Transactions of the Materials Research Society of Japan 31[2] 533-536 (2006)

Improvement of High Temperature Ductility in Oxide Ceramics by Grain Boundary Nanostructure Control

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It has been pointed out that composite synthesis is effective method to improve high temperature tensile ductility in oxide ceramics partly because of its retarded grain growth rate. On the other hand, our group has recently found that the high temperature ductility in oxide ceramics is very sensitive to small levels of doping by various cations. For example, doping of 0.2-4mol% TiO_2 and/or GeO_2 enhances the ductility in tetragonal ZrO_2 polycrystals (TZP) up to about 1000%. High resolution transmission electron microscopy (HRTEM) observations combined with nano-probe X-ray energy dispersive spectrometry (EDS) analysis confirmed that grain boundaries were free from amorphous layer or secondary phase particles, and the doped cations tend to segregate along the grain boundaries. Since the high temperature superplastic flow in TZP takes place by grain boundary sliding, the consequent change of the chemical bonding state must affect the matter transport at the grain boundaries and improve the high temperature ductility in TZP.
Key words: tetragonal zirconia, superplasticity, grain boundary, segregation, molecular orbital calculations

1. INTRODUCTION

Considerable interests have developed in recent decades in high temperature plastic flow behavior of polycrystalline ceramics.[1-3] In particular, since the super-plastic flow in a tensile manner has been experimentally demonstrated,[4] special interests in superplastic ceramics have arisen because remarkable tensile ductility can be achieved even in the brittle materials. A significant number of studies on the superplastic ceramics have been made, and large tensile elongation to failure has been achieved in various ceramics and ceramic composites.[5-7] Of the superplastic ceramics, tetragonal ZrO_2 polycrystals (TZP) have been extensively studied because of its excellent mechanical properties.[8-11] One of the reasons for the high tensile ductility in TZP is attributed to its grain size stability during high temperature deformation.[10]

It has been pointed out that composite synthesis is effective method to improve high temperature tensile ductility in oxide ceramics, because dynamic grain growth is highly suppressed by pinning effect. For instance, a maximum elongation to failure of more than 2500% was recently achieved in ZrO_2-Al_2O_3-spinel composite[12]; the enhanced ductility is directly attributed to suppressed cavity propagation, and suppressed grain growth essentially contributes to the superplastic flow as a necessary condition.

On the other hand, our group has recently found that the high temperature ductility in oxide ceramics is very sensitive to small levels of doping by various cations.[13,14] According to the results, the flow stress in TZP strongly depends on type of doping cations; amongst various dopant cations, TiO_2 and GeO_2-doping is particularly effective to reduce the high temperature flow stress and to improve tensile ductility.[13-16] The present study aims to examine the TiO_2 and/or GeO_2 doping dependence of the high temperature plastic flow behavior in TZP. The doping dependence was systematically investigated in TiO_2 or GeO_2 singly doped TZP as well as TiO_2 and GeO_2 co-doped TZP with the doping amount of 0.2-4 mol%.

2. EXPERIMENTAL PROCEDURE

The materials used in this study were tetragonal ZrO_2 polycrystals (TZP) and TiO_2 and/or GeO_2-doped TZP. Starting powders were tetragonal ZrO_2 powders containing 3mol% Y_2O_3 (TZ3Y; Tosoh, Japan), titanium oxide (high-purity grade TiO_2) and germanium oxide (purity>99.999%). TZP powders were mixed with 0.5-4mol% TiO_2 and/or GeO_2 powders by ball-milling for 24 hours. The green compacts of the mixed powders were sintered at 1400°C for 2 hours in air.

High temperature uniaxial tensile tests were carried out in air at a constant cross-head speed using an Instron-type testing machine with a resistance-heated furnace. Microstructure of the present materials was observed by a scanning electron microscopy (SEM) and a transmission electron microscopy (TEM). For further analysis on the grain boundaries in TZP, high-resolution transmission electron microscopy (HRTEM) obser-vations were performed. An energy-dispersive X-ray spectroscopy (EDS) analysis was carried out with the probe size of about 1nm.

3. RESULTS

Relative density of more than 99% and an average grain size of about 0.4μm were obtained in the sintered materials. Fairly uniform and equiaxed grain structure was obtained in the present materials, and dispersion of second phase particles was not observed at least in SEM images of TiO_2 and/or GeO_2-doped TZP.

