Effect of Crystal Structure on High-Temperature Deformation Behavior of Silicon Carbides

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It is well known that many polytypes occur in SiC. However, they can be classified into two groups; one is \(\beta\)-SiC with a cubic structure, which satisfies the von Mises criterion for plastic deformation of polycrystals, and the other \(\alpha\)-SiC with a hexagonal structure, which does not satisfy the criterion.

In order to clarify the effect of crystal structure on high-temperature deformation behavior of SiC, pressureless sintered \(\alpha\) and \(\beta\)-SiC with B + C additives as sintering aids have been deformed by compression and stress-relaxation tests have been conducted at temperatures from 1920 to 2190 K and at strain rates from \(1 \times 10^{-4}\) to \(3 \times 10^{-4}\) s\(^{-1}\). Microstructures were examined by transmission electron microscopy and X-ray diffraction.

It was found that there was no marked difference in high-temperature deformation behavior between them. Many stacking faults and microtwins were observed before deformation. These faults increased by deformation. X-ray diffraction analysis and high resolution TEM observations revealed that \(\alpha\) type structure was produced in \(\beta\)-SiC by deformation as a form of very thin twin-like layers. The similarity in deformation behavior between \(\beta\)-SiC and \(\alpha\)-SiC may arise from the restricted dislocation motion due to dense stacking faults and twins produced in \(\beta\)-SiC.

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I. Introduction

It is well known that silicon carbide exists in many polytypic forms such as 3C, 4H, 6H and 15R in terms of the Ramsdell notion, where the number refers to the number of close-packed Si-C double layers in the unit cell and the letter to the crystal symmetry. However, they can be classified into two groups; cubic 3C polytype is referred to as \(\beta\)-SiC and all of the remainingcollectively as \(\alpha\)-SiC. In \(\beta\)-SiC, each of Si atoms and C atoms forms fcc sublattice. Hence, \(\{111\}\langle110\rangle\) octahedral slip systems are activated at high temperatures. If five independent slip systems operate, a polycrystal can be ductile. This is called in general von Mises criterion. At high temperatures where dislocation motion is thermally activated, \(\beta\)-SiC polycrystals should become ductile. On the other hand, the primary slip system in \(\alpha\)-SiC is limited to only \(\{0001\}\langle1120\rangle\) basal slip. There are only two independent slip systems in this case, and then deformation can not occur along the C axis perpendicular to the basal plane. Thus, \(\alpha\)-SiC polycrystals are believed to have low ductility even at high temperatures, though \(\alpha\)-SiC single crystals show fairly good ductility\(^{10}\). In this way, it may be expected that there is a marked difference in high temperature deformation behavior between \(\alpha\) and \(\beta\)-SiC.

Many investigations concerning high-temperature deformation behavior of various polycrystalline silicon carbides have been conducted so far\(^{13}\). To the present authors' knowledge, however, there are no reports on the effect of crystal structure (polytypes) on the high temperature deformation behavior of silicon carbide. The mechanical properties of silicon carbide are known to depend markedly on extrinsic factors, such as additives, impurities and sintering procedure and so on. Therefore, it is difficult to discuss the relationship between the mechanical properties and crystal structure on the basis of the experimental results reported hitherto using materials with various extrinsic factors. For obtaining reliable results on the effect of crystal structure on high temperature deformation behavior, it is necessary to use the well-characterized specimens with negligible effect of various extrinsic factors.

In the present study, \(\alpha\) and \(\beta\)-SiC with additions of B and C, which were pressureless sintered under the same condition, were deformed by compression and stress-relaxed at high temperatures under various strain rates. Transmission electron microscopic observation and X-ray diffraction analysis were carried out to reveal the internal structure, and the mechanical behavior is discussed in connection with the structure. Contrary to expectation, it is found that there is little difference in high temperature deformation behavior between \(\alpha\) and \(\beta\)-SiC.
The probable explanation is that dense stacking faults and microtwins produced in β-SiC by deformation, resulting in partial structure change to α-SiC polytypes, are responsible for the absence of significant difference between α and β-SiC.

