

Compressive Deformation of Partially Crystallized Amorphous Si-B-C-N Ceramics at Elevated Temperatures

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The deformation behavior of Si-B-C-N ceramics derived from a polymer precursor has been investigated by compression tests at high temperatures. The hot isostatic pressing of pyrolyzed powder compact was conducted at 1450°C and at 900 MPa in order to obtain a dense ceramic monolith. The material consisted of the amorphous matrix and the dispersed Si₃N₄ particles with the diameter of about 20 nm. While only apparent elastic deformation was observed at the testing temperatures up to 1500°C, significant plastic deformation occurred at temperatures higher than 1650°C. The plastic deformation is considered to be caused by the viscous flow of the amorphous matrix. The flow stress at the testing temperatures in the range of 1650 to 1750°C increased with initial strain rate. The flow stress was not proportional to the strain rate. The shear viscosity at 0.02 strain was about 10¹¹–10¹³ Pa s and decreased proportionally to about –0.75 power of the strain rate. The decrease in shear viscosity is considered to show a strain localization behavior. Strain hardening was observed during the plastic deformation. As the reason of the strain hardening, the crystallization can be considered, in addition to the decrease in atomic site defects during the deformation.

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1. Introduction

It is known that oxide glass materials such as silicate glasses show remarkable ductility at high temperatures. Large ductility at high temperatures by viscous flow of amorphous materials has been reported also in metals prepared by techniques such as rapid solidification.^{1–3)} On the other hand, it is difficult to deform silicon carbide and silicon nitride ceramics which adopt regular network structures with connected tetrahedra even at high temperatures. A Si atom is located at the center of each tetrahedron and bound with C or N atoms by strong covalent bonds. The strong covalent bonds of tetrahedra are the origin of their excellent mechanical properties even at high temperatures. The networks are not restricted to be crystalline arrangements of connected polyhedra. Non-crystalline structure can be formed by aperiodic connection of such tetrahedra. The deformation behavior of covalent amorphous ceramics at high temperatures has been less studied. It is a very interesting question whether the deformation behavior of covalent amorphous materials is similar to the behavior of oxide glass materials and metallic amorphous alloys or not.

Many kinds of ceramic fibers and films have been obtained by polymer precursor method which fabricates inorganic materials by thermolysis of preceramic compounds.^{4–6)} Bulk amorphous ceramics such as Si-C-N and Si-B-C-N have been developed by pyrolyzing the isostatically pressed and warm pressed preceramic powders.^{7–11)} However, it is difficult to fabricate no porosity ceramic monoliths by these processes since porosity is necessary to remove the gas species during pyrolysis.

The deformation of precursor-derived Si-C-N and Si-B-C-N amorphous monoliths prepared by pyrolyzing the warm

pressed preceramic powders has been studied by several researchers.^{9,12–17)} The analysis of intrinsic plastic deformation of such amorphous ceramics is difficult, because both viscous flow of the matrix and shrinkage by the elimination of residual pores, sintering, occurred concurrently. In order to characterize the nature of viscous flow of the covalent amorphous ceramics, it is necessary to study the deformation of dense materials.

We developed the dense Si-C-N ceramic monolith by hot isostatically pressing the compacts of amorphous ceramic powder derived from polyvinylsilazane.¹⁸⁾ However, the amorphous phase in the monolith crystallized during the hot isostatic pressing (HIP). The crystallization of amorphous phase depends on the relative thermodynamic stability of the crystalline phases and the kinetics of their formation. It is known that the incorporation of boron into the Si-C-N ceramics enhances the stability of amorphous phase at the elevated temperatures.¹⁹⁾ In this report, we investigated the deformation of dense monolith which was consolidated by isostatic pressing of pyrolyzed amorphous Si-B-C-N powder.

