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Analysis of the Deformation Behavior in Nanocrystalline Y_2O_3 Stabilized Tetragonal ZrO_2

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Abstract, The deformation behavior of 3mol% Y_2O_3 stabilized tetragonal ZrO_2 polycrystals (nano Y-TZP) were studied at 1273-1373K in compression test. Both materials were "high purity" material with impurities less than 0.1 wt%. The stress exponent of nano Y-TZP with grain size of 60nm was 2.7 in higher stress region, and increased with decreasing stress. The transition of the stress exponent with stress was similar to the deformation of high-purity Y-TZP with grain size of 200 - 400nm at 1673K - 1723K (submicron Y-TZP). Constitutive equation for the deformation of nano Y-TZP was examined by a detailed analysis of the deformation data. Experimental results were correlated with a single deformation process, which incorporates a threshold stress. The deformation of nano Y-TZP was characterized by the grain size exponent p=3 and the activation energy of grain boundary diffusion, while the deformation of submicron Y-TZP was associated with p = 2 and the activation energy of lattice diffusion.

Key words: Zirconia, Superplasticity, Deformation, Nanocrystalline ceramics

1. INTRODUCTION

The occurrence of high ductility in tension or superplasticity is now well documented in a wide range of fine grained ceramics. The strain rate $\dot{\varepsilon}$ is conveniently expressed as a function of the applied stress σ, the absolute temperature T, and the grain size d as follows,

$$\dot{\varepsilon} = A\frac{Gb}{RT}\left(\frac{\sigma}{G}\right)^n\left(\frac{\mathbf{b}}{d}\right)^p D_0 \exp\left(\frac{-Q}{RT}\right) \qquad (1)$$

where D_0 is the frequency factor, Q the activation energy, R the gas constant, G the shear modulus, b the Burger's vector, p the exponent of the inverse grain size, n the stress exponent and A is a dimensionless constant.

Y_2O_3-stabilized tetragonal ZrO_2 polycrystals (Y-TZP) have been frequently serected as a model for investigating ceramics superplasticity, because very small grain sizes are retained at elevated temperatures. In superplasticity of Y-TZP, the experimental data revealed the variation of stress exponent with stress, which was similar to metals [1-4]. In order to investigate the intrinsic mechanism of superplasticity, the deformation of "high-purity" Y-TZP has been extensively studied, because the deformation of Y-TZP is significantly affected by the addition of small amount of impurities, especially, Al_2O_3 and SiO_2 [5, 6]. The high-purity Y-TZP with impurity content less than 0.1 wt% is characterized by a stress exponent of $n \simeq 2$ at comparatively higher stresses, whereas the deformation at lower stresses is associated with $n \simeq 3$ (transition of the stress exponent). The critical stress for the transition of stress exponent increases with decreasing the grain size [2,3]. On the other hand, the deformation behavior of the material, in which the impurity content is more than 0.1 wt %, is characterized by $n = 2$ and $p = 2$ over a wide stress range [2,3]. The following models have been proposed to explain the transition of stress exponent in high-purity Y-TZP: 1) two different deformation mechanisms [1], 2) threshold stress [2,3], 3) interface-controlled Coble creep [7], 4) dislocation mechanism [4]. However, they are still controversial, and there is no firm concensus on the deformation mechanism of high-purity Y-TZP.

The primary requirement for superplasticity is fine grain size. The superplasticity of Y-TZP has been investigated by using high purity materials with grain size of 400-300 nm (submicron Y-TZP) at temperatures from 1673 K to 1723 K. The reduction of grain size to the nanometer range (less than 100 nm) will lead to the enhancement of strain rate at lower temperatures as predicted by Eq.1. High-strain rate superplasticity and low-temperature superplasticity are of great technological interest for the shape forming of engineering materials. Furthermore, the comparison of the deformation of nanocrystalline Y-TZP (nano Y-TZP) to that of submicron Y-TZP may give the key to identify the deformation mechanism. In the present study, we obtained nano Y-TZP with the grain size of 60 nm by hot isostatically pressing, and the deformation behavior of nano Y-TZP was studied at temperatures from 1273 to 1373 K, which were 300 – 400 K lower than the temperature for superplasticity of submicron Y-TZP.

