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Microstructure and superplastic behavior of TiO_2-doped Al_2O_3–ZrO_2 (3Y) composite ceramics

Chen Guoqing[a,*], Zu Yufei[a], Luo Junting[b], Fu Xuesong[a], Zhou Wenlong[a]

[a] School of Materials Science and Engineering, Dalian University of Technology, Dalian 116085, PR China
[b] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, PR China

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ABSTRACT

Compression deformation behavior and mechanism of as-sintered Al_2O_3–ZrO_2 (3Y) composite ceramics doped with four different amounts of TiO_2 (0, 1, 4, and 8 wt.%, designated as 0T, 1T, 4T, and 8T) were systematically investigated in this work. It was found out that the strain rate significantly increased by doping TiO_2 addition. The stress-jump deformation data showed that the strain rate of 8T was about two orders of magnitude higher than that of the undoped ceramic under the same flow stress. Then, the microstructures were examined. After deformation, texture was developed but its intensity decreases with increasing TiO_2 concentration. Moreover, liquid phases (about 50–100 nm) were observed along the edge facets and at the junction pockets in deformed 4T and 8T specimens. Based on the microstructural features and deformation behavior, it is suggested that for 0T and 1T, the deformation mechanism was texture-controlled grain boundary sliding accompanied by diffusion; for 4T and 8T, it was grain boundary sliding accompanied by the liquid phases.

1. Introduction

Ceramics are structural materials with extensive applications owing to their excellent mechanical properties, such as low density, high strength, high hardness, and high-temperature performance. In recent years, superplastic flow was expected to be used for fabricating ceramic parts with complex shapes. However, due to the low strain rate and high temperature during deformation, reducing the production cost and improving the efficiency are the key issues for the industrial applications of superplastic ceramics. Thus, the development of superplastic deformation in ceramics at high strain rate and low temperature is required.

Attempts to improve the superplasticity in ceramics have been made using dopants such as SiO_2 [1,2], CuO_2 [3], and TiO_2–GeO_2 [4]. Doping the different cations can influence diffusion, grain growth, and stress concentration during deformation [5]. Sakka et al. [6,7] doped Al_2O_3 + MnO_4 and TiO_2 + MnO_2 in ZrO_2 to obtain a homogeneous microstructure, and failure elongations of 608% and 280% are obtained, respectively. Morita et al. [8] reported the tensile deformation of ZrO_2 doped with 30% spinel at 1350–1550 °C, and the largest elongation of 660% is achieved at 1550 °C and a strain rate of 0.02 s^{-1}. The addition of SiO_2 [1] and Al_2O_3 [9] to ZrO_2 as dopants to improve superplasticity results in ~500% and ~1000% elongation at ~1450 °C, respectively. The enhancement of ductility is due to the diffusion improvement and grain growth limitation by intergranular phases via the addition of dopants such as MgO_2, SiO_2, and Al_2O_3. Recently, TiO_2 dopants in ZrO_2 have been found to improve the ductility significantly [10,11]. However, TiO_2 addition reportedly promotes grain growth. The tensile ductility in ZrO_2 is enhanced and the flow stresses decrease with TiO_2 addition, although the resultant grain size is larger than that of undoped ZrO_2. The failure elongation of ZrO_2 (8Y) increases from ~10% to ~200% by doping with TiO_2 [10,11]. Yoshida et al. [4] doped 2.2 mol.% TiO_2–GeO_2 in ZrO_2 (3Y) and obtained a large elongation of 1053%. Xue and Chen [12] studied the benefit of (Ti, Mn) charge-compensating dopants in enhancing diffusion in deformation processes, and found that Ti/Mn co-doped Al_2O_3 with 3 mol.% ZrO_2 has excellent superplastic formability. This material can be shape formed under biaxial tension to 100% strain at temperature as low as 1280 °C [12].

Superplastic tensile and compression deformation behaviors in Al_2O_3–ZrO_2 composite were investigated by many researchers [13,14] because the composite has extensive applications owing to its excellent mechanical properties. In 1989, Wakai and Kato [15] reported that Al_2O_3–ZrO_2 ceramic has superplastic ability, and its elongation is about 200% during deformation at 1450 °C. For the Al_2O_3–ZrO_2 ceramic doped with the spinel, a large tensile elongation to failure is attained at significantly high strain rates. The elongation at 1650 °C exceeds 2500% at an initial strain rate of 0.08 s^{-1} and 390% at 1.0 s^{-1} [16,17].

* Corresponding author. Tel.: +86 411 84707970; fax: +86 411 84709967.
E-mail address: gqchen@dlut.edu.cn (G.Q. Chen).

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The deformation parameters in superplastic ceramics are calculated by the following constitutive equation:

$$\dot{\varepsilon} = A\sigma^n d^{-p} \exp\left(-\frac{Q}{RT}\right) \quad (1)$$

where $\dot{\varepsilon}$ is the strain rate, A is a constant, σ 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.

Ghosh et al. [18] investigated the superplastic behavior of ZrO_2 doped with SiO_2, and believed that the deformation mechanism is Coble diffusion creep at high stress and interface-controlled Coble diffusion creep at low stress. Sharif and Mecartney [19] studied the superplasticity of 10 wt.% Al_2O_3–ZrO_2 ceramics, in which the static grain growth is prevented by the binary composite. The stress exponent, about 2 in this material, indicates that the main deformation mechanism is grain boundary sliding accompanied by diffusional creep. Jimenen-Melendo et al. [20,21] and Dominguez-Rodriguez et al. [22] studied the superplastic deformation in Y-TZP, and believed that the deformation mechanism is grain boundary sliding accompanied by a threshold stress for intragranular dislocation nucleation. Morita et al. [8] agreed with this mechanism and demonstrated that the deformation rate is controlled by the rate of dislocation recovery. Although there is no unambiguous superplastic mechanism accepted for ceramics, grain boundary sliding is generally considered the dominant deformation mechanism in fine-grained ceramics [8]. To attain high strain rate superplasticity, grain growth, stress concentration, cavity nucleation, cavity growth, and cracking should be eliminated. Thus, some accommodation mechanisms are needed to accompany the deformation, such as diffusional creep, dislocation motion, solution-precipitation, second phases, liquid phases, and so on [23].

