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Research Article

Grain Boundary Resistivity of Yttria-Stabilized Zirconia at 1400°C

J. Wang,[1] A. Du,[2] Di Yang,[1] R. Raj,[3] and H. Conrad[1]

[1] *Materials Science and Engineering Department, North Carolina State University, Raleigh, NC 27695-7907, USA*
[2] *Materials and Metallurgy Department, Kunming University of Science and Technology, Kunming, Yunnan 650093, China*
[3] *Department of Mechanical Engineering, Engineering Center, ECME 114, University of Colorado, Boulder, CO 80309-0427, USA*

Correspondence should be addressed to H. Conrad; hans_conrad@ncsu.edu

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The grain size dependence of the bulk resistivity of 3 mol% yttria-stabilized zirconia at 1400°C was determined from the effect of a dc electric field $E_a = 18.1$ V/cm on grain growth and the corresponding electric current during isothermal annealing tests. Employing the brick layer model, the present annealing test results were in accordance with extrapolations of the values obtained at lower temperature employing impedance spectroscopy and 4-point-probe dc. The combined values give that the magnitude of the grain boundary resistivity $\rho_b = 133$ ohm-cm. The electric field across the grain boundary width was 28–43 times the applied field for the grain size and current ranges in the present annealing test.

1. Introduction

In view of its high ionic conductivity, polycrystalline yttria-stabilized zirconia (YSZ) is attractive for application in solid oxide fuel cells (SOFCs) and sensors [1, 2]. The conductivity however, decreases with decrease in grain size d [1–3], which is attributed to the greater resistivity of the grain boundaries compared to that of the grain interior.

The grain boundary resistivity in ceramics is usually determined employing impedance spectroscopy, which along with the cubic brick layer model of the grain microstructure gives for the bulk resistivity ρ at constant temperature [4–7]

$$\rho = \rho_g + \rho_b^* = \rho_g + \frac{\rho_b \delta_b}{d}, \quad (1)$$

where ρ_g is the resistivity of the grain interior, ρ_b^* *the contribution of the grain boundaries* to the *bulk resistivity*, d the grain size, ρ_b the actual grain boundary resistivity (the so-called "specific grain boundary resistivity"), and δ_b (= 1–10 nm) the grain boundary width including the space charge zone. An important feature of impedance spectroscopy is that it provides a measure of both the bulk resistivity and the grain boundary contribution. Employing this technique along with (1) has given values of ρ_b that are one-to-three orders of magnitude greater than those of ρ_g [1–3].

Impedance spectroscopy measurements on YSZ are difficult to perform at high temperatures and have been limited for the most part to temperatures below ~1000°C. In this paper, we will present a method for determining ρ_b at higher temperatures. The method is based on measuring the grain size and concurrent electric current in isothermal annealing tests with a dc applied electric field. The method also provides the magnitude of the electric field acting across the grain boundary width.

2. Experimental

Test specimens were prepared from 3 mol% yttria-stabilized zirconia (3Y-TZP) powder purchased from Tosoh, having initial grain size $d_0 = 26$ nm and the following chemical composition in wt% (see Table 1).

The as-received powder was cold-compacted (98 MPa) in a stainless steel die having a dog-bone-shaped cavity. The binder was removed by heating the compacted powder in air to 800°C in 72 hr and then holding at this temperature for 1 hr. Following binder burnout, the lower tab of the specimen was cutoff giving the geometry shown in Figure 1, which was then

Table 1

Y_2O_3	Al_2O_3	SiO_2	Fe_2O_3	Na_2O	I_g loss	ZrO_2
5.21	<0.005	0.005	0.002	0.022	0.73	Remainder

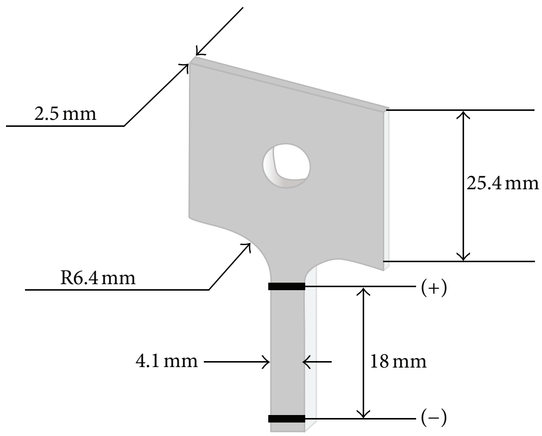

Figure 1: Schematic of test specimens geometry and the electric connections.

sintered by heating in air at a rate of 11°C/min to 1400 ± 1°C both without and with a constant dc voltage $V = 25 \pm 0.1$ V. The sintered specimens were then directly annealed at this temperature for various times without and with the applied dc electric field, the magnitude of which due to the sintering shrinkage had increased from 13.9 to 18.1 V/cm. The relative density ρ_r at the beginning and throughout the isothermal annealing was determined from measurements of the length change due to the shrinkage of the specimen during sintering and subsequent annealing.

