Enhancement of high-temperature deformation in fine-grained silicon carbide with Al doping

Takuya Tokiyama *, Yutaka Shinoda,
Takashi Akatsu, Fumihiro Wakai

*Secure Materials Center, Materials and Structures Laboratory, Tokyo Institute of Technology,
R3-23, 4259 Nagatsuta, Midori, Yokohama 226-8503, Japan*

Abstract

Fine-grained SiC was hot-pressed with Al, B, and C additives under 150 MPa at 1850 °C. The grains had an equiaxed shape and the average grain size was 360 nm in as-sintered SiC. Al was detected at grain boundaries of Al, B, C-doped SiC by using energy-dispersive X-ray spectroscopy. The uni-axial compression tests were performed at constant crosshead speed at 1772 °C in He. The strain rates of Al, B, C-doped SiC in the low-stress region were ∼1 order of magnitude faster than those of B, C-doped SiC. The stress exponent of Al, B, C-doped SiC was 1.4 in the higher stress region, and increased to 2.6 with decreasing stress. The transition of the stress exponent, which is often observed in the superplasticity of metals and oxides, e.g., ZrO_2, appeared in fine-grained SiC also.
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1. Introduction

Fine-grained boron (B), carbon (C)-doped silicon carbide (SiC) can exhibit superplastic elongation at elevated temperatures [1]. Gu [2] reported that B, C-doped SiC had no intergranular amorphous phase, so that SiC could exhibit superplastic deformation without the help of intergranular liquid phase in a similar way to that of metals. The creep and superplasticity of SiC is significantly influenced by the grain-boundary structure [3,4] and the segregation of impurities at grain boundaries. Shinoda [5] studied the effect of boron doping on compression deformation of SiC, and showed that the grain-boundary diffusion coefficient was increased with increasing amount of boron segregation at grain boundaries. Ohtsuka and co-workers [6] reported the effect of cosegregation of both boron and oxygen at grain-boundary on deformation of SiC, and suggested that the cosegregation accelerated grain-boundary diffusion further.

Aluminum (Al) has been known as an effective sintering aid, and SiC with the addition of Al is easily densified by hot-pressing [7]. Zhou et al. [8] reported that the pressureless sintering of SiC could be achieved at 1850 °C, which was 250 °C lower than the sintering temperature of B, C-doped SiC by using aluminum, boron, and carbon as additives, because this sintering process was enhanced by a liquid phase which was formed at 1800 °C [9].

The purpose of the present study is to promote the strain rate of SiC by controlling the grain-boundary chemistry. We conducted compression tests to investigate the effect of Al segregation at grain-boundaries on the deformation of B, C-doped β-SiC.

2. Experimental procedure

Ultrafine β-SiC powder (T-1 grade, Sumitomo-Osaka Cement Co., Tokyo, Japan) with a mean particle size of 30 nm was used as the raw material. The powder contained 3.5 wt% free carbon and 0.4 wt% oxygen, and other impurities were <0.0041 wt% N_2, <0.9 ppm Ca, <0.1 ppm K, <0.3 ppm Al, <1 ppm Na, and <1 ppm Zn. Amorphous boron with a mean particle size of 0.3 μm (Kojundo Chemical Laboratory Co., Saitama, Japan) and

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* Corresponding author. Tel.: +81 45 924 5335; fax: +81 45 924 5339.
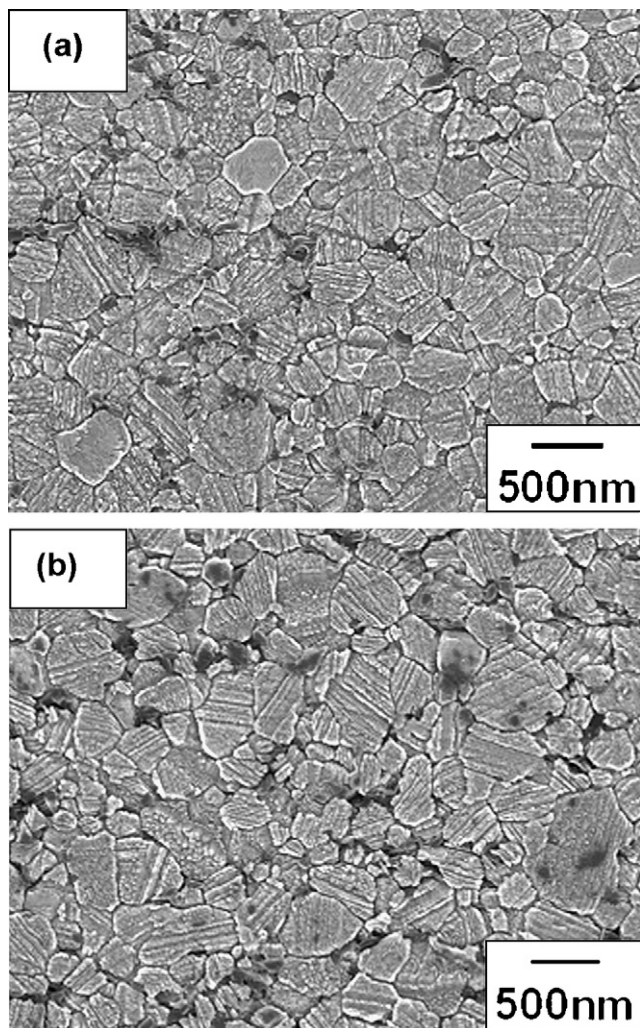*E-mail address:* tokiyama.t.aa@m.titech.ac.jp (T. Tokiyama).

