Contribution of the space charge to the grain boundary energy in yttria-stabilized zirconia

Jun Wang · Hans Conrad

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Abstract A model based on the effect of a modest applied dc electric field on grain growth is proposed for the contribution of the space charge to the grain boundary (GB) energy in 3 mol % yttria-stabilized zirconia (3 YSZ). The model considers that the total GB energy γ_b^0 (the capillary driving force for grain growth) consists of three major components: (a) γ_b^z due to the misorientation between neighboring grains, (b) γ_b^s due to the size misfit between the segregated solute and the solvent cations, and (c) γ_b^e the electrostatic (space charge) component, which results from the segregation of the aliovalent yttrium ions to the grain boundaries. The former two components combined comprise 40 % of the total GB energy in 3 YSZ and the electrostatic component 60 %. Based on the model, the calculated magnitudes of the three components were in qualitative accord with theoretical considerations and with values reported in the literature. A reduction in γ_b^e , and in turn in γ_b^0 , results from the bias exerted by the applied field on the space charge potential that occurs with the segregation of the yttrium ions to the grain boundaries. The observed reduction of grain growth in 3 YSZ by an applied electric field is attributed mainly to the reduction in γ_b^e by the field.

Introduction

It is well-known that grain size (GS) is an important microstructure parameter in the processing and properties of ceramics [1]. It was discovered by Yang and Conrad [2]

and subsequently confirmed by Ghosh et al. [3] that a modest applied dc electric field retards grain growth in 3 mol % yttria-stabilized zirconia (3 YSZ). Subsequent work by Conrad and Yang [4, 5] established that the retarding effect increased with field strength up to ~ 26 V/cm and then remained essentially constant to ~ 60 V/cm, the effect being similar in the processing methods of sintering, annealing, and plastic deformation; see Fig. 1. Furthermore, the retarding effect by the field during sintering was found to be relatively independent of the relative density and in turn of the temperature and porosity. Based on these characteristics, it was proposed [4, 5] that the retardation of grain growth in 3 YSZ by an electric field results mainly from a reduction in the capillary driving force (namely, the grain boundary (GB) energy) by the interaction of the field with the space charge at the grain boundaries. Stereology studies gave that the field had no detectable influence on the grain shape, nor on the GS distribution [6, 7]. In this article, we develop a model for the retardation of grain growth in 3 YSZ by an electric field and perform isothermal annealing tests on 3 mol % yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) at 1300 and 1400 °C to ascertain its validity.

The model

It was now well-established that yttria segregates to the grain boundaries in polycrystalline yttria-stabilized zirconia (YSZ) [8–16]. A major factor proposed to be responsible for the segregation is the GB space charge. In view of the segregation, it is generally considered that the mechanism governing the grain growth rate in YSZ is “solute drag” [16]. Theoretical considerations give for this mechanism [17, 18]

J. Wang · H. Conrad (✉)
Materials Science and Engineering Department, North Carolina
State University, Raleigh, NC 27695-7907, USA
e-mail: hans_conrad@ncsu.edu

Fig. 1 The effect of applied dc electric field strength on the ratio of the grain size with field (d_E) to that without (d) for various processing conditions. From Conrad and Di Yang [4]

$$\dot{d} = P^m M = \frac{A}{k_B T} \left(\frac{\gamma_b^0}{r} \right)^m D \quad (1)$$

where $\dot{d}$ is the grain growth rate, and $P = \gamma_b^0/r$ is the capillary driving force, with γ_b^0 the GB energy and $r = \alpha d$ ($\alpha \approx 0.5$) the average GB radius of curvature. M is the GB mobility, A is a constant, D is the diffusion coefficient of the rate-controlling ion, k_B is the Boltzmann's constant, and m is the driving force exponent, which is given by the slope of a plot of $\log \dot{d}$ vs. $\log P$ at a constant temperature. The parameter “ m ” depends on solute content and thus may vary with P or $\dot{d}$. Employing Eq. 1, and assuming that a major effect of an applied electric field E on $\dot{d}$ is through a reduction in γ_b^0 [4, 5], and dividing the grain growth rate $\dot{d}_E$ with an applied field by that without ($\dot{d}$), one obtains