2. Experimental Procedure

The material used for this experiments was derived from a boron containing polysilazane polymer with the molecular structure shown in Fig. 1. The polymer was converted into ceramic by pyrolysis at 1400°C. The pyrolyzed powder was milled by planetary ball milling, and sieved to 32 µm or less. These processes were carried out in argon atmosphere in order to prevent the oxidation. The sieved powder was die pressed at the pressure of 40 MPa into a rectangular bar with dimensions of 10 mm × 12 mm × 48 mm. The powder compact was coated with boron-nitride powder, densified by cold isostatic pressing (CIP) under 200 MPa, and, vacuum encapsulated with a PyrexTM type glass tube at a temperature of about 760°C. The encapsulated sample was held at 800°C

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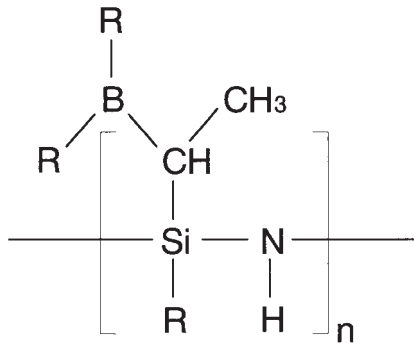


Fig. 1 Molecular structure of the boron containing polysilazane polymer used for the precursor of the ceramic material (R: H or CH₃).

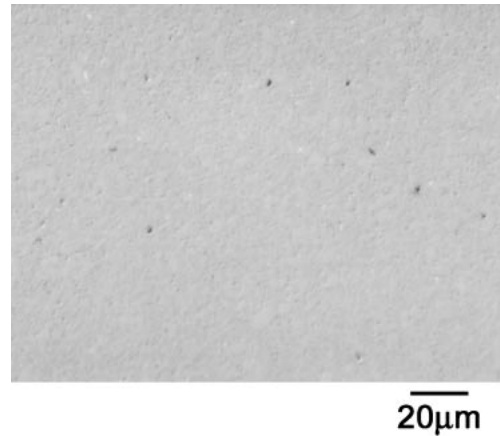


Fig. 2 Cross-sectional structure of the HIP-treated Si-B-C-N sample.

for 1.2×10^3 s in a special HIP equipment for the softening of the glass capsule, and isostatically pressed at 1450°C and 900 MPa for 1.8×10^3 s.

The material was characterized by using an optical microscope and X-ray diffraction (Rigaku, RINT2000). The microstructural observation was carried out by transmission electron microscopy (Hitachi, HF2000, accelerating voltage: 200 kV). The HIP-treated sample was cut into rectangular specimens (3 mm × 2 mm × 2 mm) using a diamond wheel along with the compression test direction parallel to the powder compacting direction, and were polished with diamond abrasive. The compression tests were conducted at temperatures from 1200 to 1750°C in N₂ atmosphere with a servo-hydraulic type testing machine (Shimadzu, EHF-EG10kNT-10L type Servo-pulser) at constant cross-head speed in an induction heating furnace.

3. Results

The chemical composition of the sample was Si_{3.0}B_{1.0}C_{4.3}N_{2.0}. Figure 2 shows the cross-section observed by optical microscopy. Although a few pores with the size of about 1 μm still remained in the structure, the micrograph indicates that the densification during the HIP treatment achieved a level of almost full density. The X-ray diffraction pattern of the sample after the consolidation by HIP is shown in Fig. 3. Some crystalline peaks were detected in addition to the broad peaks of the amorphous phase which has similar structure to β-SiC. This indicates the partial crystallization of

the initial amorphous phase. The crystalline phase is considered to be α-Si₃N₄ phase as shown by marks and each index with peaks of the diffraction pattern. The results of the transmission electron microscopy (TEM) observation are shown in Fig. 4. Fine particles of about 20 nm were dispersed in the matrix. The selected area diffraction pattern from the matrix (Fig. 4-c) shows halo rings typical of an amorphous phase, and that from the dispersed particles (Fig. 4-b) indicates that the particle is crystalline. The crystalline particle is considered to be α-Si₃N₄ phase with taking account of the result of X-ray diffraction.