2. EXPERIMENTAL PROCEDURE

The Y-TZP sample was prepared from a tetragonal ZrO_2 powder containing 3 mol% Y_2O_3 (TZ-3Y, Tosoh Co., Japan: <0.005 Al_2O_3, <0.005 SiO_2, <0.002 Fe_2O_3, <0.023 Na_2O in wt%). The starting powder was "high purity" material. The powder compacts were formed by die-pressing at 20 MPa, followed by cold-isostatically pressing (CIP) at 200 MPa. The green compacts (ϕ 20 mm × 7 mm) were coated with BN powder (GP, Denka Co., Japan), and then encapsulated by borosilicate glass at 1043 K. The glass-encapsulated specimens were hot isostatically pressed (HIP) under Ar gas. They were heated up to 1063 K, then the pressure was applied to 196 MPa. The temperature was increased up to 1373 K, and kept for 30 min. The bulk density of sintered body was 6.05 g/cm^3, which was 99% of the theoretical density. The X-ray diffraction (XRD) showed that the sintered body consisted of tetragonal phase only.

The sintered bodies were polished and thermally etched for microstructural observation by scanning electron microscope (Model S4500, Hitachi Co., Japan). The average grain size was defined as the linear intercept length. The average grain size of sintered body was 60 nm. In this paper we refer to this material as nano Y-TZP. The sintered body was cut into rectangular bars with dimension of 2 mm × 2 mm × 3 mm. The specimens were heated to a temperature 100 K lower than the deformation temperature at a rate of 30 K/min, then to deformation temperatures (1273-1373 K) at 5 K/min. After keeping for 30 min, the specimen was compressively deformed by the universal testing machine (AG-I, Shimadzu Co., Japan) in air.

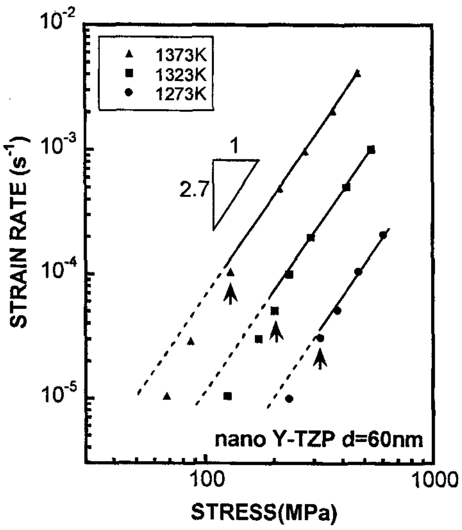

Fig.1, Logarithmic plot of flow stress vs. strain rate for nano Y-TZP at 1273-1373 K.

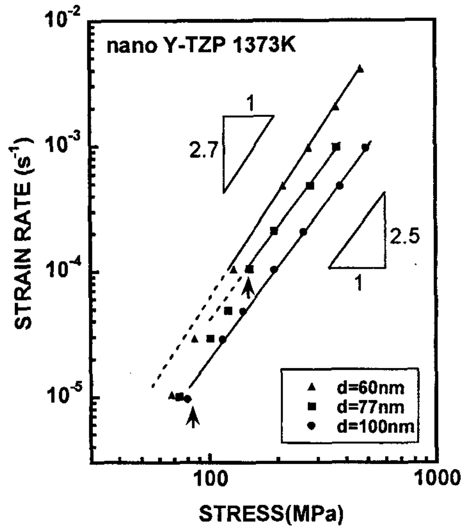

Fig.2, Variation in strain rate with stress for nano Y-TZP at 1373 K with three different grain sizes (d = 60, 77 and 100 nm).

The compression tests were conducted at constant crosshead speed. From the stress-strain curves the flow stress was defined as the intersection of two lines extrapolated to the elastic and the plastic strain regions [8].

3.RESULTS AND DISCUSSION

3-1 Deformation of nano Y-TZP

Fig. 1 illustrates the variation of strain rate with flow stress for nano Y-TZP at 1273-1373 K. The flow stress of nano Y-TZP at low temperatures was higher than 100 MPa, and decreased with increasing temperature. The apparent stress exponent of nano Y-TZP was 2.7 at high stress region and increased with decreasing flow stress. The stress, at which the stress exponent becomes n > 2.7 (arrows in Fig.1), increased with decreasing temperature. Morita also reported the region with n = 2.7 at high stress region for Y-TZP with d = 200 nm [4]. The region of n= 2 was not observed in nano Y-TZP, while submicron Y-TZP with $d \simeq$ 400 nm at 1673 K exhibited the apparent stress exponent of $n \simeq$ 2 [2,3].