$$\frac{\dot{d}_E}{\dot{d}} = \frac{\frac{A E D_E}{k_B T} \left[\frac{(\gamma_b^0 - \Delta \gamma_b^E)}{d_E} \right]^{m_E}}{\frac{A D}{k_B T} \left[\frac{\gamma_b^0}{d} \right]^m} \quad (2)$$

where $\Delta \gamma_b^E$ is the reduction in γ_b^0 by the applied field E . The subscript E in Eq. 2 refers to the parameter with applied field, its absence without field. In prior work [4, 5, 19], it was found that the parameters A , D , and m are relatively independent of E . Rearranging Eq. 2 then gives for a constant temperature

$$\Delta \gamma_b^E \cong [1 - (\dot{d}_E/\dot{d})^{1/m} (d_E/d)] \gamma_b^0 \quad (3)$$

The magnitude of $\Delta \gamma_b^E$ as a function of E at a constant T can then be obtained experimentally from a knowledge of γ_b^0 and the effect of E on the GS ratio d_E/d at a constant grain growth rate $\dot{d}$, which then avoids the need to know the magnitude of the parameter m .

In our model, we take that γ_b^0 in YSZ consists of the sum of three major components (see Fig. 2), namely

Fig. 2 Schematic of a large angle grain boundary in an ionic ceramic (MgO) illustrating the three major contributions to the grain boundary energy. Dark shaded atoms are aliovalent solutes

$$\gamma_b^0 = \gamma_b^c + \gamma_b^s + \gamma_b^e \quad (4)$$

where γ_b^c results from the crystallographic misorientation between contacting grains, γ_b^s from the ionic size misfit between the solute (yttrium) and solvent (zirconium) ions and γ_b^e is the electrostatic (space charge) component, which results from the segregated, aliovalent yttrium ions at the GB.

A rough, theoretical estimate of γ_b^c is [20]

$$\gamma_b^c = \lambda_b^c k_B T / \Omega \quad (\text{J/m}^2) \quad (5)$$

where λ_b^c is the width of the GB core, Ω is the atomic volume of the host lattice, and k_B is Boltzmann's constant.

Regarding the solute ion size misfit component, estimates of the elastic strain energy U [9, 21] based on considerations by Eshelby [22, 23] are shown in Table 1; included are the calculated magnitudes of U for 3Y-TZP. Taking into account, the number of solute ions in the GB core width one obtains for the size misfit energy per unit GB area

$$\gamma_b^s \approx U \lambda_b^c C_b^* / \Omega \quad (\text{J/m}^2) \quad (6)$$

where C_b^* is the solute ion concentration segregated at the core.

Table 1 Estimates of the ionic size misfit energy U in yttria-stabilized zirconia

Authors	Equation	Ref.	U (10^{-21} N m)
Yan et al. [21]	$U = \frac{6\pi r_1^3 (2-\nu)^2 B}{(1+3B/4\mu)}$	Eshelby [22]	5.7
Hwang and Chen [9]	$U = \frac{2}{9} \mu \Omega \left[\frac{(1+\nu)}{(1-\nu)} \right] \Gamma^2$	Eshelby [23]	6.9
		Avg.	6.3

μ = shear modulus (80 GPa), B = bulk modulus (174 GPa), ν = Poisson's ratio (0.3), r_1 = ionic radius of the host (0.084 nm), r_2 = ionic radius of the solute (0.102 nm), Γ = Vegards slope for volume misfit (0.077), Ω = molecular volume (3.5×10^{-29} m³)

Regarding the electrostatic component of the GB energy, the number of *excess* (compared to the lattice) segregated aliovalent solute ions per unit GB area is

$$N_b^s = \delta_b \overline{\Delta C_b} / \Omega \quad (\text{m})^{-2} \quad (7)$$

where $\overline{\Delta C_b}$ is the integrated average *excess* segregated solute concentration. The corresponding electrostatic energy per unit GB area is then

$$\gamma_b^e = N_b^s Z^* e \phi = \delta_b \overline{\Delta C_b} \Delta Z^* e \phi / \Omega \quad (\text{eV}/\text{m}^2) \quad (8)$$

where ΔZ^* is the effective valence of the solute cation. Assuming that $\Delta \gamma_b^E$ (in Eq. 2) results from the reduction in γ_b^e by the applied field, Eq. 8 gives for the applied field E

$$\Delta \gamma_b^E = \gamma_b^e = \delta_b \overline{\Delta C_b} Z^* e \phi / \Omega \quad (\text{eV}/\text{m}^2) \quad (9)$$