The true stress-true strain curves in the compression tests are shown in Fig. 5. The compression tests were carried out at various temperatures at an initial strain rate of 4×10^{-5} s⁻¹. The symbol of bold arrow (→) represents that the test has been interrupted at the end of the curve and the strain will be able to continue. When there is no symbol (→), the specimen has failed at the end of the curve. Only the elastic deformation was apparently observed at temperatures up to 1500°C. On the other hand, a little plastic deformation was obtained at 1600°C. The stress-strain curves exhibited significant plastic deformation at temperatures higher than 1650°C. The flow stress gradually increased with strain during the deformation. The flow stress was reduced with increasing temperature. Figure 6 shows the true stress-true strain curves at various initial strain rates and at 1650°C. A compressive deformation larger than 0.09 was obtained at

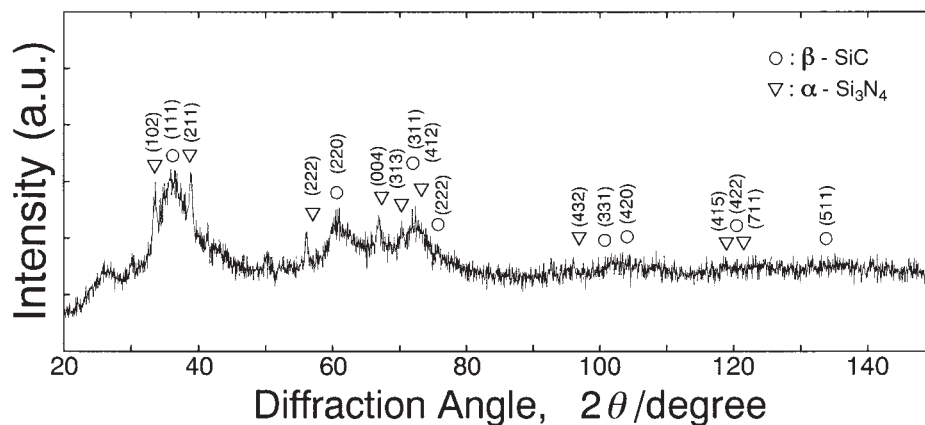


Fig. 3 X-ray diffraction pattern of the HIP-treated Si-B-C-N sample.

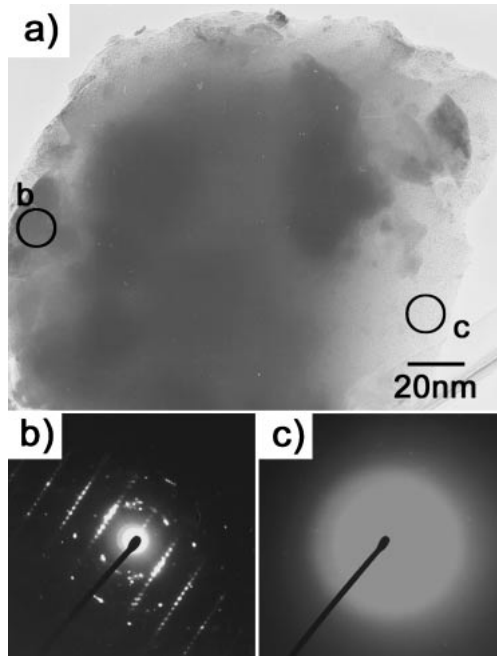


Fig. 4 TEM micrograph of the HIP-treated Si-B-C-N sample (a): bright field image, b): selected area diffraction pattern from the dispersed particles and c): selected area diffraction pattern from the matrix).

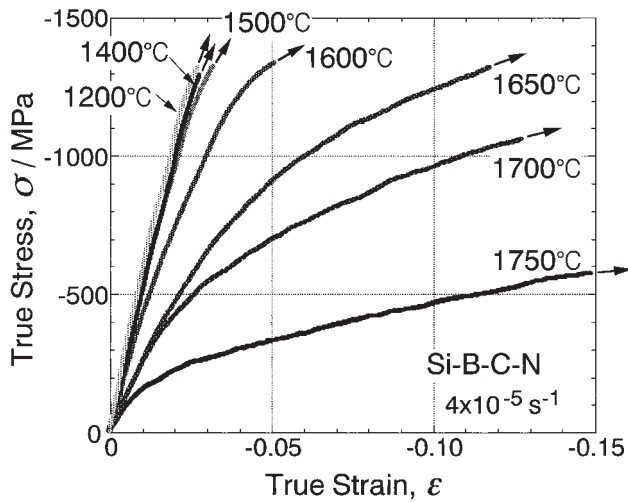


Fig. 5 Stress-strain curves of the Si-B-C-N material tested in compression at high temperatures.

initial strain rates lower than $2 \times 10^{-4} \text{ s}^{-1}$. However, the specimen fractured without significant plastic deformation at $4 \times 10^{-4} \text{ s}^{-1}$. The true stress-true strain curves at 1700 and 1750°C are also shown in Figs. 7 and 8, respectively. The ductility was enhanced by increasing the temperature, so that large true strain of 0.2 was achieved without fracture at the initial strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ at 1750°C.

