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Growth of single crystalline seeds into polycrystalline strontium titanate: Anisotropy of the mobility, intrinsic drag effects and kinetic shape of grain boundaries

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ABSTRACT

We present a suite of measurements and combined analyses of grain growth in $SrTiO_3$ for oriented single crystals into polycrystals. The growth distance and standard deviation and the microstructure evolution along the single crystal–matrix interface are used to locally characterize the change in migration behavior as a function of temperature, time and interface orientation. The relative grain boundary mobility was determined between 1250 °C and 1600 °C for four crystallographic orientations {100}, {110}, {111} and {310}. An absolute mobility of these orientations is estimated. Under fast growth conditions the morphology of single crystals shows macroscopic stepping with parts of the interface rotating to low mobility orientations. This effect represents a kinetic influence on the grain boundary morphology. The results also indicate dragging effects on microstructure coarsening, which indicate the existence of a critical driving force for grain growth. This critical driving force seems to be related to an 'intrinsic' interface drag similar to the solute drag, but based on intrinsic defects. At 1460 °C the growth of single crystals was significantly faster than expected from the mobility of the polycrystal and was identified as exaggerated grain growth. The findings give new insights into the recently published grain growth anomaly of strontium titanate, leading to a hypothesis based on the temperature dependent relative mobility of {100} oriented grain boundaries.

1. Introduction

Grain growth in polycrystals is frequently analyzed much as proposed by Turnbull and Hillert: the kinetics of grain growth are represented by a temperature-dependent kinetic factor k used to relate grain radius R and time t according to

$$R^2(t) - R^2(t = 0) = \frac{1}{4}kt \qquad (1)$$

with deviations from expected results often ascribed to changes in the behavior of a specific set of grain boundary energies and/or mobilities [1–3]. However, this experimental approach based on characterizing the mean behavior of a microstructure is unable by itself to reveal the underlying causes of the local grain growth behavior. As can been seen in the materials science literature,

changes in grain boundary migration behavior are being related to an increasingly wide range of factors, including, but not limited to, transitions in grain boundary structures and mobilities as a function of temperature, misorientation, boundary plane and composition and coupled grain boundary migration and stress generation. In alumina, for example, adsorption (complexion) transitions of the grain boundaries with dopant composition have been shown to change the grain boundary mobility and thereby change the local grain growth rate by several orders of magnitude [4–6]. Bicrystal experiments have shed considerable light on the static and dynamic properties and migration behavior of grain boundaries. For example, Kim et al. observed three distinct facetted structures, including completely dewetted regions, as a function of the grain boundary plane along a low angle bicrystal grain boundary in alumina containing a liquid phase [7]. Using a grain boundary half loop bicrystal in Zn, Sursaeva et al. observed transitions in interface shape from rough-faceted to a "rough–rough" shape with a first-order ridge as temperature decreased [8]. The coupling between grain

boundary migration and shear stresses observed in experiments and molecular dynamics simulations introduces another level of complexity to grain growth in polycrystals: normal grain boundary migration is often coupled to tangential translation of grains, leading to the creation of a shear stress along the boundary, which in a constrained system can retard grain boundary migration [9–12].

While grain growth simulations using MD and non-MD techniques can be useful tools in examining the role of anisotropic grain boundary properties on microstructure evolution in polycrystalline materials [13–16], the quantitative information needed to account for the different types of transitions in behavior among different boundaries during grain growth in polycrystals does not currently exist. With one set of assumptions there may be general agreement with the observed grain growth kinetics in a polycrystal, but it is not likely to be unique: another set of assumptions will likely give the same evolution, within the level of microstructural detail and accuracy of experiments.

In this paper we present a suite of measurements and combined analyses of grain growth of large, oriented single crystals into polycrystals which are themselves undergoing grain growth, to provide additional insights into the origins of growth rate transitions in strontium titanate [17–21]. The initial orientation of the interface between the single crystal and the polycrystal can be set by polishing the single crystal at a particular orientation before joining and the polycrystalline matrix provides the driving force for growth of the single crystal at any point in time at temperature. Experiments in this geometry have been used for more than three decades in measuring growth rate anisotropy in ceramics, e.g. Alumina [22–29], Barium titanate [30–33] and Strontium titanate [34–36]. In some of these previous experiments and in this paper, measurements of the mean migration distance of different single crystal orientations into the polycrystalline matrix and of the matrix grain size as a function of time, temperature, and single crystal surface orientation are obtained. Using these data, effective grain growth coefficients k and relative mobilities can be calculated to compare the behavior of different interface orientations as well as grain growth in the matrix.