Fig. 1. SEM micrographs of (a) B, C-doped SiC and (b) Al, B, C-doped SiC.

aluminum with a mean particle size of 3 μm (Kojundo Chemical Laboratory Co., Saitama, Japan) were added as sintering aids. Two kinds of samples, SiC-doped with 0.82 mol% boron (B, C-doped SiC) and SiC-doped with 0.55 mol% boron and 0.27 mol% aluminum (Al, B, C-doped SiC), were prepared from the starting materials. The mixed powders were then hot-pressed at 1850 °C under Ar gas with a stress of 150 MPa for 0.5 h.

The bulk density of B, C-doped SiC and Al, B, C-doped SiC was >3.10 g/cm^3, which was >96% of the theoretical density of SiC (3.21 g/cm^3). X-ray diffraction (XRD) measurements revealed that the SiC consisted of the β-phase. The microstructures were examined by scanning electron microscope (SEM; S4500, Hitachi Co., Japan) after mirror-polishing and subsequent etching with Murakami solution. The sintered body was composed of equiaxed grains as shown in Fig. 1. The average grain size was defined as 1.56L, where L was the average intercept length [10]. The average grain sizes of B, C-doped SiC and Al, B, C-doped SiC were 340 and 360 nm, respectively.

Specimens for transmission electron microscopy (TEM) were prepared by polishing and argon ion beam thinning. High-resolution TEM (HRTEM) was performed by using 200 kV microscope (2010F, JEOL Ltd., Tokyo, Japan). The chemical composition of grain-boundary in Al, B, C-doped SiC was analyzed by energy-dispersive X-ray spectroscopy (EDS). While only silicon and carbon were detected in the grain interior, aluminum was detected at the grain-boundary also.

The sintered body was cut into rectangular bars with dimension of 2 mm × 2 mm × 3 mm for compression testing. Compression tests were conducted at a constant crosshead speed at a temperature of 1772 °C, with initial strain rates from 1×10^{-5} to 2×10^{-3} s^{-1} in a He atmosphere by an electrically controlled hydraulic machine (Model EHF-EG10kNT-10L Servo Pulser, Shimazu Corp., Kyoto, Japan). Each sample was heated up to the test temperature at a rate of 50 °C/min and maintained at that temperature for 30 min to remove the thermal expansion of the machine system. True stress was calculated by assuming that the volume of the specimen was constant during deformation.

3. Results and discussion

Boron segregation to grain boundaries in B, C-doped SiC was detected by Gu [2] by using spatially resolved electron microscopy. Boron took the place of silicon, and formed bonds in a local environment that were similar to those in B$_4$C [11]. We assume that boron segregated to grain boundaries in both B, C-doped SiC and Al, B, C-doped SiC.

Aluminum was detected at grain boundaries in Al, B, C-doped SiC by EDS analysis. Inomata [9] reported that a liquid phase formed around Al$_8$B$_4$C$_7$ (in which the molar ratio of Al$_4$C$_3$/B$_4$C was 2) at 1800 °C in the SiC–Al$_4$C$_3$–B$_4$C system. The combination of Al, B, and C as sintering additives has been effective for densification. We believe that only boron segregates at grain boundaries in B, C-doped SiC, while both boron and aluminum co-segregate or form an amorphous layer at grain boundaries in Al, B, C-doped SiC.

The stress–strain curves of B, C-doped SiC and Al, B, C-doped SiC at 1772 °C and at an initial strain rate of 1×10^{-4} s^{-1} are shown in Fig. 2. After the samples were kept at 1772 °C for 30 min before the compression test, the grain sizes of B, C-doped SiC and Al, B, C-doped SiC became 360 and 400 nm, respectively. The flow stress of Al, B, C-doped SiC with grain size of 400 nm was lower than that of B, C-doped SiC with grain size of 360 nm. The flow stress was reduced by Al-doping. The strain hardening, that is, an increase in the stress with increasing strain, was more pronounced in B, C-doped SiC than in Al, B, C-doped SiC.