II. Experimental Procedure

1. Specimen

The materials used here are pressureless sintered α-SiC (6H polytype: 96.4%) and β-SiC (3C polytype: 98.1%) with additions of 0.37 mass% B and 3.1 mass% C (supplied by Japan Fine Ceramics Center). The samples were sintered at 2320 K for 7.2 ks in an Ar atmosphere and are ca. 97% of theoretical density and ca. 1 μm in mean grain size.

The specimens were cut out from the sintered materials with a low-speed diamond cutter. They were fixed with an instant glue in a special polishing jig and then polished with emery paper of grades of #240 to #1500 and finally buffed with diamond paste of 1 μm in particle size. The final size of specimen is approximately 2 mm × 2 mm × 3 mm. The parallelism of the top and bottom sides of specimens is so good that no leakage of light is observed when the specimen is put in a micrometer.

Sintering aids are liable to segregate and form a second phase of low melting point at grain boundaries, resulting in decrease of high temperature strength. When B and C are simultaneously added as sintering aids, an amorphous-like layer is also seen along the grain boundary. However, the fracture strength of the sintered SiC with B+C does not decrease but rather increases at high temperatures. From the difference in deformation behavior at high temperatures, the layer observed in the sintered SiC with B+C is considered not to be a second phase but to be a relaxed structure formed to decrease the boundary energy. Therefore, it is thought that high temperature deformation behavior of SiC with B and C additives should reflect the intrinsic nature of silicon carbide.

2. Compression test

Compression tests were conducted under a vacuum of approximately 1.3 mPa at temperatures from 1940 to 2190 K and strain rate of 3 × 10^{-4} s^{-1} using an electrically controlled hydraulic machine based on Shimadzu Servo Pulser EHF-2 type. The details of the experimental procedure were the same as those described in a previous paper. In the present study, however, sintered TiC-8.5 mol%Mo-3.5 mol%WC was used as compression rods. At the tip of the rods, a melted TiC-10 mol%Zr alloy, which is extremely strong at high temperature, was joined. The compression faces of the rods were painted with high purity graphite for lubrication and seizure proof.

3. Relaxation test

As mentioned in the following sections, both of the α and β-SiC were poor in ductility, and cracks were formed by compression under the conditions described above. In order to clarify the intrinsic properties without the effect of crack, the relaxation tests were carried out at temperatures between 1920 and 2100 K. None of cracks were observed in both the α and β-SiC after relaxation tests in this case. The details of the experimental technique are the following.

When a specimen is deformed to yield and subsequently the cross-head is arrested, the stress is relaxed. The stress relaxation rate, \( \dot{\varepsilon} \), is experimentally determined from the slope of the stress relaxation curve. Since the apparent strain, \( \varepsilon_a \), is expressed as sum of the elastic strain, \( \varepsilon_e \), of the specimen and machine and the plastic strain, \( \varepsilon_p \), of the specimen.

\[
d\varepsilon_a = d\varepsilon_e + d\varepsilon_p, \tag{1}
\]

or dividing the two sides of eq. (1) by the time increment \( dt \),

\[
\dot{\varepsilon}_a = \dot{\varepsilon}_e + \dot{\varepsilon}_p, \tag{2}
\]

when the cross head is stopped, \( \dot{\varepsilon}_e = 0 \), but the specimen is plastically deformed with a rate of \( \dot{\varepsilon}_p = - \varepsilon_e - \sigma / K \). Where \( K \) is the apparent Young's modulus or combined machine stiffness.

4. Transmission electron microscopy observation

Thin foils suitable for TEM observations were prepared from as-sintered and deformed specimens by the ion-milling technique. Thin sheets approximately 0.5 mm thick were cut out with a low-speed diamond cutter and polished mechanically to 50 μm in thickness, and then buff-polished with diamond paste. Disks, 3 mm in diameter, were trepanned from the sheets with a ultrasonic machine and Ar\(^+\) ion-milled into foils at 4 kV and 0.4 mA. The accelerating voltage for ion-milling was made as low as possible to prevent the radiation damage of the foils. For TEM observation, JEOL JEM-2000EX/T was used.