Taking $E = E_c$ and rearranging Eq. 9 gives for the space charge potential energy due to the segregated aliovalent ions

$$Z^* e \phi = \Delta \gamma_b^{E_c} \Omega / \delta_b \overline{\Delta C_b} \quad (10)$$

where E_c is the critical field shown in Fig. 1.

Experimental

Procedure

The starting material in the present isothermal annealing tests was 3Y-TZP powder (GS $d_0 = 26$ nm) purchased from Tosoh having the following chemical composition in wt%:

Y ₂ O ₃	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	Na ₂ O	ZrO ₂
5.21	<0.005	0.005	0.002	0.022	Remainder

The powder compaction (98 MPa at room temperature), specimen geometry, and electrical connections for the present tests without and with electric field were the same as those employed previously [4]. The thermal history in the present tests is shown in Fig. 3. Following binder burn-out at 800 °C the specimens were furnace-cooled to room temperature and then sintered at a constant heating rate of 11 °C/min without and with a constant applied dc voltage $V = 25 \pm 0.1$ V to 1300 ± 1 °C and 1400 ± 1 °C and then directly annealed at these temperatures for various times up to 24 h, following which they were again furnace cooled. The linear shrinkage (optical measurement), which gave the relative density ρ_r and the corresponding GS $\bar{d}$ (SEM) were measured during the annealing. As a result of the shrinkage during sintering the applied electric field E increased from the initial 14 V/cm following binder removal to ~ 18 V/cm at the beginning of the isothermal anneal.

Fig. 3 Schematic of the thermal history of the specimens in the present isothermal annealing tests without and with dc electric field

For each annealing time, the mean linear intercept GS $\bar{d}$ was determined from SEM micrographs of mechanically polished and thermally etched (1 h at 1200 °C) cross sections of the test specimens. The SEM micrographs were taken at three locations on each specimen: (a) ~ 5 mm below the positive upper electrode, (b) midway between the two electrodes, and (c) ~ 5 mm above the lower negative electrode. Approximately 200 GS measurements were made at each location, giving a total of ~ 600 measurements for each annealing time. To establish the scatter in the measurements, the GS counts were made independently by *three investigators* for each of the three locations representing each annealing condition, giving a total of ~ 1800 counts. The GS reported is the mean value of the 1800 counts made independently by the three investigators; the reported scatter is the maximum and minimum values of the mean GS for each of the three locations.

An estimate of the grain shape anisotropy Γ was taken to be the ratio of the mean GS determined from counts along lines parallel to the bottom edge of the SEM micrographs ($\bar{d}_{\parallel}$) to those along perpendicular lines ($\bar{d}_{\perp}$), i.e., $\Gamma = \bar{d}_{\parallel} / \bar{d}_{\perp}$. Again, for each location and annealing condition Γ was independently measured by the three investigators.

Results

An example of the grain structure in a specimen annealed with field compared to without is presented in Fig. 4. To be noted are: (a) the grains in both micrographs are relatively equiaxed and (b) the grains with field are significantly smaller than those without. Plots of ρ_r and $\bar{d}$ vs. annealing time t_a without and with applied electric field ($E = 18$ V/cm) at 1300 and 1400 °C are presented in Fig. 5. The data points are the combined mean values for the three locations by the three investigators; the error bars are the maximum and minimum values of the means. To be noted in Fig. 5 is

Fig. 4 SEM micrographs at the location midway between the electrodes of the specimens annealed for 12 h at 1300 °C: **a** $E = 0$ and **b** $E = 18$ V/cm

Fig. 5 Relative density ρ_r and mean linear intercept grain size $\bar{d}$ vs. annealing time t_a for the isothermal annealing of 3Y-TZP without and with an applied dc electric field $E = 18$ V/cm: **a** 1300 and **b** 1400 °C

that $\bar{d}$ and ρ_r increase in a parabolic fashion with t_a . At both temperatures, $\bar{d}$ decreases and ρ_r increases with the application of E . Further, the effect of E on the difference $\Delta\bar{d}_E = \bar{d} - \bar{d}_E$ increases with annealing time. For all test conditions, the measured grain isotropy $\Gamma = 1.05 \pm 0.05$, i.e., the grains were essentially isotropic. Further, there was no consistent trend in GS nor in Γ , regarding the three locations, i.e., from one electrode to the other.