Figures 1 and 2 show examples of the stress-strain

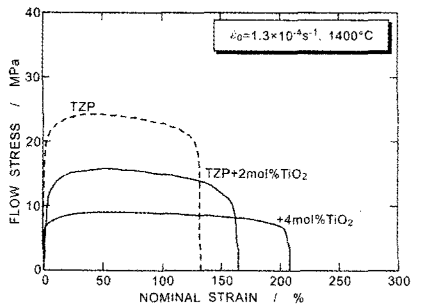

Fig. 1 Stress-strain curves in TZP and TiO_2-doped TZP at 1400°C and an initial strain rate of $1.3\times10^{-4}s^{-1}$.

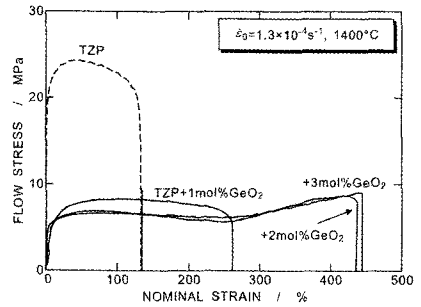

Fig. 2 Stress-strain curves in TZP and GeO_2-doped TZP at 1400°C and an initial strain rate of $1.3\times10^{-4}s^{-1}$.

curves in TiO_2-doped and GeO_2-doped TZP respectively under the initial strain rate of $1.3\times10^{-4}s^{-1}$ at 1400°C. The doping of TiO_2 and GeO_2 is effective to reduce the flow stress in TZP; the flow stress in 1mol% GeO_2-doped TZP is about one third of that in TZP. The increment in the flow stress with the nominal strain over 300% in 2 or 3mol% GeO_2-doped TZP is likely to result from the dynamic grain growth during deformation. The flow stress decreases, and elongation to failure in TZP increases with the increasing amount of TiO_2 or GeO_2-doping. For instance, 3 mol% GeO_2-doped TZP exhibits the elongation to failure of about 450% in nominal strain, which is more than three times larger than that in undoped TZP. The high temperature tensile ductility is fairly related to the doping amount; the higher doping amount provides the lower flow stress and the larger elongation to failure. However, the doping effect on the tensile ductility seems to level off over 2 mol% doping in GeO_2-doepd TZP. On the other hand, TiO_2-doping effect seems not to level off over 4 mol% doping.

Figure 3 shows the stress-strain curves in TiO_2-GeO_2 co-doped TZP under an initial strain rate of 1.3×10^{-4} s^{-1} at 1400°C. The flow stress in TZP decreases, and the elongation to failure increases with the increasing amount of TiO_2 and GeO_2 co-doping; in particular, 2.2mol% TiO_2-GeO_2 co-doped TZP exhibits the lowest flow stress and the largest elongation to failure of 993%. The flow stress in 1.5 mol% and 2.2 mol% TiO_2-GeO_2 co-doped TZP increase in the latter stage of the deformation. The co-doping effect on the tensile ductility levels off over about 2 mol% TiO_2 and GeO_2, which will be discussed elsewhere. The leveling-off behavior must be related to solubility limit of TiO_2 and GeO_2 into TZP.

As previously reported, dopant cations tend to

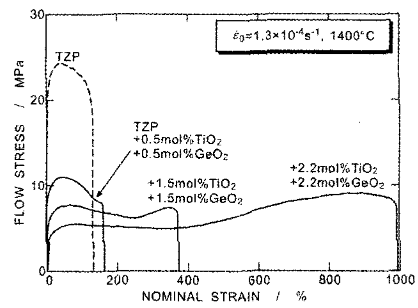

Fig. 3 Stress-strain curves in TZP and TiO_2-GeO_2 co-doped TZP at 1400°C and an initial strain rate of $1.3\times10^{-4}s^{-1}$.

segregate along the grain boundaries in TZP.[14,16,17,18] Figure 4 (a) shows a HRTEM image of a grain boundary in 1mol% TiO_2-doped TZP. The grain boundary is viewed almost at an edge-on condition. Distinct lattice images can be seen in the grains, and no amorphous layer is observed along the grain boundary. Figure 4 (b) and (c) shows the typical EDS profiles taken from the grain boundary and the grain interior region (5nm off the grain boundary) respectively in 1mol% TiO_2-doepd TZP. The EDS analysis was made using a focused probe size of about 1nm. The intensity of the Ti^{4+} spectrum at the grain boundary is much higher than that of the grain interior. This result indicates that the Ti^{4+} cations segregate along the grain boundaries. Similar results are also obtained in GeO_2-doped and TiO_2-GeO_2 co-doped TZP.[16,17]