The electric field was applied to the specimen by wrapping fine Pt wire (0.13 mm dia.) around each end of the gage section as shown in Figure 1. Along with the voltage, the electric current I during the anneal was measured to an accuracy of 1 mA. The corresponding current density j was determined by taking

$$j = \frac{I}{A_j} = \frac{I}{\left[A_0(1+\epsilon)^2\rho_r\right]}, \quad (2)$$

where A_j is the effective cross-section area for the current passage, A_0 is the specimen cross-section area following bake-out, the quantity $(1+\epsilon)$ is the reduction due to shrinkage with ϵ the relative longitudinal contraction, and ρ_r accounts for the reduction in cross-section area due to the porosity.

The magnitude of Joule heating ΔT_J during the annealing with electric field was estimated from the relationship which considers the heat loss by black body radiation, namely [8],

$$\frac{\Delta T_J}{T} = \frac{W_j}{(4A_S\sigma T^4)}, \quad (3)$$

where W_j is the electric energy in watts, $A_S = 8.7 \times 10^{-5}$ m^2 is the surface area of the specimen between the electrodes, and $\sigma = 5.67 \times 10^{-8}$ W m^{-2} K^{-4} is the Stefan-Boltzmann

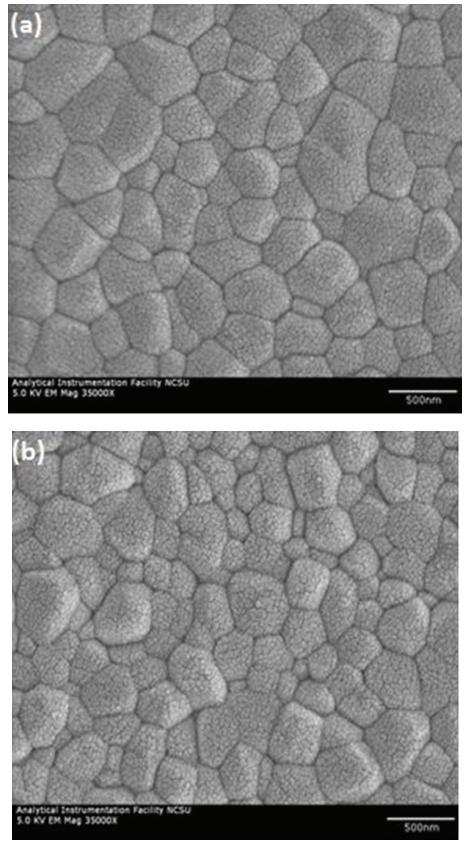

Figure 2: SEM micrographs taken at the middle location of specimens annealed 12 hr at 1400°C: (a) $E = 0$ and (b) $E_a = 18.1$ V/cm.

constant. Taking $W_j = 5$ watts at $t_a \approx 0$ hr and 8.3 watts at $t_a \approx 12$ hr ($V = 25$ V, with $I = 0.22$ A and 0.33 A, resp.), (2) gives $\Delta T_J = 54$ K and 89 K, respectively, which are ~3% and ~5% of the 1673 K annealing temperature. In view of the heat loss by conduction from the region between the electrodes to the specimen tab (see Figure 1) and by conduction and convection to the surrounding air, it is expected that ΔT_J will be appreciably less than that given by (3). A temperature rise of only ~5°C was measured by a Pt-PtRh thermocouple contacting the midsection between the two electrodes.

Following each scheduled annealing time the specimen was furnace-cooled to room temperature. To determine the grain size, cross-sections were taken at three locations: (a) ~5 mm below the upper positive (+) electrode, (b) midway between the two electrodes, and (c) ~5 mm above the lower negative (−) electrode. The cross-sections were mechanically polished, thermally etched (1 hr at 1200°C), and observed by scanning electron microscopy (SEM). An example of the microstructure without and with field is shown in Figure 2. Approximately 200 linear intercept measurements with a resolution of 5 nm were made on each of the three SEM micrographs for a specific annealing time, giving a total of ~600 measurements for each annealing time. The reported grain size is the mean linear intercept value $\bar{d}$ for the combined three locations.