III. Results and Discussion

1. Stress-strain curve

Figure 1 shows the stress-strain curves obtained by compression tests at various temperatures at a strain rate of 3 × 10^{-4} s^{-1}. Contrary to expectation, there is no appreciable difference in the stress-strain curves between the α and β-SiC. The flow stress shows a peak and subsequently decreases monotonously. At the peak stress, cracks were formed even in the β-SiC which should satisfy the von Mises criterion. The crack formation should have caused the observed decrease in flow stress. In spite of the early crack formation, the specimen could be much deformation by compression without fracture.

2. Relaxation test

Figure 2 shows the stress-dependence of the strain rate obtained by the relaxation test. The flow stress, \( \sigma \), is
Figure 3(a) and (b) show the Arrhenius plot of plastic strain rate, \( \dot{\varepsilon} \), at constant stresses for \( \alpha \) and \( \beta \)-SiC, respectively. Here the strain rates at various temperatures were obtained from Fig. 2. When the strain rate estimated for a constant stress exceeded the experimental range, the strain rate was determined by extrapolating the straight line in Fig. 2.

For \( \alpha \) and \( \beta \)-SiC, a relatively good linear relationship between \( \log \dot{\varepsilon} \) and \( 1/T \) is seen and those slopes are almost independent of \( \sigma/G \). From the above results, the mechanical equation of state can be expressed as

\[
\dot{\varepsilon} = A(\sigma/G)^n \exp\left(-Q/RT\right)
\]

(3)

where \( A \) is a constant, \( Q \) the activation energy for deformation, \( R \) the gas constant and \( T \) absolute temperature.

The activation energies represented by the slope of the straight lines in Fig. 3 are 500±10 kJ/mol and 440±10 kJ/mol for the \( \alpha \) and \( \beta \)-SiC, respectively. These values are larger than the reported activation energy for deformation of \( \alpha \)-SiC single crystals (328±68 kJ/mol\(^{39}\)), which is relevant to reflect the partial dislocation glide motion, but are lower than those for lattice self-diffusion of C (715±5 kJ/mol\(^{10}\)) and Si (697±7 kJ/mol\(^{11}\)) in \( \alpha \)-SiC, and those of C (814±14 kJ/mol\(^{12}\)) and Si (912±5 kJ/mol\(^{13}\)) in \( \beta \)-SiC.

The fact mentioned in the following section that partial structure change, \( \beta \to \alpha \) polytypic transformation, occurs as a resultant of deformation also strongly suggests that the partial dislocation glide motion is responsible for the deformation. Because the motion of Shockley partial dislocations is considered to play an important role in the \( \beta \to \alpha \) transformation\(^{16-18}\), it is considered that the deformation of \( \beta \)-SiC may be controlled by the partial disloca-

![Fig. 1 Stress-strain curves for (a) \( \alpha \)-SiC and (b) \( \beta \)-SiC compressed at various temperatures with a strain rate of \( 3 \times 10^{-4} \) s\(^{-1} \).](image)

![Fig. 2 Log(\( \sigma/G \)) vs log \( \dot{\varepsilon} \) at various temperatures, (a) \( \alpha \)-SiC and (b) \( \beta \)-SiC.](image)
tion motion to overcome the Peierls barrier, though the activation energy measured by the present relaxation test is larger than that reported for single crystal deformation. The deformation of α-SiC is also considered to be controlled by the Peierls mechanism. Because (0001) 〈1120〉 slip system in α-SiC is equivalent to the (111) 〈110〉 slip system in β-SiC, it is understood that the obtained activation energies for deformation of the α and β-SiC are not much different.

3. Microstructures

The fact that there is unexpectedly little difference in high temperature deformation behavior between the α and β-SiC, is discussed below from the viewpoint of microstructures.

Figure 4(a) and (b) are bright field images of undeformed α and β-SiC, respectively. The TEM micrographs reveal that many stacking faults and microtwins are present ubiquitously. In particular, these defects are noticeable in β-SiC. It is thought, therefore, that these defects must be the cause of the unexpected result. 〈111〉 〈110〉 slip in β-SiC should be restricted by these dense stacking faults and microtwins. Consequently, the ductility of the β-SiC becomes as low as that of the α-SiC, and the β-SiC shows deformation behavior similar to that of the α-SiC.