4. DISCUSSION

The mechanism of the superplastic flow in crystalline materials has been phenomenologically analyzed by the steady-state stress-strain behavior based on the constitutive equation,

$$\dot{\varepsilon} = A\sigma^n d^{-p}\exp(-Q/RT)$$

where $\dot{\varepsilon}$ is the strain rate, σ is the flow stress, d is the grain size, n and p are the stress and grain size exponents, Q is the activation energy for plastic flow and RT is the gas constant times absolute temperature.[1] In addition, it has been pointed out that the superplastic elongation to failure ε_f in ceramics is well described by the Zener-Hollomon (ZH) parameter of $\dot{\varepsilon}\exp(Q/RT)$.[19] Since the ZH parameter is proportional to the flow stress for a constant grain size, the above description indicates that a lower flow stress provides a larger elongation to failure. This elongation-stress rule is satisfied over a fairly wide temperature and strain rate range.[19] Figure 5 shows a logarithmic plot of the elongation to failure versus converted flow stress in the present materials and in TZP obtained at 1300°C and 1500°C.[20] Here, since the flow stress depends on the grain size for a constant strain rate and temperature, the flow stress is defined as the value at the nominal strain of 10% to neglect the effect of microstructural change such as the dynamic grain growth. Moreover, in order to compare the flow stress in the present materials, the flow stress in the present materials is converted to the normalized value for a grain size of 0.38μm using $p/n=1$.[13] The slope of the line in Fig. 5 is the theoretical value of −0.66.[19] The elongation to failure roughly tends to increase with the decreasing flow stress,

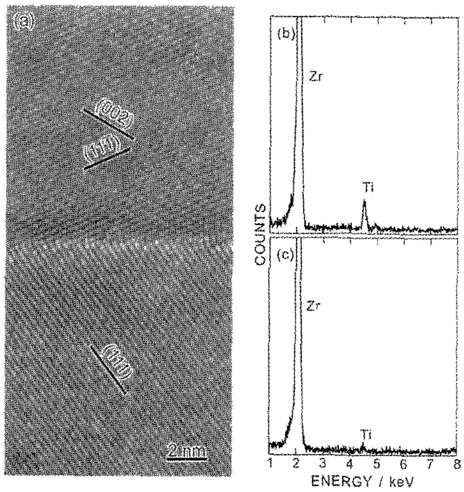

Fig. 4. (a) A high-resolution transmission electron microscopy image of a grain boundary, together with an energy- dispersive X-ray spectroscopy profiles obtained from (b) grain boundary and (c) grain interior region in 1 mol% TiO_2-doped TZP.

though the data are a little bit scattered. The improved high temperature ductility in TZP is attributed to the flow stress reduction due to TiO_2 and/or GeO_2 doping.

The doping effect on the flow stress must be attributed to the grain boundary segregation of the dopant cations. In our recent study, Ge^{4+} cations content at the grain boundaries and the grain interior regions has been investigated in 0.2-3mol% GeO_2-doped TZP by HRTEM-EDS analysis using a focused beam size of about 1nm.[16] According to the results, the Ge^{4+} content at the grain boundaries increases with the increasing amount of GeO_2 addition, but levels off over 2 mol% GeO_2 addition. The doping dependence of Ge^{4+} content at the grain boundaries is similar to that of the flow stress in GeO_2-doped TZP. The flow stress in TZP is probably dominated by the chemical composition in the grain boundaries. TiO_2 and/or GeO_2-doping is supposed to enhance the grain boundary atomic diffusion as an easy accommodation process for the superplastic flow, and consequently to decrease the flow stress in TZP.

McLean has proposed the equilibrium grain boundary solute segregation isotherm in metals:

$$C_{gb} = C_0 \exp(\Delta G_{seg}/RT)/\{1+C_0 \exp(\Delta G_{seg}/RT)\}$$

where C_{gb} is the solute concentration at the grain boundary in equilibrium with a bulk solute concentration, C_0 , and ΔG_{seg} is the change in internal energy on segregation or the segregation energy.[21] The above relationship indicates that the grain boundary segregation is proportional to the bulk solute content at a constant temperature. Grain boundary segregation amount is probably related to their solid solubility limit in TZP; the amount of the dopant cation segregation must increase with the increasing dopant addition, but level off near the solubility limit in matrix. Solid solubility limit of TiO_2 and/or GeO_2 in 3 mol% Y_2O_3-stabilized TZP has not been examined so far, but the solubility limit of TiO_2 in pure ZrO_2 was about 16 mol% at 1400°C,[22] and that of GeO_2 in 2 mol%

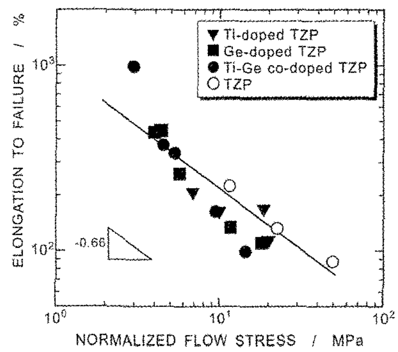

Fig. 5 A logarithmic plot of elongation to failure versus normalized flow stress in TZP and TiO_2 and/or GeO_2-doped TZP.

