The final stage of densification of SiC with Yb2O3, Y2O3 and Gd2O3 may be dominated by liquid phase sintering controlled by the diffusion of SiC in the liquid. The SiC with Sm2O3, Nd2O3 and La2O3 was still densified by the dissolution-reprecipitation mechanism.

3.2 Microstructures and mechanical properties of SiC compacts

Figure 3 shows the microstructures of SiC with (a) Yb2O3, (b) Y2O3, (c) Gd2O3, (d) Sm2O3, (e) Nd2O3 and (f) La2O3, hot-pressed at 1950°C. The microstructures consisted of SiC grains of small aspect ratios. The grain size, measured on 200 grains, is shown in Fig. 4. The grain size of sintered SiC was smaller for the addition of R2O3 with smaller R3+ ion. This result is closely related to their sintering mechanisms. Formation of the SiO2–R2O3 liquid with larger R3+ ion accelerated the grain growth of SiC.

Figure 5 shows the Weibull plots of the strengths for the SiC hot-pressed with Yb2O3, Y2O3 and Gd2O3. The strength at fracture probability of 50% and the Weibull modulus were 612 MPa and 5.1 for Gd2O3 addition, 719 MPa and 6.7 for Y2O3 addition and 731 MPa and 9.8 for Yb2O3 addition, respectively. The decrease in the fracture toughness was improved the strength and Weibull modulus. The measured strengths of SiC compacts are discussed in relation to the microstructures. The strength (σ) of SiC depends on the fracture toughness (KIC) and flaw size (a). The fracture toughness was 5.7±0.3, 5.8±0.2 and 5.6±0.2 MPa·m1/2 for Gd2O3, Y2O3 and Yb2O3 addition, respectively. That is, no significant difference of the fracture toughness was measured for these three sintering additives. The fracture toughness of SiC compact reflects the fracture energy (KIC = (2EY)1/2, E : Young’s modulus, Y : fracture energy). It is reported that the fracture energy of SiC compact increases with decreasing grain size, resulting in the increased fracture toughness. However, the change in the grain size of SiC compacts with Yb2O3, Y2O3 and Gd2O3 (Fig. 4) is small and this result explains the similar fracture toughness for these three types of SiC compacts. Therefore, the strength distribution in Fig. 5 is influenced by the flaw size distribution. The linear fracture mechanics (σ = KIC/Ya1/2, Y : shape factor of flaw) is coupled with the Weibull distribution function to yield Eq. (3).
\[ F = 1 - \exp \left\{ - \left( \frac{Y}{Y_0} \right)^m \right\} = 1 - \exp \left\{ - \left( \frac{Y}{Y_0} \right)^m \left( \frac{a}{a_0} \right)^{m/2} \right\} \] (3)

The \( \sigma_o, Y_0 \) and \( a_0 \) represent the strength, shape factor of flaw and flaw size at the fracture probability \( F = 0.632 \). When the flaw size is comparable to the grain size, the strength is dominated by the grain size. Figure 6 shows the typical flaws observed in the SiC hot-pressed with Gd\(_2\)O\(_3\) (a, b) and Yb\(_2\)O\(_3\) (c, d). Most of the flaws (\( > 200 \mu m \)) in the SiC with the lowest strength were observed near the surface of SiC and were identified to be the porous parts. The flaws (\( < 100 \mu m \)) observed in the SiC with the highest strength were the solidified regions of the liquid during the cooling process (b, d). Thus, the flaw size was very large as compared with particle size. This observation indicates that the flaw size in Eq. (3) is not associated with the grain size in Fig. 3. As discussed in Section 3.3, the sinterability of SiC compact is influenced by the reactivity and wettability of the SiO\(_2\)–\( R_2\)O\(_3\) liquid to SiC particles. Increased chemical interaction between SiC particles and the SiO\(_2\)–\( R_2\)O\(_3\) liquid with smaller \( R^3+ \) ion enhances the sinterability of SiC. The increased chemical interaction is effective to reduce the flaw size and leads to the increase in the strength and Weibull modulus.