What is unique in this paper is the use of both the standard deviation of growth distance and the microstructure along the single crystal–matrix interface to characterize locally the change in migration behavior as a function of temperature, time, and interface orientation. The measured distributions of migration distance for a given single crystal interface orientation into the polycrystal provide a convolution of local differences in driving force and mobility, as a result of the spatial variation in grain size and grain size distribution, as well as in grain boundary energies and local mobilities. Examining the standard deviations relative to the grain size and the local microstructures along the interface as a function of single crystal orientation, temperature, and time provides additional information on the heterogeneity of the matrix microstructure and its role in creating heterogeneous grain growth behavior.

Such analyses can lead to testable hypotheses for the possible causes of the observed "grain growth anomaly" in undoped strontium titanate: in strontium titanate, the grain growth constant does not show the classical Arrhenius-type behavior, but instead shows a decrease in growth rate in the temperature range of 1350 °C–1425 °C with increasing temperature, followed by an increase again as temperature increases [17–21]. Although no dopants are introduced that might lead to the observed behavior, transitions in grain boundary structure, stoichiometry, and coupling may occur with temperature alone and could account for this behavior. For example, TEM investigation of a small subset of grain boundaries in a polycrystal indicated that slower moving grain boundaries in undoped strontium titanate had higher grain boundary Ti-concentrations than faster moving grain boundaries [21]. Unfortunately, no clear relationship has yet been established between the grain growth anomaly, and differences in grain boundary chemistry, character and structure with temperature.

A temperature-induced change in grain boundary energy/faceting was proposed as an explanation of the non-Arrhenius behavior in strontium titanate [20]; it is well known that both grain boundary energy and mobility are anisotropic in strontium titanate [34,35,37–39]; a temperature induced faceting/defaceting transition close to 1590 °C is known as well [40,41]. Bäurer et al. suggested a decrease of the relative grain boundary energy of low mobility boundaries with increasing temperature [20]. This transition would result in an increasing frequency of low energy, low mobility grain boundaries which would lead to a changing distribution of curvatures in the system and a corresponding decrease of the grain growth constant. The relationship between the anisotropy of surface energy and the grain boundary plane distribution (GBPD) in strontium titanate was recently explored as a function of temperature [39]. Between 1300 °C and 1650 °C the anisotropy in the GBPD increases with temperature, particularly the frequency of the {1 0 0} oriented grain boundary planes. The scope of the current paper is (i) to provide the temperature dependent anisotropy of the grain boundary mobility and thereby (ii) to clarify whether the grain growth anomaly originates in the anisotropy of the grain boundary mobility.

2. Experimental procedure

2.1. Fabrication of embedded single crystals

The seeded polycrystal method requires joining a single crystal and a high density polycrystal. The stoichiometric polycrystalline ceramic material was prepared by a mixed oxide/carbonate route based on $SrCO_3$ (99.9+%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany) and TiO_2 (99.9+%, Sigma Aldrich). The green bodies were sintered at 1425 °C for 1 h in oxygen to obtain a relative density of 99.5 ± 0.2%. Further details of the preparation are published elsewhere [42]. Samples were cut into disks and polished (diamond slurry, 0.25 μm) and then scratched with a polishing disk (30 μm diamonds) to create pore channels.

Strontium titanate single crystals (impurity content: <10 ppm Si, <2 ppm Ba, <1 ppm Ca, SurfaceNet GmbH, Rheine, Germany) were chemically–mechanically polished and placed between two polished and scratched polycrystalline disks. Stacks were joined at 1430 °C for 20 min in air with a load of 1 MPa. During diffusion bonding the pore channels created by the scratches break up into rows of small pores. As the single crystal grows into the polycrystalline matrix, pores become isolated within the single crystal, marking the original interface of the single crystal (Fig. 1) and are used as a reference for measuring the growth distance. A set of samples was prepared for the four different surface orientations {1 0 0}, {1 1 0}, {1 1 1} and {3 1 0} of single crystals.

2.2. Grain growth experiments and data acquisition

Growth experiments were carried out between 1250 °C and 1600 °C in an oxygen atmosphere. The dwell time was interrupted at specific intervals to determine the position of the interface at a given time, with the growth distance measured by SEM on polished slices which were cut perpendicular to the single crystal interface. The heating rate was 20 K/min and the cooling rate 10 K/min for experiments below 1460 °C. For annealing above 1460 °C, samples were quenched with ~200 K/min to room temperature to minimize the influence of microstructural changes during cooling.

Typical microstructures are shown in Fig. 1. The grain size of the polycrystalline matrix was measured close to the interface with