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A reversible wetting transition in strontium titanate and its influence on grain growth and the grain boundary mobility

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A B S T R A C T

The impact of the oxygen partial pressure on grain growth in high purity strontium titanate is evaluated by observing microstructures, the grain growth constant k and the relative mobility of strontium titanate. The microstructures indicate a reversible wetting transition between 1460 °C and 1500 °C. The wetting second phase is titania-rich and free from any detectable solutes. Exaggerated grain growth was found close to the wetting transition and is explained by a temperature dependent anisotropy of the grain boundary mobility in conjunction with a high mobility of wetted grain boundaries.

The grain growth constant in reducing atmosphere shows two transitions at 1350 °C and at 1460 °C. At the first transition the grain growth constant decreases with temperature. A strong increase of k with temperature at the second transition is attributed to the wetting transition.

The relative grain boundary mobility of different orientations ({1 0 0}, {1 1 0}, {1 1 1}, and {3 1 0}) was measured in oxidizing and reducing atmosphere by observing the growth of oriented single crystals into polycrystals. At 1550 °C in reducing atmosphere the wetting liquid phase enhances the mobility by a factor of ∼10 compared to oxidizing atmosphere. Additionally, the atmosphere changes grain growth kinetics: in oxidizing, but not in reducing atmosphere growth stagnation occurs for long dwell times.

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1. Introduction

Wetting of grain boundaries in polycrystals is a phenomenon of great importance in sintering [1–3] and is known to change grain boundary characteristics and grain growth considerably [4]. For example, diffusion, faceting and grain boundary motion are fundamentally changed by a wetting second phase. In dense high purity solids grain growth is expected to show parabolic time dependence due to the linear coupling of driving force and boundary migration [5,6]. This is the case different high purity ceramics, e.g. alumina [7,8], BaTiO$_3$ [9] and SrTiO$_3$ [10,11]). However, if the relationship between driving force and boundary migration is more complex, the kinetics is changed toward cubic or even higher exponents [5,6]. In the presence of a wetting liquid film, grain growth kinetics depends on the type of the rate controlling mechanism: interface reaction controlled grain boundary motion results in parabolic kinetics; if diffusion limits coarsening the kinetics change to cubic [3,12–14]. Additionally, a wetting liquid phase influences the local orientation of grain boundary planes: since the geometric constraints for both adjacent interfaces are lowered, the grain

boundary planes can rotate freely to low energy or low mobility orientations [15–18].

A special case of second phase segregation at interfaces is known as "complexions": adsorption transitions of segregants at the grain boundary change the grain boundary characteristics, grain boundary mobility and hence grain growth drastically [7,19–23]. These complexion transitions are thermodynamically stable [24] and exist at temperatures below the wetting transition of the grain boundaries [21]. In sintering these transitions can be used to optimize the shrinkage behavior [19,25,26].

In general, wetting is based on a minimization of the interfacial energy. Perovskite ceramics include good model materials (e.g. barium titanate and strontium titanate) to study energetically driven interface effects in detail, since the grain boundary energy can be influenced by the defect chemistry (i.e. dopants and oxygen partial pressure [27–30]). Additionally a variety of useful data is available e.g. for strontium titanate. For instance, the grain growth constant is documented [10,11]: grain growth does not follow classical Arrhenius behavior, instead a decrease of the grain growth constant with temperature was found between 1350 °C and 1425 °C. The temperature dependent anisotropy of the grain boundary mobility was also measured recently [31]. Several studies observed the grain boundary energy via the inverse correlation

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of the frequency of a specific grain boundary plane and its energy (Grain Boundary Plane Distribution, GBPD [27,32–36]). The GBPD shows an increase of the grain boundary energy anisotropy with temperature. In contrast, the Wulff shape shows a decrease of the surface energy anisotropy with temperature, which points toward a change of the relationship between the binding energy and the absolute surface energy [27].

However, almost all studies are confined to oxidizing atmosphere; little information is available on the impact of the atmosphere on grain growth. The Wulff shape is available for reducing atmosphere [27]. Some information on the atmosphere and dopant dependent mobility was also published [28], however, this study does not use high purity raw materials and no quantification of growth is given. The purity of raw materials is crucial for grain boundary wetting: small amounts of SiO_2 or other dopants can result in a wetting second phase in strontium titanate [37,38] and barium titanate [39]. Even a wetting transition at the eutectic point of 1440 °C [40] was reported [41,42]. In high purity strontium titanate a titania-rich phase is known to exist, but no wetting was observed in oxidizing atmosphere [43–45].

The current study completes the data on grain growth by observing the grain growth constant and relative grain boundary mobility in reducing atmosphere. It is shown that a control of atmosphere and temperature can result in the formation of a wetting titania-rich second phase. The wetting is shown to be a reversible process and seems to be anisotropic. In different applications a controlled change of the oxygen partial pressure is important, e.g. for PTC materials [46,47] or cofiring of layered structures with base metal electrodes [48–50]. In all these application the role of a wetting transition would be of great interest.

