Brittle-to-Ductile Transition and High-Temperature Deformation in $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ and Al_2O_3 Ceramics as Evaluated by Small Punch Test

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Temperature dependence of fracture behavior in two representative oxide ceramics, 3 mol% Y_2O_3 -partially stabilized ZrO_2 and pure Al_2O_3 , was investigated to explore the high-temperature deformation mechanisms associated with ceramic superplasticity. Both the zirconia and alumina ceramics were found to show apparent brittle to ductile transitions. The transition temperatures (BDTT) were determined by means of the Small Punch (SP) test. Linear relationships were obtained between the BDTT and the logarithmic deforming rate in both ceramics. The high-temperature deformation mechanisms were discussed on the basis of the relationship between BDTT and deforming rate, and they were found to be intrinsically the same both in the present zirconia and alumina ceramics. Superplasticity can be easily achieved in tetragonal zirconia ceramics mainly because of the stability of the fine-grained microstructures. High ductility and even superplasticity can be achieved also in alumina, provided that its grain growth can be suppressed during deformation at high temperature.

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I. Introduction

Brittle ceramics may become ductile above a specific temperature, which is referred to as brittle-to-ductile transition temperature (BDTT)⁽¹⁾⁻⁽⁴⁾. Below BDTT catastrophic fracture occurs by crack propagation in a busting mode, whereas above BDTT a certain amount of plastic deformation can be obtained prior to the eventual failure. Moreover, some ceramics exhibit superplasticity⁽⁵⁾⁻⁽⁷⁾ with an elongation rate exceeding 300%, at temperatures high enough above their BDTTs. The brittle to ductile transition behavior of ceramic materials has received considerable attention in the last decade, although recent studies have been focused on ceramic superplasticity because of its possible applications in ceramic processing. To attain a full understanding of high-temperature deformation and superplasticity of ceramic polycrystals, investigations on brittle-to-ductile transitions should be of primary importance.

In the present study, the brittle-to-ductile transition behavior of two representative oxide ceramics, Y_2O_3 -partially stabilized zirconia and pure alumina polycrystals, was investigated and discussed in relation to their high-temperature deformation mechanisms. A recently developed and now rather popular method, the small punch test (SP)⁽⁸⁾, was applied to determine the brittle-to-ductile transition temperatures of the present ceramics. This method, using miniaturized specimens, was originally developed for the evaluation of materials for nuclear plants⁽⁸⁾, and it has been successfully used to

investigate the ductile-to-brittle transition in metallic alloys due to nuclear irradiation⁽⁸⁾ and the embrittlement of intermetallic compounds⁽⁹⁾. Among numbers of oxide and non-oxide superplastic ceramics, the highest superplasticity has been achieved in Y_2O_3 -partially stabilized zirconia, whereas alumina shows much lower ductility than that found in zirconia. Questions still remained about what is really responsible for this difference, although some explanations can be found from the literature⁽⁷⁾⁽¹⁰⁾⁽¹¹⁾. The present study was also intended to clarify this point.

II. Experimental Procedure

1. Sample preparation

Commercial ZrO_2 -3 mol% Y_2O_3 (TZ-3Y, Tosoh Co., Tokyo, Japan) and Al_2O_3 (TM-DA, Taimei Chemicals Co., Nagano, Japan) powders, with crystallite sizes of 26.7 and 100 nm respectively, were used as the starting materials. The TZ-3Y powder contained about 1.5 mass% HfO_2 , which is difficult to be separated from ZrO_2 , and the other impurities were less than 0.01 mass% (<0.005 mass% Al_2O_3 , <0.002 mass% SiO_2 , <0.002 mass% Fe_2O_3 , and 0.013 mass% Na_2O). The purity of the TM-DA Al_2O_3 was $>99.99\%$. Cylindrical powder compacts of 14 mm in diameter were formed by die pressing at 100 MPa, and followed by cold-isostatic pressing at 200 MPa. The TZ-3Y and Al_2O_3 green compacts were sintered in air for 2 h at 1673 and 1573 K, respectively, and they subsequently were subjected to post hot-

isostatic pressing (post-HIP) under a pressure of 200 MPa (Ar gas) for 2 h at 1773 and 1573 K, respectively. The post-HIP treatment was conducted to produce fully dense materials so that any possible influence of residual porosity on the relevant high-temperature properties can be eliminated. Density measurement by Archimedes' method confirmed that fully dense samples were obtained.