Y_2O_3-stabilized TZP was reported to be about 4 mol% at 1350°C.[23] The solubility of TiO_2 or GeO_2 in 3 mol% Y_2O_3-stabilized TZP is supposed to be not so different from the reported values. On the assumption that the flow stress reduction in TZP is attributed to the cation grain boundary segregation, the flow stress reduction in TiO_2 and/or GeO_2-doped TZP is consistent with the above speculation about the doping dependence of the grain boundary segregation. The sluggish change of the flow stress in TiO_2 can be explained by the relatively high solid solubility limit of TiO_2 in ZrO_2. TiO_2-doping effect on the flow stress will be saturated at the doping level more than 4 mol%.

Concerning the mechanism of the doping effect on the grain boundary atomic diffusion, it is reasonable to assume that change in chemical bonding state due to the dopant cations segregation affects the grain boundary diffusion in TZP; it has been recently reported that the grain boundary diffusion coefficient in 0.1mol% cation-doped polycrystalline Al_2O_3 is correlated well with ionicity.[24] A first-principle molecular orbital calculation was recently performed for cation-doped TZP model clusters[15] using a discrete-variational (DV)-Xα method developed by Adachi *et al.*[25] From the Mulliken population analysis, a good correlation has been found between the flow stress and the net charge products; the lower net charge products provides the lower flow stress in TZP.[15] The calculations suggest that the grain boundary segregation of Ti^{4+} and Ge^{4+} cations reduces the ionic bonding strength in the vicinity of the grain boundaries. The grain boundary atomic diffusion in TZP must be enhanced by the reduction in the ionic bond strength, and the flow stress consequently decreases in TiO_2 and/or GeO_2 doped TZP.

The present results indicate that the TiO_2 and/or GeO_2 doping effect of the high temperature plastic flow behavior in TZP is attributed to the grain boundary segregation of the dopant cations. Figure 6 shows a schematic illustration of polycrystalline oxide ceramics doped with small amount of cations. The dopant cations tend to segregate along the grain boundaries with the segregation width of less than 5 nm in oxide ceramics such as TZP and Al_2O_3.[14,16,18,26] The grain boundary segregation affects the grain boundary diffusion and the superplastic flow behavior. In other words, grain boundary nanostructure control by cation-segregation is very effective to improve the high temperature

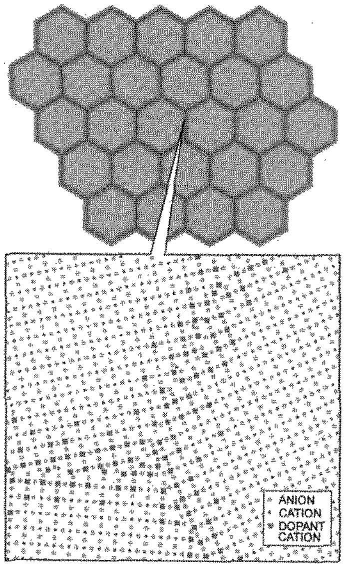

Fig. 6 A schematic illustration of TZP doped with small amount of dopant cations which tend to segregate along the grain boundaries.

mechanical properties in oxide ceramics; it is partly because the high temperature plastic flow and failure in oxide ceramics takes place mainly by grain boundary sliding which is often rate-controlled by matter transport through the grain boundaries. However, the present study is still the preliminary step toward the grain boundary atomistic structure analysis. Further quantitative investigations on the segregation behavior and chemical bonding state are necessary to elucidate the doping effect on the high temperature plastic flow behavior in superplastic ceramics, and to develop new structural ceramics based on grain boundary nanostructure control in the near future.

5. SUMMARY

The flow stress in TZP decreases with the increasing TiO_2 and/or GeO_2 doping amount, but the flow stress reduction levels off over 2 mol% doping. The improved high temperature ductility in TZP is roughly related to the flow stress reduction. The doping dependence of the flow stress is attributed to the grain boundary segregation of the dopant cations. The change in the chemical bonding state due to the grain boundary segregation is supposed to enhance the grain boundary atomic diffusion in TZP, and the flow stress consequently decreases. The present results are expected to give theoretical guidelines necessary for development of new structural ceramics by nanostructure control.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Japan Society for the Promotion of Science for the financial support by a Grant-in-Aid for Encouragement of Young Scientists. The authors also express the deepest gratitude to Professor Taketo Sakuma of Kochi University of Technology for his instructive discussions on the present work.

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(Received December 10, 2005; Accepted January 26, 2006)