The relation between the flow stress and strain rate is plotted on linear scales in Fig. 9. The flow stress was determined as proof stress at 0.02 strain. The flow stress increased with initial strain rate at each testing temperature. The flow stress was not proportional to the strain rate. The shear viscosity η can be calculated by the equation;

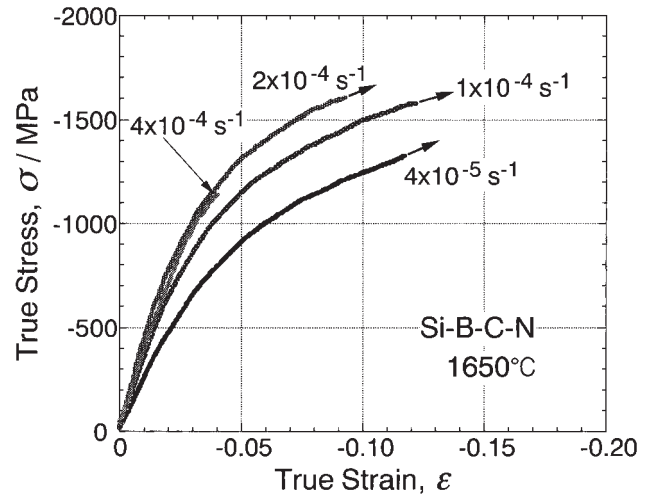


Fig. 6 Stress-strain curves of the Si-B-C-N sample tested in compression at 1650°C.

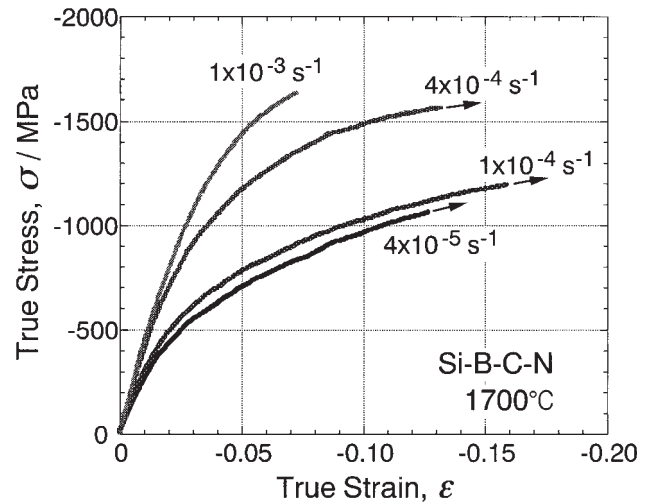


Fig. 7 Stress-strain curves of the Si-B-C-N sample tested in compression at 1700°C.

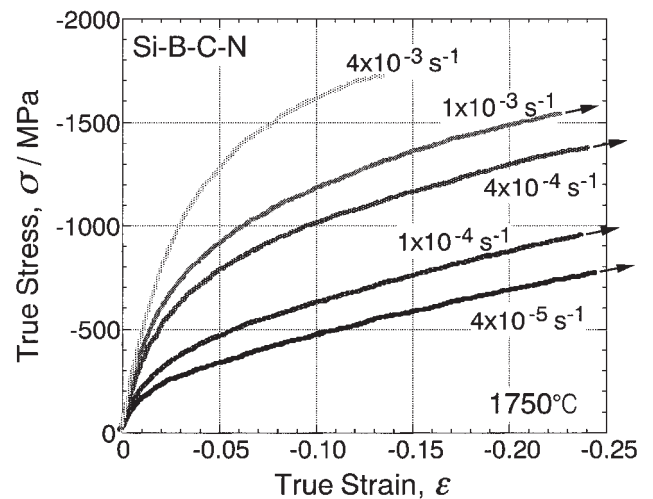


Fig. 8 Stress-strain curves of the Si-B-C-N sample tested in compression at 1750°C.