The HIPed nano Y-TZP was annealed to have the different grain size; 77 nm and 100 nm. The relationship between flow stress and strain rate was plotted on a logarithmic scale in Fig. 2. The strain rate decreased with increasing grain size. The apparent stress exponent at 200 MPa slightly decreased from 2.7 for d= 60 nm to 2.5 for d= 77 nm and d= 100 nm. The stress at which the apparent stress exponent was higher than n= 2.5 (arrows in Fig.2) decreased with increasing grain size.

Many investigations have been conducted on the deformation of high purity Y-TZP. In the deformation of submicron Y-TZP with grain size of 200-400 nm, the apparent stress exponent increased from 2 to 3 with decreasing flow stress. Jiménez-Melendo and coworkers suggested that the stress for transition from n= 2 to n= 3 (transition stress) was dependent on grain

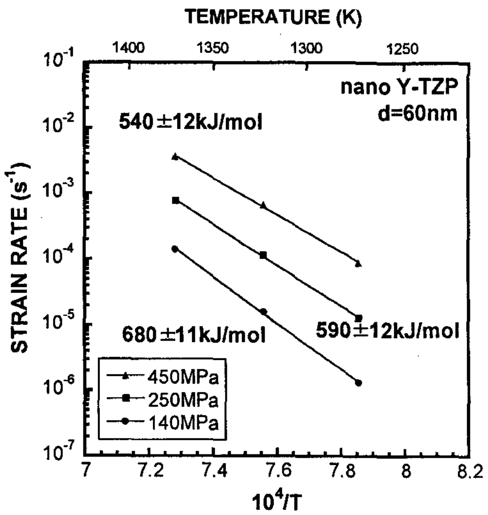

Fig.3, Variation of strain rate with reciprocal temperature at various stress for nano Y-TZP.

size and temperature. The transition stress between n= 2 and n= 3 decreased from 30 MPa for d= 280 nm to 10 MPa for d= 674 nm in the deformation of submicron Y-TZP at 1623 K [2]. As the temperature decreased, the transition stress increased. The apparent stress exponent (n= 2.7) of nano Y-TZP at high stress region was higher than that of submicron Y-TZP. But the transition stress of both nano Y-TZP and submicron Y-TZP were dependent on grain size and temperature, in the same way.

Fig. 3 shows that the variation of strain rate with reciprocal temperature at various stresses for nano Y-TZP with grain size of 60 nm. The apparent activation energy increased from 540 kJ/mol to 680 kJ/mol with decreasing flow stress. Jiménez-Melendo and coworkers also reported that the apparent activation energy of submicron Y-TZP increased with decreasing flow stress [2,3].

For the deformation of submicron Y-TZP, the activation energies are 500-600 kJ/mol at 1673K. There is no direct measurement of grain boundary diffusion of Zr^{4+} in Y-TZP by tracer diffusion, but the activation energy for lattice diffusion in 2.8Y-TZP was reported recently as 607 kJ/mol [9]. Sakka reported the activation energy of grain boundary diffusion (506 kJ/mol) for polycrystalline tetragonal CeO_2-ZrO_2-HfO_2 solid solutions [10]. The reported values of activation energy for deformation of Y-TZP were intermediate between the activation energy of grain boundary diffusion and that of lattice diffusion.

Fig. 4 illustrates the variation of strain rate with grain size for nano Y-TZP at the temperature of 1373 K. The apparent exponent of inverse grain size for nano Y-TZP decreased from p = 3 at 360 MPa to p = 1.5 at 80 MPa with decreasing flow stress. In the deformation of submicron Y-TZP, the apparent grain size exponent decreased with decreasing flow stress [2,3]. The relationship between the apparent grain size exponent and the flow stress in nano Y-TZP exhibited similar tendency to that in the submicron Y-TZP.

3-2 Threshold stress

Recently, Jiménez-Melendo [2,3] and Morita [4] reported that the flow behavior ($\dot{\varepsilon}$-σ relationship) of Y-TZP exhibited similar characteristics to that observed in superplastic metals. The logarithmic plot of $\dot{\varepsilon}$-σ relationship in Y-TZP is characterized by three deformation region; in region II (high stress region) the stress exponent is close to 2; in region I (intermediate stress region) the stress exponent is n > 3; in region 0 (low stress region) the stress exponent is 1. Microstructural observation of superplastically deformed Y-TZP indicated that the grains retained their equiaxed shapes after the very large tensile deformation. It has been considered that in region II (n = 2), the deformation occurs by a grain boundary sliding process. The region I (n > 3) was interpreted as the transition region near the threshold stress. The experimental data in both region I and II can be correlated with a single deformation process which incorporates a threshold stress σ_0,

$$\dot{\varepsilon} = A\left(\frac{Gb}{kT}\right)\left(\frac{\sigma-\sigma_0}{G}\right)^n\left(\frac{b}{d}\right)^p D \qquad (2)$$