In order to further verify the change in crystal structure by deformation, X-ray diffraction analyses were carried out. Figure 5 shows X-ray diffraction patterns of the α-SiC (Fig. 5(a)) and β-SiC (Fig. 5(b), (c) and (d)); Fig. 5(a) and (b) were obtained before deformation, Fig. 5(c) after deformation of 28% at 2190 K and 5(d) after annealing at 2190 K for 7.2 ks without deformation. Each peak intensity in Fig. 5 is normalized by the intensity of (111) or (006) reflection occurring at 2θ = 36°. After deformation of the β-SiC, some peaks corresponding to 6H and 4H polytypes are observed (Fig. 5(c)), whereas no such peaks occur before deformation (Fig. 5(b)). According to the stability diagram for the occurrence of SiC polytype, 6H structure is the most thermally stable one above ca. 2270 K, so that the polytypic transformation of 3C→6H could occur during heating at 2190 K. From Fig. 5(d), however, there is no definite sign of α structure occurring even after the annealing; namely, the β structure is retained, which strongly suggests that the deformation should be responsible for the occurrence of hexagonal structures in the original β-SiC.

The crystal structure of α-SiC is possible to be characterized by a certain sequence of twining of 3C structure. Figure 6 shows a high-resolution image of the β-SiC deformed by 28% at 2190 K. The image reveals that the hexagonal structures exist as the form of twin-like layers. Figure 7 shows an enlarged image of the square area shown in Fig. 6. The crystal structure between arrows indicated in Figs. 6 and 7, for example, can be characterized by stacking sequence of 6H structure (...ABCABC...). X-ray diffraction peaks corresponding to α type structures in Fig. 5(c) may arise from these regions. Hence, those twin-like layers, which may be produced by glide of Shockley partial dislocations, must be the precursor to the β→α transformation.

As a consequence, the similarity between the deformation behavior of the β-SiC and that of the α-SiC may also arise from such twin formation and partial structure changes in β-SiC. Therefore, in order to provide polycrystalline β-SiC with expectant high ductility, it is
necessary to increase the stacking fault energy, and eventually 3C structure must be stabilized. Nitrogen doping which has been reported to be effective for stabilization of 3C structure (1990), for instance, may be one of the applicable methods.

IV. Conclusion

In order to clarify the effect of crystal structure on the high temperature deformation behavior of sintered silicon carbides, \( \beta \)-SiC, which satisfies the von Mises criterion, and \( \alpha \)-SiC, which does not satisfy the criterion, were deformed by compression and relaxation, and further transmission electron microscopy observation and X-ray diffraction analysis were carried out. The obtained results are summarized as follows.

(1) There is no significant difference in the high temperature deformation behavior between the \( \alpha \) and \( \beta \)-SiC. Even in the \( \beta \)-SiC, cracks were formed by a slight deformation. The probable explanation for the unexpected result is the dense stacking faults and microtwins produced in \( \beta \)-SiC by deformation. \( \{111\}\langle110\rangle \) dislocation glide motion in the \( \beta \)-SiC should be restricted by these defects. It is believed, therefore, that the ductility of the \( \beta \)-SiC becomes low and that the \( \beta \)-SiC shows a deformation behavior similar to the \( \alpha \)-SiC.

(2) As a result of X-ray diffraction analysis and high-resolution TEM observation, it is found that a partial structure change of \( \beta \rightarrow \alpha \) occurs by deformation. This structure change must be relevant to the motion of Shockley partial dislocations. Such a structure change is responsible for the absence of a significance difference between the \( \alpha \) and \( \beta \)-SiC.

(3) In order to provide \( \beta \)-SiC with high ductility, it is necessary to increase the stacking fault energy and then 3C structure must be stabilized.

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Fig. 6  High-resolution image of $\beta$-SiC deformed by 28% at 2190 K.

Fig. 7  Enlarged image of the square area shown in Fig. 6.
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