Compressive Deformation of Precursor-Derived Si–C–N Ceramics at Elevated Temperatures

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The deformation behavior of Si–C–N ceramics derived from polyvinylsilazane polymer precursor has been investigated by compression tests at elevated temperatures. The dense Si–C–N ceramic monolith was fabricated by hot isostatic pressing of a compact prepared from pyrolyzed powders at 1500°C and at 950 MPa without any sintering additives. The microstructure of the ceramic monolith was a nano-composite structure consisting of α-Si₃N₄ crystalline grains and turbostratic graphite-like phases. Only slight plastic deformation was observed at 1500°C in spite of high compressive stress over 1000 MPa. On the other hand, the sample showed plastic flow at 1600 and 1700°C with a compressive strain of about 11% was obtained at 1700°C and 4 × 10⁻³ s⁻¹. The feature of the microstructure was maintained after the compressive deformation, although the grains were coarsened during the deformation. The strain rate exponent of the compressive stress during the deformation at 1600 and 1700°C was about 0.1. The deformation mechanism of the ceramic material is thought to be different from those of creep deformation in amorphous Si–C–N ceramics and of superplastic deformation in silicon nitride ceramics containing glassy grain boundary phases.

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1. Introduction

Silicon nitride based ceramics are one of the most promising candidates for mechanical applications at elevated temperatures. Since the diffusion coefficients of silicon nitride is low, oxides are usually added as sintering aids. The additives form silicon oxynitride glasses at grain boundaries during sintering.¹,² These intergranular oxynitride glasses impair the strength at elevated temperatures. On the other hand, the intergranular glassy phase promotes deformation at elevated temperatures, and leads to superplasticity.³–⁷

The thermolysis of organometallic polymers provides an alternative method to fabricate the ceramics for high temperature applications.⁸ The absence of intergranular oxynitride glass leads to excellent mechanical properties, which are quite different from those of conventionally sintered materials.⁹,¹⁰ Si–C–N based bulk amorphous ceramics, for example, have been developed by pyrolyzing the isostatically pressed and warm pressed preceramic powders.¹¹–¹³ Such bulk amorphous materials, however, still include open and closed pores which are necessary to release volatile species through the bulk monolith by diffusion during pyrolysis.

We developed a process to fabricate dense Si–C–N ceramic monolith by hot isostatic pressing compacts prepared from amorphous ceramic powders derived from polyvinylsilazane without any sintering additives.¹⁴ The monolith had a nano-composite structure consisting of Si₃N₄ and graphite-like phases, which were formed by crystallization of the amorphous phase during hot isostatic press (HIP) treatment. Such a fine nano-composite structure is different from the amorphous bulk materials. In addition, the nano-composite is different from conventional silicon nitride ceramics, because the nano-composite does not contain intergranular oxynitride glass. Here, we first report the compressive deformation of the precursor-derived nano-composite at high temperatures.

2. Experimental Procedure

The material used for this experiment was derived from a polyvinylsilazane polymer (VT50, Hoechst AG). The polyvinylsilazane polymer was thermally crosslinked at 250°C, and pyrolyzed at 1050°C. This treatment results in black ceramic powders with a chemical composition of Si₁₀C₁₆N₁₃ in atomic ratio. Details of the preparation process and the ceramization behavior are described by Seitz et al.¹⁵ The hot isostatic pressing of pyrolyzed powder compact was conducted at 1500°C and 950 MPa without any sintering additives. Details of the consolidation process and the densification behavior are described in Ref. 14.

The HIP-treated sample was cut into rectangular specimens (3 mm × 2 mm × 2 mm) using a diamond wheel so that the compression test direction was parallel to the powder compacting direction, and were polished with diamond abrasive. The compression tests were conducted at temperatures from 1400 to 1700°C in a nitrogen atmosphere with a servo-hydraulic type testing machine (EHF-EG10kNT-10L type Servo-pulsar, Shimadzu Co.) at constant cross-head speed in an induction heating furnace. The microstructure was observed by scanning transmission electron microscopy (HB601UX/R2, VG Scientific, accelerating voltage: 100 kV) and transmission electron microscopy (HF2000, Hitachi, accelerating voltage: 200 kV).

3. Results

Figure 1 shows the stress-strain curves obtained by the compression tests at various temperatures and at the initial strain rate of 4 × 10⁻⁵ s⁻¹. The symbol (→) represents that the test was interrupted at the end of the curve. When there is
no symbol (→), the specimen has failed at the end of the curve. Only slight plastic deformation was observed at 1400 and 1500°C in spite of high compressive stress over 1000 MPa. On the other hand, the sample showed a compressive strain of about 7% at 1000 MPa at 1600°C. The compressive strain of about 11% was achieved at 1700°C at lower compressive stress. The stress-strain curves at 1600 and 1700°C for various strain rates are shown in Figs. 2 and 3. The sample could be deformed with compressive strain over 5% at the initial strain rates less than $4 \times 10^{-5}$ s$^{-1}$ at 1600°C. Larger compressive strain of about 8% was obtained at a higher initial strain rate of $4 \times 10^{-4}$ s$^{-1}$ at 1700°C.

In order to compare the deformation stress among the testing conditions, the compressive stress values at the compressive strain of 0.035 on these true stress-true strain curves are plotted in Fig. 4 as a function of initial strain rate.

The compressive stress at 1700°C is lower than that at 1600°C at any initial strain rate. Although the compressive stress at $2 \times 10^{-5}$ s$^{-1}$ is higher than that at $1 \times 10^{-5}$ s$^{-1}$, the compressive stress at both the testing temperatures of 1600 and 1700°C decreased a little as increasing strain rate from $2 \times 10^{-5}$ s$^{-1}$ to $4 \times 10^{-5}$ s$^{-1}$. In the range of initial strain rates over $4 \times 10^{-5}$ s$^{-1}$, the compressive stress value increased as initial strain rate. The strain rate exponent of the compressive stress in the strain rate range over $4 \times 10^{-5}$ s$^{-1}$ at 1600 and 1700°C is about 0.1.