The strain rate $\dot{\varepsilon}$ is conveniently expressed as a function of the applied stress σ, the absolute temperature T, and the grain size d as follows:

$$\dot{\varepsilon} = A \frac{Gb}{RT} \left(\frac{\sigma}{G} \right)^n \left(\frac{b}{d} \right)^p D_0 \exp \left(-\frac{Q}{RT} \right) \tag{1}$$

where D_0 is the frequency factor, Q the activation energy, R the gas constant, G the shear modulus, b the Burger's vector, p the exponent of the inverse grain size, n the stress exponent, and A is a dimensionless constant.

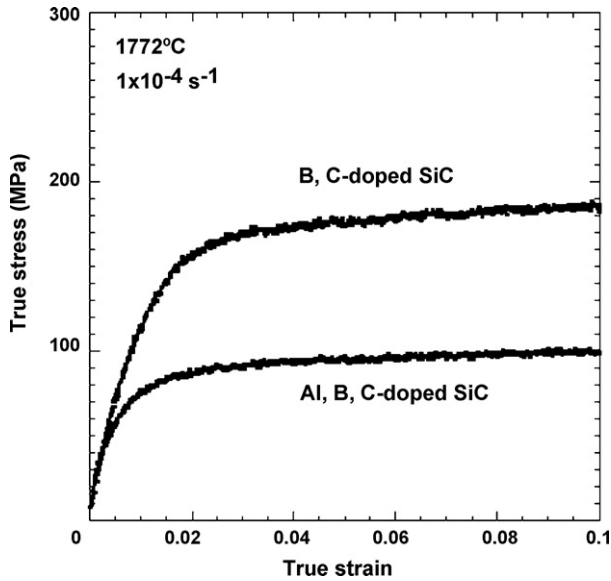Fig. 3 illustrates the variation in strain rate with true stress for B, C-doped SiC and Al, B, C-doped SiC at 1772 °C. The

Fig. 2. True stress–true strain curves of compressive tests under initial strain rate of $1 \times 10^{-4} \, s^{-1}$ at 1772 °C for B, C-doped SiC and Al, B, C-doped SiC.

strain rates of Al, B, C-doped SiC ($d = 400$ nm) in the low-stress region were ~1 order of magnitude faster than B, C-doped SiC. The slope of the curves in Fig. 3 determines the stress exponent. The stress–strain rate relationship is not given by a straight line in B, C-doped SiC and Al, B, C-doped SiC. The stress exponent of B, C-doped SiC ($d = 360$ nm) was 1.8 at the high-stress region and 3.1 at the low-stress region. On the other hand, the stress exponent of Al, B, C-doped SiC ($d = 400$ nm) was 1.4 at the high-stress region and 2.6 at the low-stress region. The Al, B, C-doped SiC samples were sintered at 1900 °C to have a grain size of 510 nm. The data of coarse Al, B, C-doped SiC were plotted in
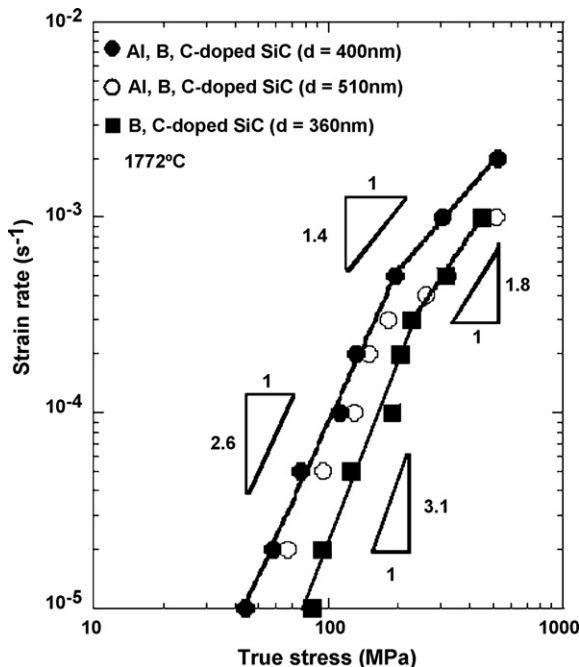