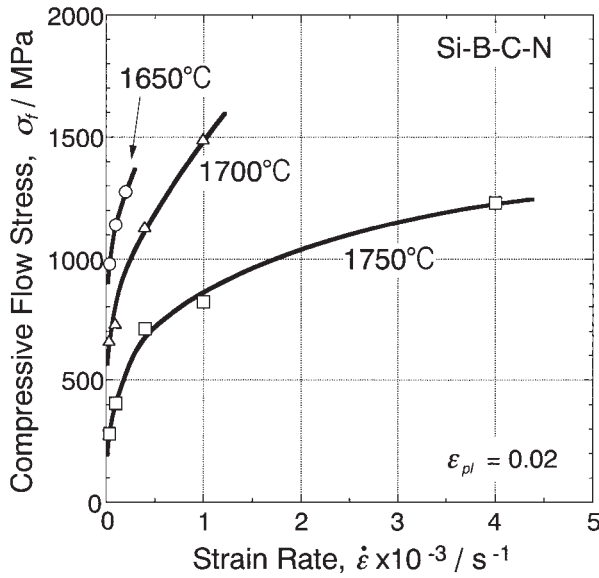


Fig. 9 Strain rate dependence of the flow stress of the Si-B-C-N material.

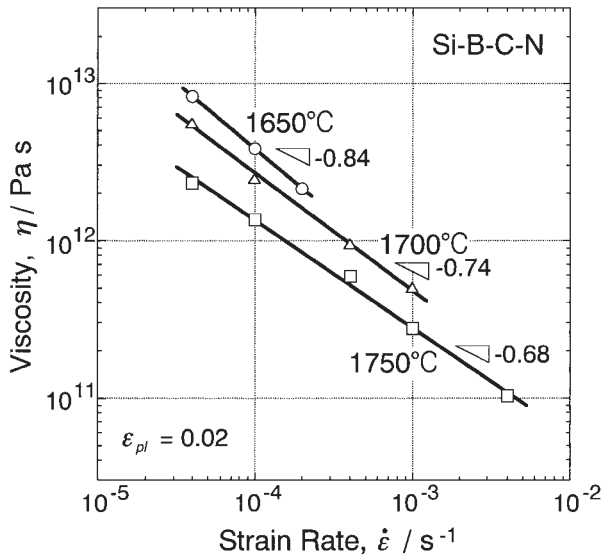


Fig. 10 Strain rate dependence of the viscosity of the Si-B-C-N material.

$$\eta = \sigma / 3\dot{\epsilon}, \quad (1)$$

where σ is the flow stress and $\dot{\epsilon}$ is the strain rate in uniaxial deformation. The shear viscosity converted from the flow stress is shown in Fig. 10, on logarithmic scales. The shear viscosity at the temperatures from 1650 to 1750°C was in the order of 10^{11} – 10^{13} Pa s and decreased with the testing temperature. The relation between the shear viscosity and strain rate was approximated by a line in the logarithmic plot. The shear viscosity η can be approximated by the equation;

$$\eta = a_T \dot{\epsilon}^k, \quad (2)$$

where a_T is a constant dependent on temperature and k is an exponent. The value of k in this study was from -0.84 to -0.68 . Such phenomena with negative k values are called shear-thinning.

The results of X-ray diffraction of the specimens after compression tests at $4 \times 10^{-5} \text{ s}^{-1}$ are shown in Fig. 11. The

diffraction pattern of the specimen tested at 1600°C was hardly altered as compared with that of before test. In the case at 1700°C, the crystallization of the amorphous phase is clearly shown in the diffraction pattern. Furthermore, the crystallization to β -SiC considerably progressed during the test at 1750°C.