The TEM micrographs of the specimens after the compression tests at 1700°C are shown in Fig. 5, together with the result of the sample before test. The microstructure before the test (Fig. 5(a)) is a fine two-phase structure which consists of roundish α-Si$_3$N$_4$ crystalline grains with the size of 20–80 nm and turbostratic graphite-like phase. These phases are homogeneously distributed. The microstructures of the
specimens after the compression tests at both the initial strain rates of $2 \times 10^{-5}$ s$^{-1}$ (Fig. 5(b)) and $4 \times 10^{-5}$ s$^{-1}$ (Fig. 5(c)) also consist of Si$_3$N$_4$ and graphite-like phases as similar to the structure before test. However, the Si$_3$N$_4$ grains in the structures tested at both the initial strain rates were considerably coarsened during the tests. The largest levels of Si$_3$N$_4$ grains after compression tests were about 200 nm for the strain rate of $2 \times 10^{-5}$ s$^{-1}$, and about 150 nm for $4 \times 10^{-5}$ s$^{-1}$. The coarsening of grains is more significant at the lower case of $2 \times 10^{-5}$ s$^{-1}$.

4. Discussion

In the results of the compression tests, only slight plastic deformation was observed at 1400 and 1500°C in spite of high compressive stress over 1000 MPa, as shown in Fig. 1. These results indicate that the material kept the excellent mechanical strength up to 1500°C where the strength of conventional silicon nitride ceramics prepared with sintering additives usually is reduced. On the other hand, the sample could be deformed at 1600 and 1700°C. The deformation stress at both the testing temperatures of 1600 and 1700°C decreased a little as increasing strain rate from $2 \times 10^{-5}$ s$^{-1}$ to $4 \times 10^{-5}$ s$^{-1}$. Such inverse dependence on strain rate is difficult to be considered as the essential deformation behavior. The grains in the TEM microstructure tested at $2 \times 10^{-5}$ s$^{-1}$ were considerably coarser as compared with that at $4 \times 10^{-5}$ s$^{-1}$. Coarsening of grains is fundamentally dependent on the testing time, although compressive stress affects on such coarsening. Stress during deformation of polycrystalline materials at high temperatures is usually affected by the grain size. The inverse dependence on strain rate from $2 \times 10^{-5}$ s$^{-1}$ to $4 \times 10^{-5}$ s$^{-1}$ might be due to the effect of grain size.

The deformation behavior of Si–C–N and Si–B–C–N amorphous monoliths has also been studied by several researchers. Since these monoliths included open and closed pores, their deformation behaviors involved shrinkage due to densification under compression loading. In contrast to these amorphous monoliths, our specimen is nanocrystalline composite without porosity. The deformation of our material is not caused by such densification of pores. The creep deformation of Si–C–N amorphous monoliths has been reported, and the deformation behavior is concluded to be Newtonian viscous flow. Superplastic deformation has been observed in silicon nitride ceramics prepared by liquid sintering with sintering additives. In cases of such silicon nitride ceramics, strain rate dependence of the flow stress was high, and the deformation behaviors by viscous flow of the grain boundary phases have been considered. In contrast, the compressive stress in the present study was much less dependent on strain rate as compared with such silicon nitride ceramics. The present material was prepared without sintering additives, and silicon oxynitride glasses were not formed at grain boundaries. Besides, the material kept the high strength against the deformation even at 1500°C where the strength of conventional silicon nitride ceramics prepared with sintering additives is reduced significantly. These results indicate that the deformation of the material in the present study is different from flow mechanisms of silicon oxynitride glasses in conventional silicon nitride ceramics prepared with sintering additives. The TEM microstructure of the material was a fine two-phase structure and the feature was also maintained after compressive deformation at 1700°C, although the grains were coarsened during deformation. The deformation behavior of the material might be affected by the grain size as mentioned above. This plastic deformation at 1600 and 1700°C is accordingly thought to be based on a mechanism related to grain boundary, such as grain boundary sliding or grain boundary diffusion, although further detailed investigation is necessary.

5. Conclusion

The deformation behavior of the Si–C–N ceramic monolith derived from polyvinylsilsazane polymer precursor has been investigated by compression tests at high temperatures. The dense Si–C–N ceramic monolith was fabricated by hot isostatic pressing a compact prepared from pyrolyzed powders without any sintering additives. The microstructure of the ceramic monolith was a nano-composite structure consisting of α-Si$_3$N$_4$ crystalline grains and turbostratic graphite-like phases. This material kept the excellent me-

![Fig. 5 TEM micrographs of the Si–C–N ceramics, (a) before test (as-HIP-treated), and after compression tests at (b) 1700°C, $2 \times 10^{-5}$ s$^{-1}$, and (c) 1700°C, $4 \times 10^{-5}$ s$^{-1}$.](image)
Mechanical strength up to 1500°C and showed plastic flow at 1600 and 1700°C. The feature of the microstructure was maintained after compressive deformation, although the grains were coarsened during the deformation. The strain rate exponent of the compressive stress in the strain rate range over $4 \times 10^{-5}$ s$^{-1}$ at 1600 and 1700°C was about 0.1. The deformation mechanism can not be analyzed simply from the strain rate exponent since the degree of grain growth during the deformation varies with strain rate. The deformation mechanism of the ceramic material might be different from those of creep deformation in amorphous Si–C–N ceramics and of superplastic deformation in silicon nitride ceramics containing glassy grain boundary phases.

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REFERENCES