Fig. 3. Logarithmic plot of true stress vs. strain rate at 1772 °C for B, C-doped SiC and Al, B, C-doped SiC.
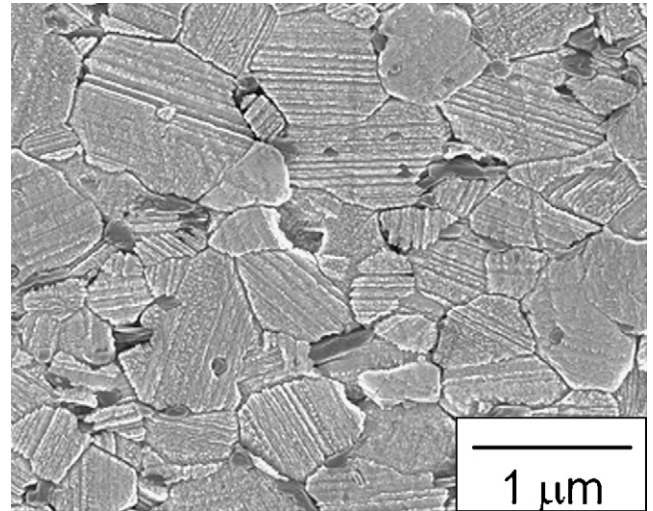

Fig. 4. SEM micrograph of Al, B, C-doped SiC after compressive deformation of $\varepsilon = 0.7$ under an initial strain rate of $1 \times 10^{-4} \, s^{-1}$. Compressive axis was vertical.

Fig. 3 also. The strain rate of Al, B, C-doped SiC ($d = 510$ nm) was lower than that of Al, B, C-doped SiC ($d = 400$ nm). The deformation of Al, B, C-doped SiC was affected by grain size more significantly at the high-stress region than at the low-stress region. This result suggests that the exponent of the inverse grain size p decreases at the low-stress region.

Fig. 4 shows SEM micrograph of Al, B, C-doped SiC deformed to a true strain of 0.7 at 1772 °C and at initial strain rate of $1 \times 10^{-4} \, s^{-1}$. No significant cavitation damage could be found after the compression test. The grains retained equiaxed shapes even after the compression test. XRD measurements revealed that the SiC consisted of the β-phase. It was suggested that the deformation mechanism was mainly caused by the grain-boundary sliding.

Backhaus-Ricoult et al. [3] studied the compression creep behavior of hot-pressed B, C-doped SiC with an average grain size of 3.5 μm at 1500–1700 °C and at 100–1100 MPa, and reported the transition of the stress exponent with increasing stress. They showed that the controlling creep mechanism at the low-stress region ($n = 1.5$) was grain-boundary sliding accommodated mainly by grain-boundary diffusion; at high-stress region ($n = 3.5$), the controlling mechanism was dislocation motion. By contraries, our results showed that the value of the stress exponent decreased with increasing stress.

The decrease of the stress exponent at higher stress region was also observed in the deformation of high-purity yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) [12–14]. For example, Berbon and Langdon [13] have proposed two sequential processes of grain-boundary sliding accommodated by diffusion at the high stresses and an interface-reaction process at the low stresses. They used a modified Coble mechanism developed by Arzt et al. [15]. The modified Coble creep model is expressed as

$$\dot{\varepsilon} = A \frac{\sigma}{d^3} \left(\frac{N^2}{N^2 + 1/2} \right) \tag{2}$$

where N is the number of dislocations in a single grain-boundary plane, and is given by

$$N = \frac{\sigma d}{2Gb_{gb}} \tag{3}$$

where b_{gb} is the Burger's vector for grain-boundary dislocations. When the N value is large, the creep equation can be expressed by $n = 1$ and $p = 3$. When the N value is small, the creep is interface-controlled and it is expressed by $n = 3$ and $p = 1$. The transition of the stress exponent of Al, B, C-doped SiC was similar to the model of the modified Coble creep. Furthermore, this model predicts low value of p at the low-stress region that is consistent with our results of Al, B, C-doped SiC. It was considered that the flow of Al, B, C-doped SiC occurred by grain-boundary sliding accommodated by the modified Coble creep.

4. Summary

In order to clarify the effect of Al-doping on the high-temperature deformation of B, C-doped SiC and Al, B, C-doped SiC were deformed in compression at 1772 °C. Our results are summarized as follows:

- The strain rates of Al, B, C-doped SiC ($d = 400$ nm) in the low-stress region were ~1 order of magnitude faster than that of B, C-doped SiC.
- The stress exponent of B, C-doped SiC ($d = 360$ nm) was 1.8 at the high-stress region and 3.1 at the low-stress region. On the other hand, the stress exponent of Al, B, C-doped SiC

($d = 400$ nm) was 1.4 at the high-stress region and 2.6 at the low-stress region. The transition of the stress exponent, which is often observed in the superplasticity of metals and oxides, e.g., ZrO_2, appeared in fine-grained SiC also.
- It was considered that Al-doping promoted grain-boundary diffusion.

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