2. Experimental procedure

2.1. Grain growth experiments on polycrystals

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 resulting powder has a very high purity; especially no silicon is detectable by ICP-OES [44]. The green bodies were presintered at 1425 °C for 1 h in oxygen to obtain a dense fine-grained microstructure (relative density of 99.5 ± 0.2%, average grain radius <1 μm, cf. Fig. 1a). Further details of the synthesis are published elsewhere [44].

All grain growth experiments were performed in tubular furnaces (Gero GmbH, Neuhausen, Germany) at temperatures between 1300 °C and 1550 °C. The atmosphere was either pure oxygen or forming gas (95% N_2 and 5% H_2, $p(O_2) \approx 8 \times 10^{-8}$ Pa) at ambient pressure. The heating rate was 20 K/min and the cooling rate 10 K/min for the experiments below 1350 °C. Above 1350 °C samples were quenched with ~200 K/min to avoid any influence during cooling. During quenching the atmosphere was not changed.

The grain size of the polycrystals was measured using the line intersection method (at least 284 grains, typically 1200). The mean grain size R at time t was used to obtain the grain growth constant k by applying a standard grain growth law [9,10,51]:

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

2.2. Grain growth experiments on embedded single crystals

The seeded polycrystal method requires joining a single crystal and a polycrystal. Stoichiometric polycrystalline ceramic material
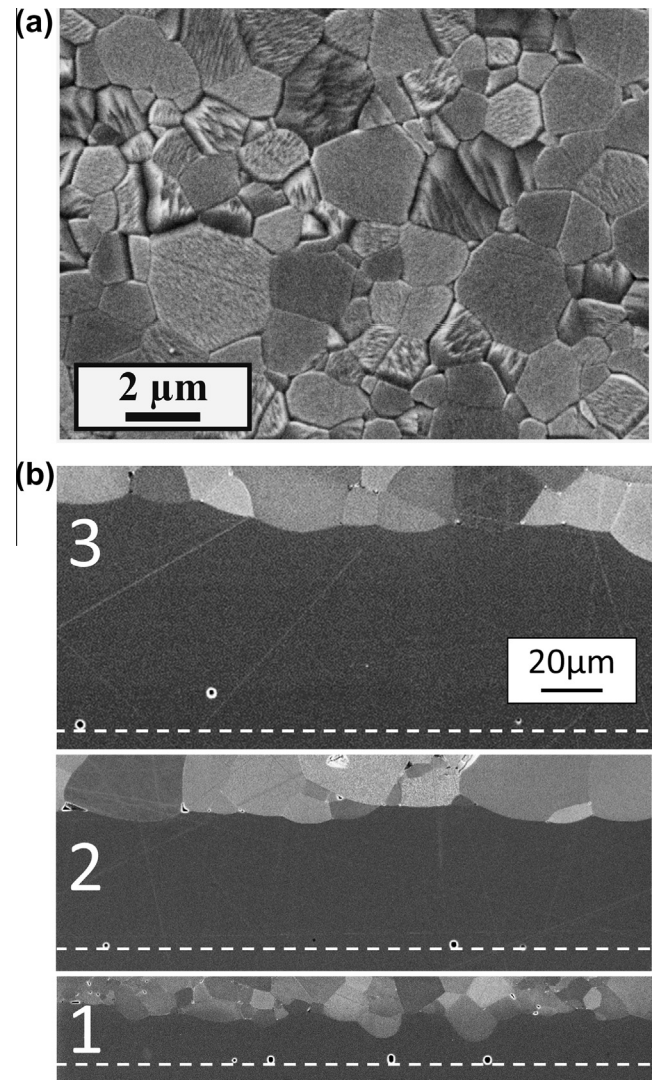

Fig. 1. (a) Microstructure of the samples presintered at 1425 °C for 1 h in oxygen and (b) a single crystal growing into a polycrystalline matrix at 1550 °C after 6 min (1), after 1.5 h (2) and after 4.4 h (3). The white dotted line highlights the rows of small pores, which indicate the original position of the interface of the single crystal at time 0.

was presintered at 1425 °C for 1 h in oxygen (Fig. 1a). Samples were cut into discs and polished (diamond slurry, 0.25 μm) and then scratched with a polishing disc (30 μm diamonds) to create pore channels [31].

The strontium titanate single crystals (impurity content: <10 ppm Si, <2 ppm Ba, <1 ppm Ca, SurfaceNet GmbH, Rheine, Germany) were chemical–mechanical polished and placed between two polished and scratched polycrystalline discs. 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 scratches break up into rows of small pores. As the interface of the single crystal migrates into the polycrystalline matrix, pores become isolated within the single crystal and appear as a row in the micrographs marking the original interface of the single crystal (white dotted lines in Fig. 1b). These pores were used as a reference for measuring the growth distance. A set of samples was prepared for the four different surface orientations {100}, {110}, {111} and {310} of the single crystals. Further details of this procedure can be found elsewhere [27,31].