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Thermodynamics versus kinetics of grain growth control in nanocrystalline zirconia



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ABSTRACT

This work presents a thorough analysis of the grain growth behavior of gadolinium doped yttria stabilized zirconia (YSZ). The effect of the dopant on the thermodynamics as well as on the kinetics of the process is reported by providing extensive experimental data. While normal grain growth following a parabolic growth relation was observed, gadolinium inhibited the process proportionally to its concentration. By using microcalorimetry, we showed that the dopant decreases the grain boundary energy of YSZ, and hence reduces the driving force for growth. Analysis of the growth profile at different temperatures and times indicate that gadolinium does not significantly affect the grain boundary mobility or the activation energy for grain growth. The results rationalize that the dopant is acting on a mostly thermodynamic basis and opens good perspective for design of coarsening control focused on the system energetics.

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1. Introduction

Ionic dopants have been extensively used to control grain growth in ionic oxides [1–3]. In attempts to retain grain sizes in the nanoscale range, several studies have been focused on understanding the role of dopants in both kinetics and thermodynamics of the process in order to optimize dopant selection and concentration [4–6]. Most interest lies on dopants that have strong tendency to preferentially segregate to the grain boundaries (GBs) due to the low solubility in the crystalline bulk [7–15]. Disregarding cases where the dopant is in such a high concentration that it forms a second phase, which could lead to a significant drag force for growth [12], a segregated dopant that represents excess concentration at the GB can affect cooperative movement of atoms from a kinetic perspective by solute drag [16–19]. If the grain growth process is expressed by the GB migration velocity, v , the kinetic impacts of dopants are seen in the mobility term, M_{gb} :

$$v = \frac{dD}{dt} = M_{gb} \cdot \frac{\gamma_{gb}}{D} \quad (1)$$

Here, γ_{gb} is the GB energy and D is the average grain size. A decrease in mobility will slow down growth [20], but a parabolic behavior arising from the integral form of this equation should still hold. On the other hand, from a thermodynamic point of view, addition of solute atoms that segregate to the GBs will affect the GB energy, thus also slowing down growth according to the equation. This concept has been modeled by Weissmuller [21], Kirchheim [22], Liu and Kirchheim [23], Millett et al. [13] and others. The reduction in γ_{gb} with solute segregation can be formulated as a function of GB energy of the host material (solvent), γ_0 , the solute excess at the GB region, Γ_B , the enthalpy of segregation, ΔH_{seg} , and the bulk solute content X_B^{bulk} :

$$\gamma_{gb} = \gamma_0 - \Gamma_B \left(RT \ln X_B^{bulk} - \Delta H_{seg} \right) \quad (2)$$

With an increase in solute excess, for a doped system having negative segregation enthalpy, the GB energy will decrease according to this equation, assuming a negligible entropic contribution over segregation enthalpy. Thus, in the presence of a suitable

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solute segregated at the GBs, it is possible to tailor the GB energy and therefore to control the grain growth behavior on a thermodynamic basis. Such behavior is evident from a number of recent theoretical and experimental studies [13,24–27]. Due to the difficulties in obtaining reliable data on the thermodynamic effects of dopants to a particular system, it is, however, not uncommon to ignore such effect and assume a prevalent kinetic contribution. Recent advances in microcalorimetry [28] have enabled a more quantitative analysis of this energetic contribution, such that one can properly address the question on the actual contributions of dopants from both kinetics and thermodynamics perspectives. In this paper, we address the problem in a cubic zirconia system.

When doped with a critical amount of yttria (Y_2O_3), the cubic polymorph of zirconia (ZrO_2) is stabilized, known as Yttria Stabilized Zirconia (YSZ). Due to the stabilization, the YSZ ceramics have high ionic conductivity [29] as well as high thermal stability [30]. Despite several applications inspired by those properties [31–33], here we focus on YSZ as a model material (host) in order to avoid phase transitions during grain growth studies and energetic assessments. We have selected Gadolinium (Gd^{3+} , ionic radius 94 pm) as an additional dopant with potential for segregation. Gd^{3+} has similar charge as yttrium (Y^{3+} , ionic radius 90 pm) but the different ionic radii hypothetically provides sufficient local stress as a driving force for segregation. The dopant was added in concentrations from 1 to 4-mol% and the GB energy for all compositions experimentally assessed using differential scanning calorimetry (DSC). Local chemical composition profiles across GBs were determined by Electron Dispersive X-ray Spectroscopy (EDS) and Electron Energy Loss Spectroscopy (EELS) using a Scanning Transmission Electron Microscope (STEM). Dopant effects on the mobility of the grain boundaries as well as activation energies were experimentally determined based on grain growth kinetics studies following validated procedure [1], but inputting the actual measured GB energies in the analysis instead of assuming arbitrary values. The results provide striking evidence of the dominance of the thermodynamic effect on grain growth behavior over mobility and diffusion terms.