As mentioned above, to avoid the need for the value of the driving force parameter m in the solution of Eq. 3 one should know the magnitude of the GS ratio $\bar{d}_E/\bar{d}$ at a constant grain growth rate ratio $\dot{\bar{d}}_E/\dot{\bar{d}}$. For this, the values of $\dot{\bar{d}}_E/\dot{\bar{d}}$ were determined from the slopes of the $\bar{d}$ vs. t_a curves in Fig. 5. The slopes (derived manually) are plotted vs. the reciprocal of the GS $(\bar{d})^{-1}$ in Fig. 6. The hatched region defines where the magnitude of $\bar{d}_E/\bar{d}$ can be obtained at a constant $\dot{\bar{d}}_E/\dot{\bar{d}}$ and in turn for a corresponding constant driving force for grain growth. Also

Fig. 6 Grain growth rate $(\dot{\bar{d}})$ vs. the reciprocal of the grain size $(\bar{d})^{-1}$ for the present annealing tests without and with applied dc electric field $E = 18$ V/cm at 1300 and 1400 °C

shown in Fig. 6 are the values of the GS ratio $\bar{d}_E/\bar{d}$ at constant grain growth rate, which values range from 0.60 to 0.71 with an average of 0.65. Of significance is that these values of $\bar{d}_E/\bar{d}$ for $E = 18$ V/cm are in accord with those in

Fig. 1 obtained at this field strength for other tests and processing conditions. The prior results (Fig. 1) and the present isothermal annealing test results thus give that the effect of an electric field on the GS ratio $\bar{d}_E/\bar{d}$ during sintering, plastic deformation and isothermal annealing is a unique function of the applied field strength, i.e., $\bar{d}_E/\bar{d} = f(E)$ independent of $\bar{d}$, T , and ρ_r . This in turn gives for a constant field strength that the difference in GS $\Delta\bar{d}_E = \bar{d} - \bar{d}_E = \bar{d}[1 - f(E)]$, i.e., $\Delta\bar{d}_E$ is proportional to $\bar{d}$.

Analysis and discussion

The GB energy components γ_b^Σ and γ_b^s represent elastic atomic displacements, which are usually essentially independent of an applied electric field E . The effect of E on grain growth in 3Y-TZP is therefore entirely through its influence on the electrostatic component γ_b^e . The form of the $\bar{d}_E/\bar{d}$ vs. E curve in Fig. 1 thus gives that the regime $E \leq E_c$ corresponds to γ_b^e and that for $E > E_c$ to $(\gamma_b^\Sigma - \gamma_b^s)$, where γ_b^s is subtracted from γ_b^Σ because the ionic radius of Y^{3+} is larger than that of Zr^{4+} [9]. Therefore, since $d_E/d = 0.4$ at $E = E_c$, Eq. 3 gives $\gamma_b^e = 0.6\gamma_b^0$, and in turn $(\gamma_b^\Sigma - \gamma_b^s) = 0.4\gamma_b^0$. Based on these magnitudes, we will compare the experimentally derived GB energy components with predictions.