3.3 Interaction between SiC and SiO\(_2\)–\( R_2\)O\(_3\) liquid

Figure 7 shows the appearance of the inside of SiC compact (a) before and (b) after the reaction with SiO\(_2\)–\( R_2\)O\(_3\) liquid. After the heating at 1950°C in an Ar atmosphere, the SiO\(_2\)–\( R_2\)O\(_3\) compact on the SiC compact changed to a liquid phase and moved into the porous SiC compact. The infiltration depth was easily measured because of the change of the color of SiC compact. This liquid also reacted with SiC compact to form the concave on the surface of the SiC compact. The microstructure of SiC infiltrated with the SiO\(_2\)–Yb\(_2\)O\(_3\) liquid (point 1) was more porous than that of SiC without the interaction with the liquid (point 2). This observation indicates the dissolution of SiC grains into the infiltrated liquid. Figure 8 shows the concaved depth (a) and infiltration depth (b), measured at three different positions, after the reaction with the SiO\(_2\)–\( R_2\)O\(_3\) liquid. The SiO\(_2\)–\( R_2\)O\(_3\) liquid with smaller \( R^3+ \) ion has a higher reactivity to SiC compact (Fig. 8(a)), indicating the higher solubility of SiC in the liquid. This result
supports the high density of SiC with Gd$_2$O$_3$, Y$_2$O$_3$ and Yb$_2$O$_3$, after the hot-pressing (Fig. 1). In addition, the infiltration depth of the liquid increased when the ionic radius of R$^{3+}$ ion decreased. This result reflects the high wettability of the liquid to SiC particles or low viscosity of the liquid with smaller R$^{3+}$ ion, and supports the uniform distribution around SiC particles. Therefore, the high sinterability of SiC with R$_2$O$_3$ of smaller R$^{3+}$ ion is due to the high solubility of SiC and the uniform distribution of the SiO$_2$–R$_2$O$_3$ liquid around SiC particles.

4. Conclusions

In this experiment, the aqueous suspension of SiC–R(NO$_3$)$_3$–PAA system at pH 5.0 was prepared to adsorb the sintering additive uniformly around the SiC particles. The powder compact was consolidated through gypsum mold to hot-press at 1950°C in an Ar atmosphere.

(1) The consolidated SiC powder compacts with 1 vol% of R$_2$O$_3$ were hot-pressed to 76–99% of theoretical density. The addition of R$_2$O$_3$ with a smaller R$^{3+}$ ion was effective to densify SiC. The grain size of SiC was smaller for the addition of R$_2$O$_3$ with smaller R$^{3+}$ ion.

(2) The densification mechanism of SiC during the hot-pressing at 1950°C changed from the dissolution-reprecipitation to the liquid phase sintering dominated by the diffusion of SiC in the SiO$_2$–R$_2$O$_3$ liquid with increasing heating time for the addition of Yb$_2$O$_3$, Y$_2$O$_3$ and Gd$_2$O$_3$. On the other hand, the dissolution–reprecipitation mechanism proceeded by 2 h of hot-pressing for the addition of Sm$_2$O$_3$, Nd$_2$O$_3$ and La$_2$O$_3$.

(3) The high sinterability of SiC with R$_2$O$_3$ of smaller R$^{3+}$ ion is due to the high solubility of SiC and uniform distribution of the SiO$_2$–R$_2$O$_3$ liquid around SiC particles.

(4) The strength at a fracture probability 50% and the
Weibull modulus of SiC were 612 MPa and 5.1, 719 MPa and 6.7 and 731 MPa and 9.8 for the addition of Gd$_2$O$_3$, Y$_2$O$_3$ and Yb$_2$O$_3$, respectively. The decreased ionic radius of R$^{3+}$ ion improved the mechanical strength of SiC. The fracture toughness of the SiC was almost independent of the ionic radius of R$^{3+}$ of the SiO$_2$–R$_2$O$_3$ liquid, and was 5.7, 5.8 and 5.6 MPa m$^{1/2}$ for the addition of Gd$_2$O$_3$, Y$_2$O$_3$ and Yb$_2$O$_3$, respectively.

References