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High-strain-rate superplasticity in nanocrystalline silicon nitride ceramics under compression

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Dense nanocrystalline silicon nitride (Si_3N_4) samples were successfully fabricated at extremely low temperature of 1300 °C with high pressure 300 MPa by spark plasma sintering (SPS). The as-sintered sample consisted of equiaxed fine grains with an average grain size of 56 ± 13 nm. Nanocrystalline Si_3N_4 samples exhibited superplastic deformation at high strain rate ranging from 10^{-3} to $10^{-2}\,s^{-1}$ under compression. Significant microstructural development was not observed in the deformed samples. There was no cavity damage after large deformation.

Keywords: High-strain-rate superplasticity (HSRS); Silicon nitride; Spark plasma sintering (SPS); Deformation

Superplasticity refers to an ability of polycrystalline materials to exhibit extraordinarily large elongations in tension. This phenomenon had been observed in fine-grained metals, alloys [1], oxide ceramics [2], and non-oxide ceramics such as silicon nitride (Si_3N_4) [3] and silicon carbide (SiC) [4]. When the materials can be deformed at strain rates higher than $10^{-2}\,s^{-1}$, it has been often referred to high-strain rate superplasticity (HSRS) [1]. For the application to superplastic forming, HSRS has an advantage of reducing the total time for processing, thereby leading to a mass production. In oxide ceramics, ZrO_2–spinel–Al_2O_3 composite with grain size around 0.2 μm exhibited a large tensile elongation 1050% at a high strain rate $0.4\,s^{-1}$ at 1650 °C, which was 250 °C higher than the sintering temperature (1400 °C) [5]. The maintenance of fine grain size, which was the microstructural requirement for superplasticity, was achieved by suppressing the grain growth by three-phase microstructure and the shortened deformation time. However, the superplastic deformation in Si_3N_4-based ceramics has been still restricted to relatively low strain rates around 10^{-6}–$10^{-3}\,s^{-1}$ [3,6–15]. The Si_3N_4 ceramics is widely used as structural components such as cutting tools and/or components for engine, bearing, etc., owing to their excellent mechanical properties associated with high fracture toughness, strength, hardness and wear resistance. The HSRS in the hard and brittle Si_3N_4 ceramics is desirable to extend the application fields of this excellent material.

The constitutive equation of high-temperature deformation is described as follows:

$$\dot{\varepsilon} = A\frac{\sigma^n}{d^p} \tag{1}$$

where $\dot{\varepsilon}$ is strain rate, A is a constant, d is grain size, p is an exponent for grain size, the value of which is typically either 2 or 3 in many superplastic metals, and ceramics, and n is a stress exponent with values from 1 to 3 usually. The flow stress is, then, a function of strain rate:

$$\sigma \propto (\dot{\varepsilon} \cdot d^p)^{1/n} \tag{2}$$

The increase of strain rate leads to an increase of flow stress, especially, when the stress exponent is low. Since superplastic forming of ceramics is conducted in compression such as forging, the flow stress in compression must be small for making large components. However, in the compressive deformation of Si_3N_4-based ceramics, the stress exponent becomes $n < 1$ at higher stresses, while it is $n = 1$ at lower stresses. The deformation characterized by $n < 1$ is called shear thickening. Chen and Hwang [10] showed the flow stress in SiAlON ceramics drastically increased in the shear thickening region ($n < 1$). The shear thickening behavior hinders the deformation at high strain rates. Therefore it is important to suppress the increase of the flow stress at high strain rate region in order to attain the HSRS. The key approach to reduce the flow stress is the grain refinement as indicated in Eq. (2). While Si_3N_4-based ceramics are sintered at temperatures higher than 1600 °C usually, the sintering at lower temperature is necessary to obtain nanocrystalline material. The use of amorphous powder is

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effective to reduce the sintering temperature, for example, Kim et al. [16] fabricated Si_3N_4 nanoceramics from amorphous Si_3N_4 nanopowder containing Y_2O_3 and Al_2O_3 by spark plasma sintering (SPS) at temperatures from 1550 to 1750 °C. The grain size of Si_3N_4 nanoceramics was within the range from 90 to 240 nm, and increased with increasing sintering temperature. In order to decrease the sintering temperature further, the application of higher pressure is necessary. In addition to the ultrafine grain size, the superplastic deformation rate is enhanced by reducing viscosity of intergranular glass phase resulting from the reaction between Si_3N_4 particles and sintering additives. The intergranular glass phase plays an important role on deformation acting as a lubricant and a diffusion path. Narimatsu et al. [17] showed that the flow stress was strongly dependent on the chemistry of Y_2O_3–Al_2O_3–SiO_2 glass system. Therefore, it is also important to design the chemistry of intergranular glass in Si_3N_4 ceramics to attain the HSRS.