4. Discussion

Only the elastic deformation was apparently observed in the compression tests at temperatures up to 1500°C in spite of high compressive stress over 1300 MPa. In the $\text{Si}_{3.0}\text{B}_{1.0}\text{C}_{4.3}\text{N}_{2.0}$ ceramics fabricated by the warm-pressing and pyrolysis method, creep deformation with strain rates of about 10^{-7} s^{-1} was observed in the temperature range between 1350°C and 1500°C.^{12,16,17)} The apparent elastic deformation at such temperatures in the present study may contain the slight plastic deformation.

On the other hand, larger plastic deformation was obtained at temperatures higher than 1600°C. The shear viscosity in the plastic deformation at the temperatures from 1650 to 1750°C is 10^{11} – 10^{13} Pa s as shown in Fig. 10. Such values of viscosity agree with the result of creep deformation in $\text{Si}_{1.7}\text{C}_{1.0}\text{N}_{1.5}$ ceramics derived from polyhydridomethylsilazane.¹³⁾ The value of about 10^{12} Pa s corresponds to the viscosity at which almost materials become to be able to flow. Viscous flow of materials is generally explained by the structural relaxation against the given strain.²⁰⁾ If the structural relaxation of a material is faster than the strain, the material can flow. The viscosity derived from the critical relaxation time of viscous flow observed experimentally for most common materials corresponds to about 10^{12} Pa s. Therefore, the plastic deformation of this material at temperatures higher than 1650°C is considered to be caused by the viscous flow of the amorphous matrix.

The flow stress at testing temperatures from 1650 to 1750°C was not proportional to the strain rate, as shown in Fig. 9. It indicates that the deformation of this material is non-Newtonian viscous flow. The deformation of amorphous Si-B-C-N monoliths prepared through the warm pressing and pyrolysis route has been studied by creep test ($\text{Si}_{3.0}\text{B}_{1.0}\text{C}_{4.3}\text{N}_{2.0}$),^{12,16,17)} ($\text{Si}_{2.0}\text{B}_{1.0}\text{C}_{3.4}\text{N}_{2.3}$)¹⁴⁾ and by compression test ($\text{Si}_{1.0}\text{B}_{0.4}\text{C}_{3.4}\text{N}_{2.4}$).¹⁵⁾ In the case of the creep tests by An *et al.* for the $\text{Si}_{1.7}\text{C}_{1.0}\text{N}_{1.5}$ material which did not contain B, the relation between the applied stress and the strain rate in the steady state was Newtonian viscous flow.¹³⁾ On the contrary, the results of the $\text{Si}_{2.0}\text{B}_{1.0}\text{C}_{3.4}\text{N}_{2.3}$ material by the similar experimental procedure to the $\text{Si}_{1.7}\text{C}_{1.0}\text{N}_{1.5}$ material exhibited non-Newtonian viscous flow.¹⁴⁾ Non-Newtonian viscous flow was also observed in the compression tests of the $\text{Si}_{1.0}\text{B}_{0.4}\text{C}_{3.4}\text{N}_{2.4}$ material.¹⁵⁾

The shear viscosity decreased with strain rate as shown in Fig. 10. Similar decrease in viscosity with strain rate has been observed at high stress and high strain rate conditions in many kinds of amorphous and glassy materials such as oxide glass materials,^{21,22)} amorphous polymer materials,²³⁾ metallic glass alloys,²⁴⁾ while these materials usually exhibit Newtonian viscous flow at low stress and low strain rate conditions at relatively high temperatures. In case of polymer materials, such decrease in viscosity with strain rate is