Important in the evaluation of γ_b^Σ and γ_b^s is a knowledge of their relative magnitudes. According to Eqs. 5 and 6 their ratio is given by

$$\gamma_b^\Sigma/\gamma_b^s = k_B T / UC_b^* \quad (11)$$

Taking $T_{avg} = 1350$ °C, $U = 6.3 \times 10^{-21}$ N m (Table 1) and $C_b^* = 0.06$ [15], Eq. 11 gives $\gamma_b^\Sigma/\gamma_b^s = 59.3$, i.e., $\gamma_b^\Sigma \gg \gamma_b^s$. The field-independent regime for $E > E_c$ in Fig. 1 thus corresponds mainly to γ_b^Σ , and therefore $\gamma_b^\Sigma \approx 0.4\gamma_b^0 \approx 0.254$ J/m² ($\gamma_b^0 = 1.215 - 0.358 \times 10^{-3}T$ J/m² [24]). Setting $\gamma_b^\Sigma = 0.254$ J/m², Eq. 5 gives $\lambda_b^c = 1.21 \Omega^{1/3}$, which is not unreasonable considering: (a) the scatter in the data in Fig. 1, (b) the atomic structure in Fig. 2, and (c) general information on the width of grain boundaries in crystalline solids. Taking $\lambda_b^c = 1.21 \Omega^{1/3}$, $U = 6.3 \times 10^{-21}$ N m (Table 1), and $C_b^* = 6 \times 10^{-2}$ [15], Eq. 6 gives $\gamma_b^s = 4.3 \times 10^{-3}$ J/m². Thus, the difference $(\gamma_b^\Sigma - \gamma_b^s) \approx 0.25$ J/m², is in accord with that given by the field-independent regime ($E > E_c$) in Fig. 1. Moreover, the small value of γ_b^s indicates that cation size misfit is not the major factor responsible for the segregation of yttria to the GBs in zirconia.

Regarding the electrostatic component γ_b^e , according to Eq. 9 $\Delta\gamma_b^e$ is proportional to $\Delta\gamma_b^E$, the latter being given by Eq. 3. Employing Eq. 3 and taking $\gamma_b^0 = 0.63$ J/m²

Fig. 7 Calculated effect of the applied dc field on the grain boundary energy in 3Y-TZP at $T_{avg} = 1350$ °C

[24] the effect of E on $\Delta\gamma_b^E$ at 1350 °C determined from the results in Figs. 1 and 6 is shown in Fig. 7. To be noted is that in keeping with Fig. 1 an approximately linear reduction in the GB energy by the applied field occurs up to the critical field $E_c \cong 26$ V/cm, with no further effect at higher fields to 65 V/cm. The rate of reduction in γ_b^0 by the field $d\gamma_b^E/dE$ is 1.46×10^{-2} (J/m²)/(V/cm)⁻¹, and the total reduction of γ_b^0 at $E_c = 26$ V/cm is ~ 0.38 J/m². Thus, the major factor responsible for the segregation of yttria to the GBs in zirconia is electrostatic in nature, as proposed by Hwang and Chen [9]. Further, since the effect of electric field on grain growth in 3Y-TZP is through its influence on the global GB energy (which per se is non-vectorial), it is expected that the field will not have a significant effect on the grain shape isotropy, as was in fact observed.

Of further interest regarding the electrostatic GB energy component γ_b^e is a comparison of the magnitude of the space charge potential ϕ_i obtained from the present isothermal annealing tests with that determined by impedance spectroscopy and by atomic simulation. Taking for the parameters in Eqs. 9 and 10, $\Delta\gamma_b^E = 0.60\gamma_b^0$ (Eq. 3), $\gamma_b^0 = 0.63$ J/m² ($T_{avg} = 1350$ °C [24]), $\Omega = 35 \times 10^{-30}$ m³, $\delta_b = 8$ nm [15], and $\overline{\Delta C}_b = 1.6 \times 10^{-2}$ [15], one obtains $Z^*e\phi = 0.66$ eV. Taking $Z^* = 3$ for the Y^{3+} ions gives $e\phi = 0.22$ eV. This value is in accord with those obtained by impedance spectroscopy [25–29] and atomic simulation [30]; see Table 2. Moreover, this value of $e\phi$ for 3Y-TZP is within the range reported for crystalline oxides in general [31–35]. These agreements provide support for the model proposed here for γ_b^e (Eqs. 9 and 10) whereby the applied electric field exerts a bias on the space charge potential due to the segregation of Y^{3+} ions to the GBs; see Fig. 8.