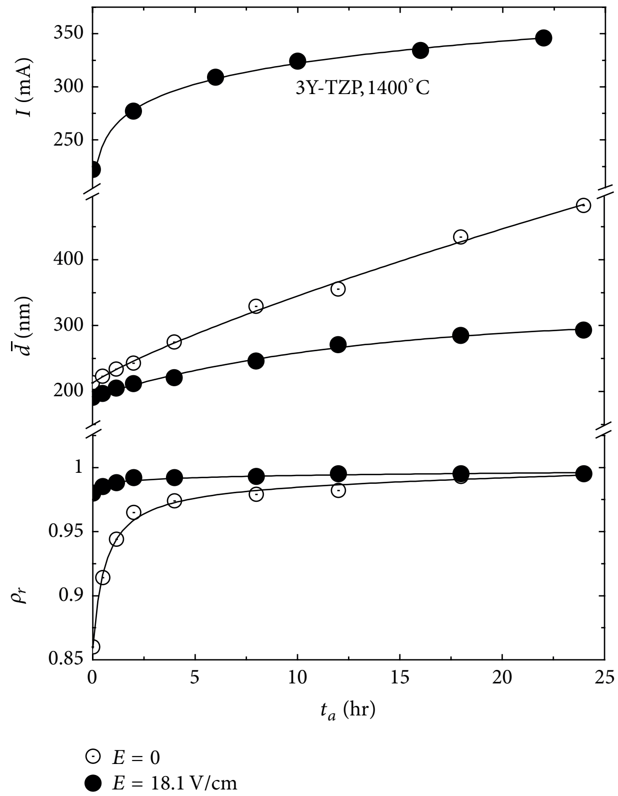

FIGURE 3: Relative density ρ_r, mean linear intercept grain size $\bar{d}$, and corresponding electric current I versus time t_a for annealing 3Y-TZP without and with an externally applied electric field $E = 18.1$ V/cm.

3. Results and Analysis

Figure 3 presents the mean linear intercept grain size $\bar{d}$ for the combined (three) locations along the gage section versus the annealing time t_a for the tests both without and with the applied electric field E_a. The variation in $\bar{d}$ between the three locations was within 10%. There was however no consistent variation from top to bottom (positive to negative electrode). To be noted in Figure 3 is that the grain growth curves are parabolic in shape and that the curve for annealing with field lies below that without, that is, the field retarded grain growth throughout the annealing. Included in Figure 3 are the corresponding relative density ρ_r (= measured density divided by 6.03 g/cm^3) and the electric current I as a function of the annealing time. The form of the I versus t_a curve is also parabolic. Without field ρ_r increases from 86% to 97% within 2 hrs and then increases more gradually to 99.5% at 24 hr. With field ρ_r increases gradually from 98.0% to 99.5% over the 24 hr period.

In keeping with (1) a plot of the bulk resistivity $\rho = E_a/j$ (j calculated employing (2)) versus the reciprocal of the three-dimensional average grain size d_{3D} (= 1.78 $\bar{d}$ for tetrakaidecahedron [9]) for the present tests is given in Figure 4. Included for comparison are extrapolated values from Arrhenius plots of the resistivity ρ for 3Y-TZP polycrystals obtained by impedance spectroscopy (IS) [10–12] at lower temperatures (from maximum temperatures of ~1323 K, ~833 K, and ~773 K, resp.) and 4-point-probe dc measurements [13] (from maximum temperature ~1253 K). Also included in Figure 4 are the range and the average values of ρ ($\equiv \rho_g$) for YSZ single crystals with 4–10 mol% yttria employing both 4-point-probe [14, 15] and IS [14, 16, 17] methods. To be noted in Figure 4 is that there exists reasonable agreement between the present results for the bulk resistivity of polycrystalline 3 Y-TZP and those obtained by IS and conventional 4-point-probe methods. Moreover, the combined results give a reasonable fit to a straight line whose intercept is in accordance with the value of ρ ($\equiv \rho_g$) for single crystals. The least-squares values of the intercept and slope of the straight line for the combined measurements on polycrystals are 0.51 (ohm-cm) and 1.33 (ohm-cm) (μm), respectively, with a correlation coefficient of 0.96.