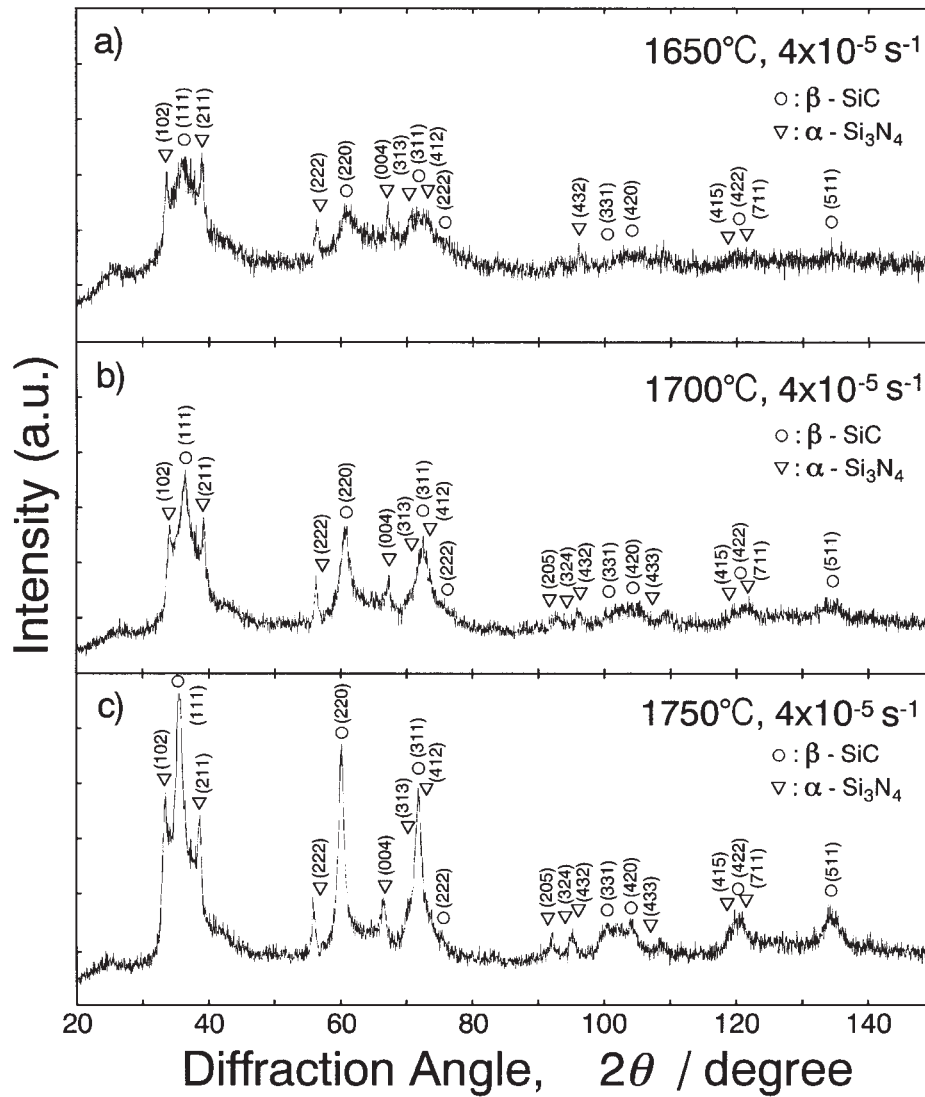


Fig. 11 X-ray diffraction patterns of the specimens after compression tests at a): 1600°C, b): 1700°C and c): 1750°C.

explained by shear-induced changes in the network of entanglements of intermolecular chains.²³⁾ It is however difficult for this Si-B-C-N ceramics to explain the decrease in viscosity by the entanglements of intermolecular chains, since the atomic configuration is not constituted of long molecular chains but is based on aperiodic connections of tetrahedral structure. On the other hand, the transient of Newtonian viscous flow to non-Newtonian viscous flow with increasing strain rate in metallic glasses is explained by strain localization.^{25,26)} The non-Newtonian viscous flow in this ceramic material is considered to show a strain localization behavior similar to that of metallic glasses. The failures of the specimens at further high strain rates also can be explained by the strain localization.

The amorphous Si-B-C-N monoliths prepared through the warm pressing and pyrolysis route shrink due to viscous sintering at elevated temperatures.^{12,14-17)} This volume change of the specimen makes it difficult to separate the intrinsic plastic deformation of the amorphous materials from the total deformation. The strain rate of those Si-B-C-N materials decreased with time in the creep tests, while the flow stress increased with strain in the compression tests. Our dense material exhibited similar strain hardening. Since our

material contains almost no porosity, the disappearance of pores can not be the origin of strain hardening. Strain hardening is usually evaluated as an exponent on stress-strain curves by the equation;

$$\sigma = K_T \varepsilon^n, \quad (3)$$

where K_T is a constant dependent on temperature and n is the strain hardening exponent. The strain hardening exponent during the compressive deformation of our material is shown in Fig. 12. The strain hardening exponent is larger at higher temperature and lower strain rate conditions where the crystallization more progress. The crystallization is also indicated in the X-ray diffraction pattern of the specimen after compression tests at 1700 and 1750°C as shown in Fig. 11. Strain hardening associated with crystallization or phase separation has been observed in silicate glass.²⁷⁾ The crystallization of the amorphous phase is considered as one of the causes of the strain hardening in this experiment.