2. Details of testing

The modified SP method (MSP) was employed for testing brittle materials⁽¹²⁾. In the modified SP (MSP) method, a disk specimen (approximately 10 mm in diameter and 0.5 mm in thickness) is pushed at its center by a small plane-headed puncher (~ 2 mm in diameter), and the deflection is detected by a rod attached onto the opposite side. The details of the testing jig used in the present study can be found in our previous reports^{(13)–(15)}. The MSP load-deflection curves were measured from room temperature to 1773 K in an argon atmosphere with the MSP jig setup in an electric furnace with a tungsten mesh heater, at punch-displacement rates (= crosshead speeds) that were changed over the range of 0.005–0.5 mm/min (0.0833–8.33 $\mu\text{m/s}$). The load was normalized as done in the previous study⁽¹³⁾ to remove the effect of the specimen thickness. The MSP method can determine the fracture strength by the the following equation⁽¹²⁾⁽¹³⁾:

$$\sigma_f = \frac{3P_{\max}}{2\pi t^2} \left[1 - \frac{1-\nu^2}{4} \frac{b^2}{a^2} + (1+\nu) \ln \frac{a}{b} \right] \quad (1)$$

where t is the thickness of a specimen, a and b are radii of the lower hole and the puncher, 2.25 mm and 0.9 mm, respectively, in the present work. ν is Poisson's ratio.

The disk specimens for the MSP test were sliced from the post-HIPed pellets using a diamond wheel. Both circular faces of the specimens were ground by SiC paper and one surface was finally polished with 1 μm diamond paste to achieve a mirror-like surface finish.

3. Microstructural observation

The microstructures of the TZ-3Y and the Al_2O_3 investigated in the present study were observed by transmission electron microscopy (TEM). The TEM samples were prepared by the usual procedure for ceramics, *i.e.*, slicing, mechanical polishing, and ion milling. The tensile surfaces of the MSP specimens after testing were observed by scanning electron microscopy (SEM).

III. Results

1. Microstructure

Figure 1 shows representative TEM micrographs of the TZ-3Y and the Al_2O_3 obtained in the present study, which were used for the following evaluation experiments. Both TZ-3Y and Al_2O_3 specimens show fully densified microstructures, with mean grain sizes of ~ 0.8 and ~ 2.0 μm , respectively. The grains of the Al_2O_3 are

Fig. 1 TEM micrographs of the TZ-3Y (A) and Al_2O_3 (B) ceramics investigated in this study.

sharply faceted, without appreciable grain boundary phases. The TEM image of the TZ-3Y is somewhat unclear, since the phase transformation induced by the radiation of an electron beam during TEM observations would cause the indistinctness⁽¹⁶⁾. Considering that grain sizes significantly affect high-temperature strength and deformation properties, it was intended to fabricate two ceramics with the same grain sizes. For that purpose, the sintering and post-HIP temperatures were set relatively high for the TZ-3Y to enhance its grain growth, whereas the Al_2O_3 was sintered and HIPed at temperatures as low as possible for its densification. However, the resultant grain sizes for the TZ-3Y and Al_2O_3 were ~ 0.8 and ~ 2.0 μm , respectively. Despite the resultant difference in the grain sizes, the present Al_2O_3 has much finer microstructures as compared with conventional alumina ceramics because a newly developed ultrafine alumina powder was used.

2. BDTT

Figure 2 shows the load-deflection curves of the TZ-3Y and the Al_2O_3 obtained at a punch-displacement rate of 0.05 mm/min at various testing temperatures. The load versus deflection relationships become nonlinear above

Fig. 2 MSP load-displacement curves of the TZ-3Y and Al_2O_3 , at a punch-displacement rate of 0.05 mm/min.

