A High-Strain-Rate Alumina-Based Ceramic Composite

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I. Introduction

Superplasticity refers to the ability of polycrystalline solids to exhibit greater than 100% deformation in tension at elevated temperatures. Superplasticity in ceramics generally requires a fine-grained microstructure with a grain size less than 1 μm. While a fine starting grain size and sluggish grain growth in 3Y-TZP make this material the perfect candidate for superplastic deformation, extensive dynamic grain growth and cavitation during high-temperature deformation prevents pure alumina from achieving superplasticity. High-temperature deformation of pure polycrystalline alumina is limited in both tension and compression.1–4

There is currently considerable interest in the improvement of superplasticity for shape-forming alumina-based composite materials, since alumina is the most widely used ceramic material for industrial applications. The prerequisite to achieving superplasticity in alumina-based materials, however, is to obtain a fine-grained microstructure that will be stable against coarsening during high-temperature deformation. Therefore, many attempts have been made to limit grain growth in alumina by solute segregation at grain boundaries5,6 or dispersion of second-phase particles.3 Those attempts have met with limited success. However, recently a strain of 390% with a strain rate of 1 s⁻¹ in tension was achieved for a three-phase zirconia–alumina–spinel ceramic composite at 1650 °C, a rare example of high strain rate superplasticity in ceramics. Microstructural examinations showed that the grain growth in each phase during deformation to failure was only 10% or less due to the three-phase dispersion.

In this current work, a fine grain three phase alumina–zirconia–mullite material with a similar volume fraction for each phase has been prepared by reaction processing and the creep behavior characterized under high-temperature compressive tests in air. The results showed that the three-phase strategy effectively limited the grain growth and enhanced the high-temperature deformation, indicating that the three-phase concept can be applied to make many different ceramic composites superplastic.

II. Experimental Procedure

Starting materials were a high-purity alumina powder (Baikowski Inter. Corp., Charlotte, NC), a 3 mol% yttria-stabilized tetragonal zirconia powder (Tosoh Co. Ltd., Tokyo, Japan), and silica sol (Nissan Chemical Industries Ltd., Tokyo, Japan), with starting particle sizes of 40, 26 and 15 nm, respectively. The amounts of the starting materials were calculated to make a material of alumina (40 vol%)-zirconia (30 vol%)-mullite (30 vol%) (AZ30M30) after sintering. Materials were ball milled, isostatically pressed, and then sintered at 1723 K for 1 h. Mullite forms from the reaction of silica and alumina during sintering. AZ10M10 with 10 vol% zirconia and 10 vol% mullite, and AZ15M15 with 15 vol% zirconia and 15 vol% mullite were also prepared. Bulk density of the samples was measured using the Archimedes method.

Compressive tests were carried out in air using an ATS commercial apparatus. Samples before and after deformation were polished to a 1 μm finish and then thermally etched at 1673 K for 1 h for scanning electron microscopy (SEM) (Philips XL 30FEG, Eindhoven, Netherlands). The grain size in 3D was determined to be 1.56L, where L is the average 2D grain size measured by Scionimage software. Transmission electron microscopy was conducted on a Philips CM20, Eindhoven, Netherlands. Crystalline phases were identified by X-ray diffraction (XRD) with CuKα radiation.

III. Results and Discussion

Backscattered electron images of the sintered and deformed AZ30M30 are shown in Fig. 1. Zirconia grains appear white, alumina grains are gray, and mullite grains are dark gray (Fig. 1(c)). No large pockets of silica were found at grain junctions. Energy-dispersive spectroscopy showed that the black areas marked by arrows in Fig. 1(a) are not silica-rich regions. Since there were fewer such areas in the deformed samples (Figs. 1(b) and (c)), these regions are most likely small voids that densified under compression. The amount of silica originally added (5.9 wt%) is similar to Zhao et al.’s study of 5 wt% SiO₂-doped 3Y-TZP, where SEM observations clearly showed the large SiO₂ pockets at grain boundary junctions. TEM studies also did not find large SiO₂ pockets at junctions in the present material. The absence of large pockets of SiO₂ indicates that the silica has reacted with alumina and formed mullite. The formation of mullite and no other reaction phases was also verified by XRD.

The grains in the sintered sample are primarily equiaxed. Mullite in silica-rich environments develops an elongated and short-fiber-like morphology, but mullite in alumina-rich environments is usually equiaxed.3,5 The average grain size for alumina and mullite was 0.39 μm before deformation and 0.42 μm after 100% deformation under 30 MPa at 1700 K. The average grain size for zirconia before and after deformation was almost the same within the experiment error, 0.23 μm. The density measured from the Archimedes method was 95% theoretical density before deformation and close to theoretical density after 100% deformation. No cavitation was found in either the plane...
normal to the compressive axis or the plane parallel to the compressive axis.