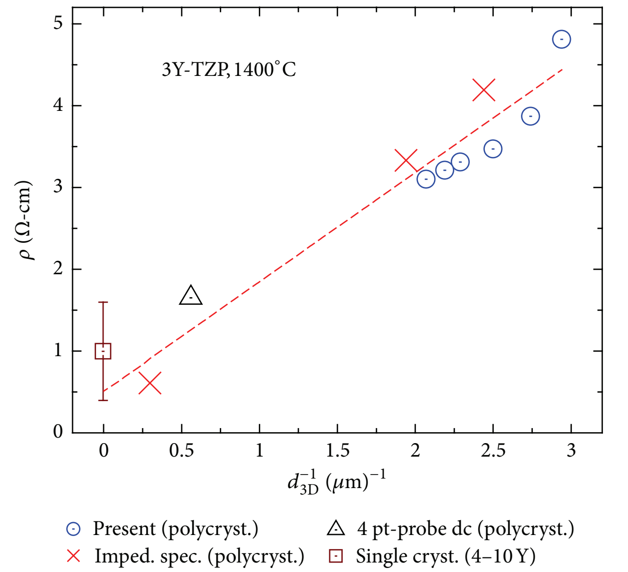

FIGURE 4: Bulk resistivity ρ versus the reciprocal of the 3D grain size d_{3D} for present results, impedance spectroscopy measurements [10–12], and 4-point-probe dc measurements [13] on polycrystals and impedance spectroscopy [14, 16, 17] and 4-point-probe measurements [14, 15] on single crystals.

According to (1) the slope of the line in Figure 4 equals the product $\rho_b\delta_b$. Taking $\delta_b = 10$ nm (based on the segregation of yttria to the grain boundaries [18]) gives $\rho_b = 133$ ohm-cm. Further, taking $\rho_g = 0.51$ ohm-cm gives for the ratio of the grain boundary resistivity to that in the grain interior $\rho_b/\rho_g = 261$, which again is in accordance with that reported for impedance spectroscopy measurements [1–3].

Knowing the magnitudes of j and ρ_b one can calculate the value of the electric field E_b across the grain boundary width by employing the conventional relation

$$E_b = \rho_b j. \tag{4}$$

Taking $\rho_b = 133$ ohm-cm and the values of j determined from the measured values of the current I, one obtains the magnitude of E_b and the ratio E_b/E_a as a function of grain size presented in Figure 5. The magnitudes of E_b and in turn the ratio E_b/E_a increase from 497 V/cm to 771 V/cm and from 27.5 to 42.6, respectively, with increase in d_{3D} from 0.340 to

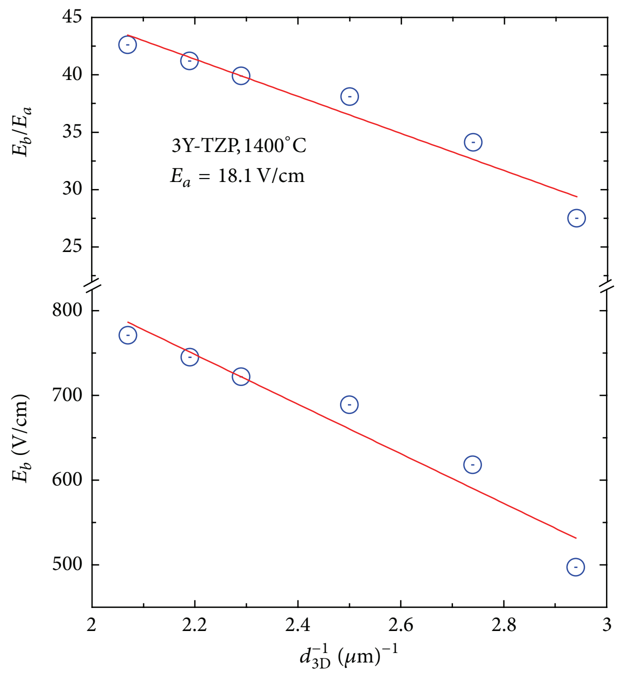

FIGURE 5: Electric field across the grain boundary width E_b and the ratio E_b/E_a versus d_{3D}^{-1} for the present tests.

0.483 μm with E_a = 18.1 V/cm and the corresponding values of the electric current.

4. Summary and Conclusions

The bulk resistivity ρ of 3 mol% yttria-stabilized zirconia polycrystals (3Y-TZP) was determined from the effect of an applied dc field on grain growth and the corresponding electric current in isothermal annealing tests at 1400°C. Employing the brick layer model, the results give for the magnitude of the grain boundary resistivity ρ_b = 133 Ω-cm, which in turn gives that the electric field across the grain boundary width $E_b \approx$ 28–43 times that of the applied electric field for the present test conditions. These values of ρ and ρ_b are in reasonable accordance with values obtained by impedance spectroscopy at lower temperatures.

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