Al_2O_3–ZrO_2 (3Y) ceramic doped with TiO_2 has excellent mechanical properties and good superplastic deformability. However, the deformation behavior and mechanism of this material have not yet been investigated and thus remain unclear. The present paper studied the superplastic behavior and mechanism of Al_2O_3–ZrO_2 (3Y) ceramics doped with different amounts of TiO_2 to clarify the effect of TiO_2 dopants on deformation.

2. Experimental materials and methods

The preparation of the TiO_2-doped Al_2O_3–ZrO_2 (3Y) composite ceramic was as follows. Al_2O_3–ZrO_2 (3Y) powders were synthesized at a mass ratio of 58:42 by heating ethanol–aqueous salt solutions [24]. The powders were then calcined in air at 1100 °C for 2 h. Rutile TiO_2 was doped in as-calcined Al_2O_3–ZrO_2 (3Y) powders by electromagnetic stirring and ultrasonic wave shaking. TiO_2 used in this study had >99.8% purity. The average particles sizes of the Al_2O_3–ZrO_2 (3Y) and TiO_2 powders were 30 and 80 nm, respectively. The amounts of TiO_2 added to the composite powders were 0, 1, 4, and 8 wt.%, designated as 0T, 1T, 4T, and 8T, respectively. The composite powders were sintered at 1400 °C, 65 MPa applied pressure, and 6 min holding time in a Spark Plasma Sintering Furnace (SPS-3.20MK-IV, Sumitomo Coal Mining Co., Ltd., Japan).

The as-sintered cylindrical specimens with densities greater than 98% of the theoretical value were used in compression deformation. The densities were measured by the Archimedes method. The uniaxial compression deformation with a constant velocity was conducted in a vacuum using an ultrahigh temperature tensile testing machine. The deformation mould was made of a high-strength tungsten alloy. When the temperature reached the deformation value, the specimens were kept at the set temperature for 10 min before compressive testing. The temperature during deformation was measured using a platinum–rhodium thermocouple. The stress-jump deformation test was conducted to evaluate the deformation characteristics using a spark plasma sintering furnace. The temperature of the ceramics during the deformation was measured with an infrared radiation thermometer. The parameters, including the initial height H_0 and the initial end face area A_0, were directly measured. The load P and the immediate height H_x at every second were recorded by the system. The true compressive strain ε, the true stress σ, and the strain rate $\dot{\varepsilon}$ of the specimens were expressed as follows:

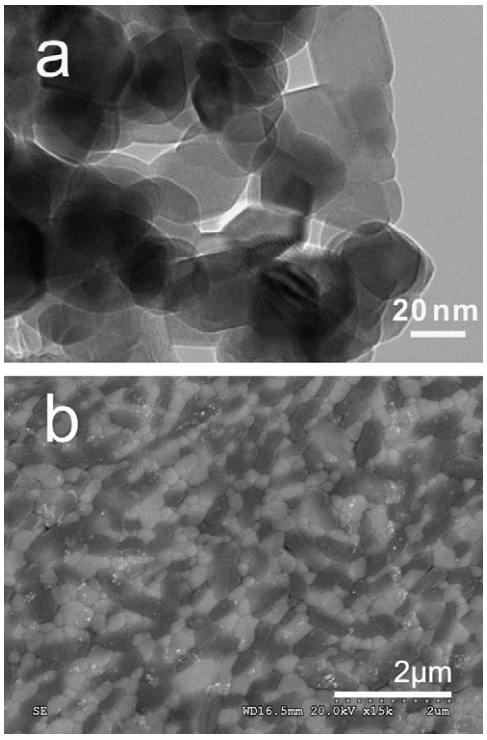

Fig. 1. TEM morphology (a) of nano-sized powders and SEM morphology (b) of as-sintered undoped Al_2O_3–ZrO_2 (3Y) ceramic.

$$\varepsilon = -\ln\left(\frac{H_x}{H_0}\right) \quad (2)$$

$$\sigma = \frac{PH_x}{A_0H_0} \quad (3)$$

$$\dot{\varepsilon} = \frac{H_x - H_{x-1}}{H_x}. \quad (4)$$

The phases in the composite were analyzed using an X-ray diffraction (XRD) system (XRD-6000, Shimadzu Corporation, Japan). The microstructure was characterized by a scanning electron microscopy (SEM) system (S-4300, Hitachi, Japan). The SEM specimens were polished with a diamond paste of 1.5 μm and then thermally etched in air for 1 h at a temperature 50 °C lower than the sintering and/or deformation temperature of each specimen. The average grain sizes of the two phases were calculated using the linear intercept method: $d = 1.56L$, where L is the intercept length.

3. Results and discussion

3.1. Powders and as-sintered ceramic of undoped Al_2O_3–ZrO_2 (3Y) composite

Fig. 1a shows the TEM morphology of the Al_2O_3–ZrO_2 (3Y) nano-sized powders made by using the method of the heating ethanol–aqueous salt solutions. The powders are mixed well without observable agglomeration. The powder sizes are relatively uniform with an average particle size of 30 nm and a specific