Figure 2 shows a typical true strain rate versus true strain graph obtained at 1700 K and 30 MPa for the samples of AZ10M10, AZ15M15, and AZ30M30. All three samples experienced primary creep. AZ30M30, with a similar volume for each phase, exhibited a constant strain rate after primary creep, which indicates that there is almost no grain growth under constant-stress deformation. Any increase in the grain size would decrease the strain rate according to the following semi-empirical equation:

\[ \dot{\varepsilon} = A \sigma^n \exp \left( \frac{-Q}{RT} \right) \]  

(1)

where \( \dot{\varepsilon} \) is the strain rate, \( A \) is a constant, \( \sigma \) is the flow stress, \( n \) is the stress exponent, \( d \) is the grain size, \( p \) is the grain size exponent, \( Q \) is the activation energy, \( R \) is the gas constant, and \( T \) is the absolute temperature.

Figure 3 plots the relationship between flow stress and strain rate for AZ30M30 at temperatures ranging from 1673 to 1773 K. The plot yields a stress exponent \( n \) of appropriately 2. This value of \( n \) is broadly consistent with the values reported in previous studies on alumina materials, including high-purity alumina, high-purity alumina with tracer zirconia, and alumina–zirconia composites. Kim et al. also reported a value of 2.2 for the alumina material codispersed by 10 vol% zirconia and 10 vol% spinel particles.

Mullite is a well-known creep-resistant material. Codispersion of mullite could be expected to increase the flow stress and lower the strain rate. But the strain rate of AZ15M15 and AZ30M30 with mullite is more than twice that of AZ30. This increase of strain rate by the co-dispersion of mullite could be explained by several reasons. First, the grain shape of single-phase mullite usually develops an elongated fiber-like morphology. The interlock of elongated grains can hinder the grain boundary sliding and decrease the strain rate, but elongated mullite grains were not observed here. Second, the tri-phase structure limits grain growth and creates new interfaces that do not exist in alumina–zirconia composites. The new interfaces may have different grain boundary mobilities. Lastly, a small amount of unreacted silica could remain at the multiple grain
was found to increase with a higher volume percent of mullite.18 Previous work, the activation energy for AZ30 and AZ15M15 compression at 1650°C was determined and contained 10–20 vol% glass. 

The calculated activation energy of AZ30M30 has an average value of 880 kJ/mol in Fig. 4, much higher than that of pure alumina (about 450 kJ/mol)12,15 and that of alumina–zirconia composites (600–700 kJ/mol).4,18,19 The higher activation energy of AZ30M30 is probably due to the codispersion of creep-resistant mullite. The activation energy for mullite has been reported to be as high as about 1000 kJ/mol.8,20 In the authors’ previous work, the activation energy for AZ30 and AZ15M15 was found to increase with a higher volume percent of mullite.18 A similar increase of activation energy with higher mullite concentration was also observed in zirconia–mullite composites.9 Wolf et al.21 studied the creep behavior of high-alumina refractories containing different amounts of a fused mullite–zirconia aggregate of eutectic composition and reported a similar value of the activation energy, although that material was large grained and contained 10–20 vol% glass.

In this current work, a strain rate as high as 0.013 s⁻¹ has been achieved under a compressive stress of 60 MPa and at 1500°C. The strain rate of 0.01 s⁻¹ is characteristic of high-strain-rate superplasticity in ceramics. Extrapolating the strain rate against the absolute temperature, the true strain rate under stress concentrations, thus promoting grain boundary sliding. Junctions or segregate along grain boundaries and minimize the stress concentrations, thus promoting grain boundary sliding.

Fig. 5. Extrapolated strain rate for AZ30M30 at 16500°C and 50MPa. Solid squares are experimental data; open square is extrapolated.

In conclusion, a submicron grain size alumina-based ceramic codispersed with 30 vol% zirconia and 30 vol% mullite (AZ30M30) was synthesized and deformed under compression to 100% strain, demonstrating a constant strain rate and minimal grain growth. Constant stress compressive creep behavior showed a stress exponent of 2 and a high activation energy of 880 kJ/mol due to the dispersion of mullite. A strain rate of 0.013 s⁻¹ was achieved at 60MPa and at 1500°C, indicating the potential for high-strain-rate superplasticity.

IV. Conclusions

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References