2. Experimental procedures

Gd free and Gd doped nanocrystalline yttria stabilized zirconia powders were synthesized by reverse strike co-precipitation [34,35]. Zirconium oxo-nitrate hydrate [$ZrO(NO_3)_3 \cdot xH_2O$] (Aldrich, 99%, St. Louis, MO), yttrium nitrate hexahydrate [$Y(NO_3)_3 \cdot 6H_2O$] (Aldrich, 99.999%, St. Louis, MO) and Gadolinium nitrate hexahydrate [$Gd(NO_3)_3 \cdot 6H_2O$] (Aldrich, 99.999%, St. Louis, MO) were used as the metal precursors and 1.0 M ammonium hydroxide (NH_4OH) as the coprecipitation agent. Powders were dried at 100 °C overnight [36] and calcined at 450 °C for 2 h. For the Gd doped samples (1–4 mol %), the yttrium content was decreased consistently with the Gd content to maintain the same trivalent dopant concentration along the samples. This was done with the purpose of maintaining overall defect content and minimizing diffusivity differences between them. Fewer oxygen vacancies are expected in the bulk when the Gd dopant ions segregate to the grain boundaries. Noteworthy, YSZ growth is controlled by cationic diffusion, which does not change significantly when comparing, for instance, 10YSZ and 8YSZ [37,38]. Hence, the trivalent ion content is not expected to have a significant effect on diffusion coefficient during growth.

Chemical compositions were confirmed by X-ray Fluorescence (XRF) spectroscopy (Rigaku, Supermini200 Sequential WD-XRF, Pd Target, 50KV/4 mA, Tokyo, Japan). X-ray Diffraction (XRD) was used (Bruker AXS Inc., Madison, WI, model D8 Advance; $CuK\alpha$ Radiation $\lambda = 1.5418 \text{ \AA}$ under 40 kV and 40 mA) to ensure phase purity and

measured the crystallite size of the nano powders around 6.0 nm by JADE 6.1(MDI) software performing a whole profile fitting. Lattice parameters were also calculated from XRD by mixing YSZ samples with a standard lanthanum boride (LaB_6) of known lattice parameter. XRD patterns for the as-synthesized nanoparticles are shown in Fig. 1S.

The calcined powders were sintered into dense pellets (5 mm diameter, ~1 mm height) using the spark plasma sintering technique (SPS, model 825S, Syntex, Tokyo, Japan) at 950 °C for 5 min with 600 MPa mechanical pressure under vacuum. The main advantage of using this technique is its ability to sinter at low temperatures and short holding times, which gives highly dense compacts with limited grain growth [39–41]. Since the powder is in contact with a conductive graphite die and SiC punches, fast heating rates are enabled while the effect of external pressure further facilitates the densification without significant grain growth [42]. After sintering, carbon residues present on the surface of the pellets that origin from the graphite parts were polished off before the sample was calcined at 750 °C for 5 h. This process was done to assure negligible strain remained in the sample after this pressure-assisted densification method and that any carbon residues and local zirconia reduction were properly eliminated. Note that the calcination condition was chosen to provide sufficient time and temperature for oxidation of any reduced zirconia and strain relaxation. Oxidation is fast at this temperature as is governed by oxygen vacancy migration. The diffusion length of the cations at the annealing temperature is estimated to ~0.9 nm, which is considered sufficient for relaxation of bonds. XRD patterns showed no distortion of the lattice, confirming the relaxation efficacy. No signs of bloating were observed in SEM due to this thermal treatment indicating carbon was mostly on the surface of the pellet. The relative density for all the pellets ranged from 95% to 96% measured with Archimedes' method. XRD patterns of crushed pellets were used to calculate crystallite sizes after sintering.

For transmission electron microscopy (TEM) characterization, electron transparent samples were prepared by focused ion beam (FIB) sectioning of a 2 mol% Gd sample with ~30 nm grain sizes. TEM lamellae were subsequently transferred to suitable specimen grids by standard in-situ lift-out techniques. Effects of ion beam damage to the electron transparent samples were minimized by routine clean-up procedures that include successive lowering of the ion beam energy and current densities. At UC Davis, a FEI Scios FIB instrument was employed for TEM specimen preparation. Subsequent annular dark field (ADF) imaging was carried out with an aberration-corrected Jeol JEM 2100F/Cs instrument, while diffraction contrast TEM experiments were performed with a Jeol JEM 2500SE instrument. Both electron microscopes were operated at 200 keV.

Local chemical composition profiles were obtained by energy dispersive X-ray spectroscopy (EDS) using Y-K, Zr-L, O-K, and Gd-L intensities. Spectra were recorded with a dual high solid angle 30 mm² windowless Si X-ray detector attached to a Jeol JEM 2800 STEM instrument operated at 80 keV at the University of Utah. The respective TEM samples were prepared using a FEI Helios Dual Beam FIB instrument. The acquisition parameters to resolve quantitative EDS spectral images were a single acquisition comprised of multiple 5 s scans over 512 by 512 pixels. Initial quantification of the collected EDS spectra utilized a Cliff-Lorimer thin film correction with an input physical density of 6.10 g/cm³ and a nominal specimen thickness of 95 nm. Weighted spectral images were calculated from the experimental data based on the following formula per pixel: $Gd(at\%)/[Gd(at\%)+Y(at\%)]$ and $Y(at\%)/[Gd(at\%)+Y(at\%)]$. The normalized maps were then superimposed on the acquired ADF survey images. This normalization, instead of actual Gd concentration mapping, was performed to better visualize Gd

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