It is well-known that 3Y-TZP is an ionic conductor (due to the high mobility of the oxygen ions) and that the so-called “specific” GB resistivity ρ_b^* is one-to-three orders of the magnitude larger than that of the grain interior ρ_g [35–

Table 2 Comparison of the space charge potential ϕ_i obtained in the present isothermal grain growth tests with those by the absolute reaction rate (ARR) theory, by impedance spectroscopy (IS) and by atomic simulation (AS)

Authors	Material	Method	d (μm)	T ($^{\circ}\text{C}$)	ϕ_i (V)	δ_b (nm)
Present	3 YSZ	Grain growth: $\dot{d} = \text{const.}$	0.1–0.5	800–1500	0.22	8.0
Conrad [5]	3 YSZ	Grain growth: ARR	0.1–0.5	800–1500	0.12–0.18	–
Verkerk et al. [25]	8 YSZ	IS	0.28	600–1000	0.20–0.23	9.0
Guo and Maier [26]	8 YSZ	IS	16	200–800	0.25	~ 5.0
Guo [27]	8 YSZ	IS	1.4	400	0.26	3.5
Guo et al. [28]	8 YSZ	IS	16	250–500	0.20–0.27	~ 4.0
Guo and Zhang [29]	3 YSZ	IS	0.12–1.3	250–600	0.18–0.24	5.6
Guo and Zhang [29]	8 YSZ	IS	0.25–13.5	450	0.21–0.27	4.8
Bingham et al. [30]	6 YSZ	AS	<0.5	1700	0.15–0.22	1.7

d = grain size, ϕ_i = space charge potential, δ_b = total grain boundary width

Fig. 8 The bias exerted at 1350 °C by the applied dc electric field E on the space charge potential ϕ_i in 3YSZ due to the segregation of yttrium ions at the grain boundary **Fig. 9** Grain boundary energy γ_b vs. the magnitudes of the space charge potential ϕ_i in 3YSZ at 1350 °C

37]. The relationship between the mechanism by which an electric field retards grain growth and that which governs ρ_b^* has yet to be determined. The present results, along with those obtained previously (Fig. 1), give that the mechanism by which a field retards grain growth is by reducing the relatively athermal GB energy through the effect of the field on the space charge potential. The higher ρ_b^* compared to ρ_g could be due to a reduction in the oxygen ion mobility through the GB as a result of reduction in the oxygen ion vacancy concentration. The mechanism by which a reduction in the oxygen vacancies might occur is presently under investigation by the authors.

The contribution of the space charge ϕ_i to γ_b^0 obtained from cross plots of the results in Figs. 7 and 8 is shown in Fig. 9. The variation of γ_b with ϕ_i in Fig. 9 thus gives that any physical property which is a function of γ_b (e.g., grain growth rate or plastic strain rate) will depend on the valence of the solute as well as its ionic size misfit. Thus, properties relating to γ_b can be varied by the addition of selected aliovalent solutes and the application of an electric field.

Summary and conclusions

The effect of an applied dc electric field E up to ~ 60 V/cm on grain growth in 3Y-TZP shows two regimes: (a) $E \leq E_c$ (26 V/cm), where the GS ratio with field compared to without (d_E/d) decreases with E and (b) $E > E_c$ where d_E/d is essentially independent of E , the transition occurring at $d_E/d \approx 0.4$. It is proposed that the former regime corresponds to the electrostatic (space charge) component γ_b^e of the GB energy and the latter to the difference between the crystallographic (γ_b^Σ) and the size misfit (γ_b^s) components. The electrostatic component accounts for 60 % of the total GB energy and the crystallographic and cation size misfits for the remaining 40 %.

A physical model is developed for determining the magnitudes of the three GB energy components in 3Y-TZP from the effect of an electric field on grain growth. Reasonable agreement occurred between the experimentally derived values of the GB energy components and predictions. Moreover, the derived value of the space charge potential $e\phi_i = 0.22$ eV was in accord with reported values from impedance spectroscopy and atomic simulation.

The present results support the idea that the segregation of yttria to the grain boundaries in 3Y-TZP is mainly due to an electrostatic factor and that the resulting retardation of grain growth by an electric field is mainly due to a reduction in the GB energy, i.e., in the capillary driving force.

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