Besides, another reason of the strain hardening can also be considered. The result of X-ray diffraction of the Si-B-C-N specimens after the creep tests by Riedel *et al.* was not significantly altered as compared with the starting material.¹⁴⁾ Such increasing of viscosity without crystallization has

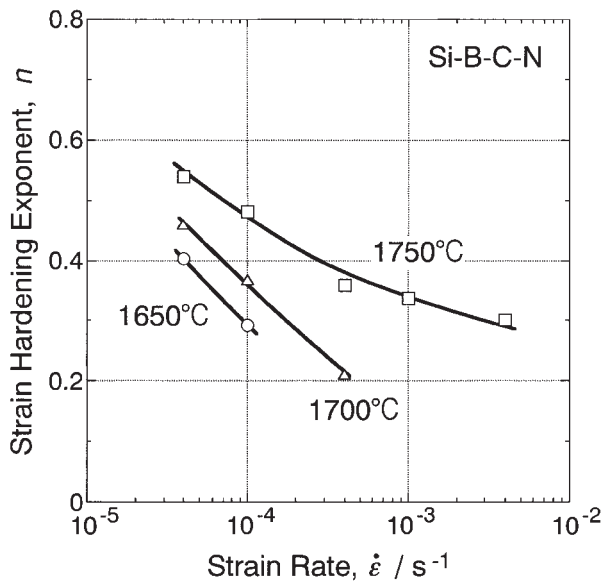


Fig. 12 Strain hardening exponent during the compressive deformation of the Si-B-C-N material.

been observed in other amorphous materials and usually explained by using free volume models.²⁵⁾ Baufeld *et al.* discussed that the increase of the flow stress was related to the decrease of free volume in the amorphous phase.¹⁵⁾ Christ *et al.* analyzed the creep data of Si-B-C-N amorphous ceramics and argued that the creep behavior was similar to that of metallic glasses.¹⁶⁾ However, the deformation behavior of amorphous ceramics derived from polymer precursors may be a little different from amorphous and glassy alloys, since some characteristics are different in the atomic structures and bonds between both kinds of materials. Amorphous and glassy alloys have relatively dense structures based on the original liquid state despite they are not equilibrium. Deformation mechanism in metallic glasses is explained by creation and annihilation of flow defects (free volume) based on a relatively stable state at which local free energy is minimum in the atomic structures.^{25,28)} On the other hand, structures in amorphous ceramics derived from polymer precursors are highly unstable and have much more atomic site defects. It is not easy to define similarly such a relatively stable state in these amorphous ceramics. Although the deformation mechanisms may accordingly be a little different, the decrease in atomic site defects during the deformation is considered as a cause of the strain hardening in this ceramics, as well as the crystallization.

5. Summary

The deformation behavior of the Si-B-C-N ceramic monolith derived from the polymer precursor has been investigated by compression tests at high temperatures. The dense Si-B-C-N ceramic monolith was obtained by hot-isostatically pressing the pyrolyzed powder at 1450°C and 900 MPa. The material consisted of the amorphous matrix and the dispersed Si₃N₄ particles (about 20 nm in diameter). The material kept the excellent mechanical strength up to 1500°C. On the other hand, it exhibited significant plastic deformation at temperatures higher than 1650°C. The stress-

strain curves showed strain hardening during the plastic deformation. The plastic deformation was characterized as non-Newtonian viscous flow from the relation between the flow stress and strain rate. The shear viscosity converted from each flow stress at temperatures in the range of 1650 to 1750°C was about 10¹¹–10¹³ Pa s and decreased proportionally to about -0.75 power of the strain rate.

Acknowledgments

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