In this study, amorphous Si_3N_4 nanopowder was selected as the starting material to fabricate nanograined Si_3N_4 sample. The intergranular glass phase of Y_2O_3 and Al_2O_3 has been reported to be effective for the superplasticity of Si_3N_4 ceramics [11,18]. MgO was used as an additional additive in Y_2O_3–Al_2O_3 glass system in order to decrease the flow stress further. Magnesium cation is the glass modifier which lowers the glass transition temperature [19] and viscosity of glass phase [20]. The amorphous nanopowder was fully densified at low temperature and high pressure by SPS. The compressive deformation at a strain rate in the HSRS range was first demonstrated in Si_3N_4 nanoceramics.

A commercially available nanoamorphous Si_3N_4 powder containing 6 wt.%Y_2O_3, 3 wt.%Al_2O_3 and 2 wt.%MgO (Metallic impurities; Fe < 0.05 wt.% and Ca < 0.01 wt.%, PCT6Y3A2M, Plasma and ceramic technologies, Salaspils, Latvia) was used as the starting material. The powder had a high specific surface area of 73 ± 5 m^2/g and small particle size of <30 nm. The powder compacts were sintered by spark plasma sintering (SPS-515S, Dr. Sinter-Lab, Fuji Electronic Industrial Co. Ltd., Saitama, Japan) at extremely low temperature of 1300 °C under high pressure of 300 MPa for 15 min in nitrogen atmosphere. SiC die was used as an outer mold for applying high pressure in SPS machine. Graphite cylinder was used as an inner mold for electrical conduction. The sintered disks (ϕ10 mm × 4 mm) were cut into rectangular shape with approximately dimensions of 2 mm × 2 mm × 3 mm, ground and then mirror polished for compression tests (Fig. 1(a)). The compressive specimen was placed between two SiC platens. Graphite sheets coated by BN powder were put between the specimen and the SiC platens to reduce friction. Uniaxial compression tests were performed in nitrogen atmosphere at a temperature of 1600 °C in a resistance furnace with tungsten heating elements using a universal testing machine (Type 4507, Instron Co. Ltd., Danvers, MA). The strain rate was kept constant during the test by controlling the cross-head speed manually.

Phase identification in nanocrystalline Si_3N_4 samples was carried out by X-ray diffraction (XRD; RINT2500, Rigaku, Tokyo, Japan). Microstructure was observed using a field emission transmission electron microscope (FE-TEM; JEM2100F, JEOL Ltd., Tokyo, Japan) at 200 kV. TEM samples were prepared by grinding to thickness of <100 μm, mirror polishing with 1 μm diamond paste, and then dimple grinding to thickness of <30 μm (Model 656; Gatan Inc., Pleasanton, CA) before argon-ion milling at 5 keV using precision ion polishing system (PIPS, Model 691, Gatan Inc., Pleasanton, CA). Before TEM analysis, both sides of TEM samples were coated by thin carbon layers using a vacuum evaporator (JEE-400; JEOL Ltd., Tokyo, Japan) to avoid charging effect under the electron beam. Cross-sectional area of the deformed samples was observed using a field-emission scanning electron microscope (FE-SEM; S4800, Hitachi, Tokyo, Japan). SEM samples were mirror polished with 1 μm diamond

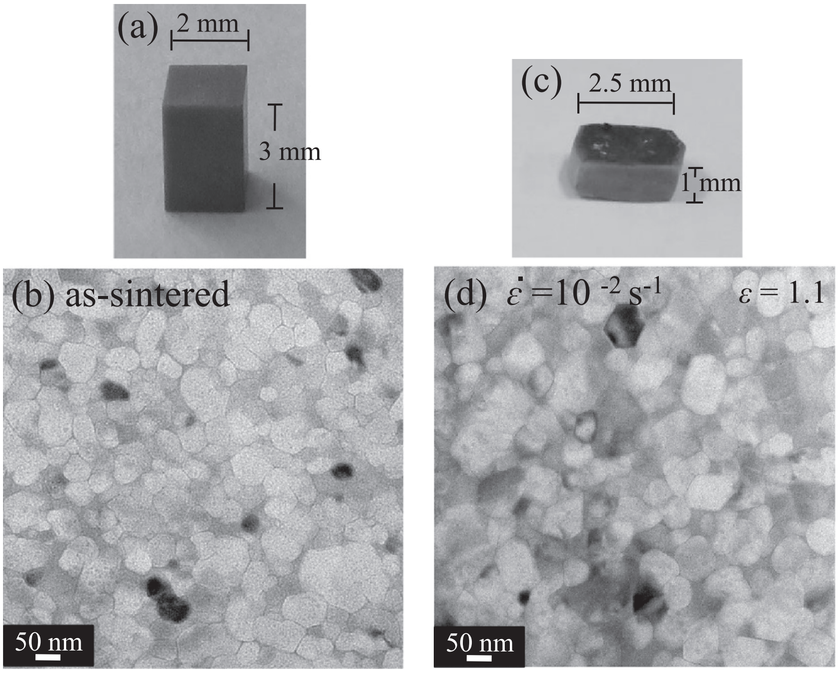

Figure 1. Nanocrystalline Si_3N_4 samples and TEM micrographs showing microstructure of (a, b) as-sintered and (c, d) deformed sample at strain rate 10^{-2} s^{-1}, respectively.

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