1373 and 1523 K, respectively for the TZ-3Y and Al_2O_3 , indicating that apparent brittle to ductile transition occurred in both two materials these temperatures. The fracture strength for the samples in the brittle state can be calculated according to eq. (1). For example, the fracture load at 1323 K in the TZ-3Y represents a fracture strength of 1112 MPa, and that at 1473 K in the Al_2O_3 corresponds to a fracture strength of 529 MPa. It was confirmed that the fracture strengths and/or flow stresses were independent of the punch displacement rates, within the range used in the present study, suggesting that the brittle to ductile transitions would occur almost at the same stress level.

Figure 3 shows the optical micrographs of the TZ-3Y specimens tested at the temperatures shown in Fig. 2(A). The appearance changed with increasing testing temperature. The specimens were fractured due to the extension of radial cracks originating from the center at temperatures where the load-deflection relationship remained linear. With increasing testing temperature, a shallow depression was formed around the center of specimen, but the eventual fracture was still brittle. At temperatures high enough (e.g. 1573 K), radial cracks disappeared and the eventual fracture tended to be due to necking. The same results were obtained also in the present Al_2O_3 specimens.

To determine ductile-to-brittle transition temperature in metallic materials, SP fracture energy, which corresponds to the area between the load-deflection curve and the deflection axis, is measured as a parameter of

Fig. 3 Macro views of the MSP specimens of TZ-3Y after testing at the shown temperatures.

fracture toughness. Figure 4 shows change in the MSP fracture energy of the TZ-3Y and Al_2O_3 as a function of testing temperature. The MSP energy increased over a narrow temperature range, showing a definite transition. With increasing punch-displacement rate, the transition occurred at higher testing temperature. It should be, however, noted that such a transition was not observed in the Al_2O_3 when tested at the fastest crosshead speed in the present temperature range; the load-deflection relationships investigated were all linear.

Figure 5 shows change in BDTTs for the TZ-3Y and the Al_2O_3 as a function of punch-displacement rate. The BDTT was defined here as a temperature where the MSP fracture energy was equal to the half of the sum of maximum and minimum values over a temperature range of transition⁽³⁾⁽⁸⁾. The BDTT increased linearly as a function of logarithmic punch-displacement rate. Figure 5 can be rewritten as shown in Fig. 6, in which a linear relationship holds between the logarithmic punch-displacement rate and the reciprocal of transition temperature. The meanings of the slopes in Fig. 6 will be described later.

Fig. 4 Change in SP fracture energy as a function of testing temperature, at various punch-displacement rates ($\circ$ $\bullet$: 0.5 mm/min, $\diamond$ $\blacklozenge$: 0.05 mm/min, $\square$: 0.01 mm/min, $\triangle$ $\blacktriangle$: 0.005 mm/min).

Fig. 5 Change in BDTT as a function of punch-displacement rate.

IV. Discussion

High-temperature ductile deformation in fine-grained ceramic polycrystals is generally considered to result from creep due to grain boundary sliding⁽⁷⁾⁽¹⁷⁾. However, if deformation speed is larger than that of the grain boundary sliding, no appreciable amount of ductile

Fig. 6 Linear relationship between the logarithmic punch-displacement rate and the reciprocal of BDTT.

deformation would be obtained. In other words, the brittle to ductile transition may occur when the loading rate (S^{ex}) is lower than the creep rate (S^{c}):

$$S^{\text{ex}} \leq S^{\text{c}} \quad (2)$$

In general, the creep rate can be expressed as⁽¹⁸⁾

$$S^{\text{c}} = A(1/d)^p \sigma^n \exp(-Q/RT) \quad (3)$$

where d is the grain size, σ is the flow stress, Q is the activation energy for the deformation, R is the gas constant, T is the absolute temperature and A , p and n are constants.