Two equations are proposed for grain boundary diffusion and lattice diffusion controlled superplastic flow. The phenomenological relations in superplastic metals are written in the following equations [11].

$$\dot{\varepsilon}_l = A\left(\frac{Gb}{kT}\right)\left(\frac{\sigma-\sigma_0}{G}\right)^2\left(\frac{b}{d}\right)^2 D_L \qquad (3)$$

$$\dot{\varepsilon}_{gb} = A\left(\frac{Gb}{kT}\right)\left(\frac{\sigma-\sigma_0}{G}\right)^2\left(\frac{b}{d}\right)^3 D_{gb} \qquad (4)$$

In superplasticity of metals, when the materials have large grain size or are deformed at high temperature, the deformation mechanism is GBS controlled by lattice diffusion. The rate controlling mechanism of GBS

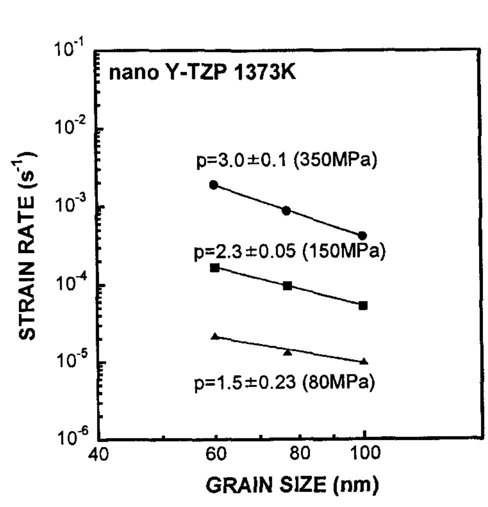

Fig. 4 Logarithmic plot of grain size vs. strain rate for nano Y-TZP at a temperature of 1373 K.

changed from lattice diffusion to grain boundary diffusion, when materials have fine grain size or are deformed at low temperatures [12].

In threshold stress model, the stress exponent, exponent of inverse grain size and activation energy are expressed as a function of flow stress. The stress exponent and the activation energy increased with decreasing flow stress. The exponent of inverse grain size decreased with decreasing flow stress. When GBS is controlled by the grain boundary diffusion (Eq. 4), the exponent of inverse grain size is 3 at high stress region. As the flow stress decreased, the exponent of inverse grain size decreased from 3 to 0. For nano Y-TZP, the exponent of inverse grain size decreased from 3 to 1.5 with decreasing flow stress. The transition of the exponent of inverse grain size in nano Y-TZP was similar to that predicted by equation (4).

Jiménez-Melendo and coworkers suggested that the deformation mechanism of submicron Y-TZP was GBS controlled by lattice diffusion, which incorporates the threshold stress. But their empirical expression of the threshold stress model can not be applicable to nano Y-TZP. The grain size of nano Y-TZP was one-tenth of submicron Y-TZP, and was deformed at lower temperatures. If the deformation mechanism map of Y-TZP is similar to that of the superplasticity of metals, it is natural to suppose that the deformation mechanism of nano Y-TZP is GBS controlled by grain boundary diffusion, which incorporates threshold stress. Despite the uncertainty on the origin of threshold stress, GBS model incorporating the threshold stress has an advantage for interpreting both submicron Y-TZP and nano Y-TZP.

4. CONCLUSIONS

Nano Y-TZP with the grain size of 60 nm was obtained by hot isostatically pressing, and the deformation behavior of nano Y-TZP was investigated at temperatures of 1273-1373 K. The conclusions obtained are summarized as follows,

1) The transition of stress exponent from 2.7 to the higher value was observed in the compressive deformation of nano Y-TZP with grain size of 60 nm at 1373 K.
2) The activation energy of nano Y-TZP increased from 540 kJ/mol for 450MPa to 680 kJ/mol for 140 MPa with decreasing flow stress.
3) The deformation behavior of Y-TZP was explained by the threshold stress model. In nano Y-TZP the strain rate was proportional to D_{gb}/d^3, while it was proportional to $D_{lattice}/d^2$ in submicron Y-TZP.

5. REFERENCES

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