At a critical point (transition temperature, BDTT), S^{c} and T in eq. (3) can be replaced with S^{ex} and T_{BDTT} . Therefore, the slopes in Fig. 6 correspond to the apparent activation energies for the deformation, which were measured to be 352 and 318 kJ/mol for the TZ-3Y and the Al_2O_3 , respectively. It should be mentioned that these values may not be so accurate because the present experimental data are not sufficient; however, they are comparable to the activation energies reported for the diffusional creep⁽¹⁹⁾. As above-mentioned in the section of results, the brittle to ductile transitions occurred almost at the same stress, regardless of the change in punch-displacement rate within the range investigated. Additionally, the grain size, d , would be unchanged at the temperatures below the maximum BDTT for the highest punch-displacement rate, because the transition phenomenon disappeared if the grain growth became significant, as will be shown below by the result obtained for the Al_2O_3 . These two facts validated the determination of the apparent activation energies from the linear relationships between the logarithmic punch-displacement rate and the reciprocal of transition temperature, as shown in Fig. 6.

The above experimental results showed that there are

Fig. 7 Tensile surface morphology of the MSP specimens of the TZ-3Y after testing: (A) at 1473 K, punched to 200 μm ; (B) at 1573 K, punched to 400 μm ; (C) at 1673 K, punched to 600 μm . The punch-displacement rate is 0.05 mm/min. Arrows indicate the grain boundary cracks.

Fig. 8 Tensile surface morphology of the MSP specimens of the Al_2O_3 after testing: (A) at 1473 K, punched to 100 μm ; (B) at 1573 K, punched to 100 μm ; (C) at 1673 K, punched to 200 μm . The punch-displacement rate is 0.005 mm/min. Arrows indicate the grain boundary cracks.

no intrinsic differences between the zirconia and alumina in the brittle to ductile transition. However, why superplasticity can be more easily obtained in zirconia-based ceramics than in alumina? The following experiments of microstructural observation will give an answer. **Figures 7 and 8** show representative SEM micrographs of the tensile surfaces of the TZ-3Y and the Al_2O_3 , which were given to a predetermined amount of deformation. When the testing temperatures were not high enough, grain boundary cracks were formed both in the TZ-3Y and the Al_2O_3 after a certain amount of ductile deformation, as shown in Figs. 7(A) and 8(A). At higher temperatures, both specimens were deformed to larger strains without crack formation. However, at further higher temperatures, the Al_2O_3 specimen contained a lot of crevices. The grain size increased significantly in the Al_2O_3 above 1573

K, but remained unchanged in the TZ-3Y. It is easy to understand why no BDTT was obtained in the present Al_2O_3 at a punch-displacement rate of 0.5 mm/min. If the grain growth had been suppressed at temperatures above 1573 K, transition behavior should have appeared in the Al_2O_3 even at the highest deformation rate (0.5 mm/min). However, the grain growth in the Al_2O_3 seems to be accelerated above 1573 K. Because the processing window (from BDTT to the temperature without significant grain growth) is very narrow, superplasticity is difficult to be achieved in the Al_2O_3 . Conventional alumina ceramics, having grain sizes of 5–10 μm , may have no BDTT under normal conditions. To achieve superplasticity in alumina ceramics, it is needed to develop a fabrication process to produce submicron-sized compacts, which may have BDTT sufficiently below 1573 K.

On the other hand, Y_2O_3 -partially stabilized zirconia exhibits high superplasticity not only because their sintered microstructures are usually very fine, but also because the initial grain sizes remained almost unchanged during deformation at temperatures higher enough above DBTT.

V. Conclusion

Fully dense Y_2O_3 -doped tetragonal ZrO_2 and pure Al_2O_3 ceramics were fabricated by pressureless sintering followed by post hot-isostatic pressing, and their brittle-to-ductile transition behavior was investigated by using a small punch testing method. The Brittle-to-Ductile Transition Temperature (BDTT) of ceramics can be determined accurately and conveniently by the MSP method. The BDTT shifts to higher temperature with increasing deforming speed. Linear relationships were obtained between the BDTT and the logarithmic deforming speed for the present zirconia and alumina ceramics, suggesting that there exist no intrinsic difference in the deformation mechanisms between the two ceramics. Superplasticity can be easily achieved in tetragonal zirconia ceramics mainly because of the stability of the fine-grained microstructures. High ductility and even superplasticity can be achieved also in alumina as in the tetragonal zirconia ceramics, provided that its grain growth can be suppressed during deformation at high temperature.

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