Grain growth in weak electric fields in strontium titanate: Grain growth acceleration by defect redistribution

Wolfgang Rheinheimer[*], Manuel Fülling, Michael J. Hoffmann

Institute of Applied Materials—Ceramic Materials and Technologies, Karlsruhe Institute of Technology, Karlsruhe, Germany

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ABSTRACT

The impact of DC electric fields on grain growth in strontium titanate is investigated between 1350 °C and 1550 °C for fields of up to 50 V/mm. To prevent joule heating by electrical currents, insulating Al_2O_3 plates separate electrodes from samples. The seeded polycrystal technique is used, which allows evaluating gradients induced by electric fields. The growth direction of the single crystalline seeds is perpendicular to the electric field; hence electrostatic forces do not influence its growth. Below 1425 °C, the influence of electric fields is very weak. Above 1425 °C the field results in an increase of the grain boundary mobility at the negative electrode.

The enhancement of the boundary mobility at the negative electrode is attributed to electric field induced defect redistribution. Oxygen vacancies migrate towards the negative electrode, while strontium vacancies accumulate at the positive electrode. This defect redistribution is connected to the defect chemistry dependent grain growth in strontium titanate.

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1. Introduction

Within the last five years considerable efforts were expended in understanding electric field assisted sintering (flash sintering). Flash sintering refers to accelerated sintering in electric fields [1,2]. This method involves high currents flowing through the sample and thereby joule heating. Different ceramic materials show this effect, for example alumina [3], silicon carbide [4], zirconia [1,5–9], barium titanate [10] and strontium titanate [11]. The mechanism of flash sintering is under debate. While most likely joule heating is involved [12–14], different defect based mechanisms were proposed as well [1,2,5,15]. Further experimental and theoretical work is ongoing in a multitude of working groups.

However, flash sintering experiments are very hard to control: shrinkage occurs within seconds and the local temperature is undefined due to joule heating. Analyzing grain growth in an electric field simplifies these experiments and provides information on the active mechanisms. Only, few studies focused on the impact of electric fields on grain growth. In experiments with an electric current flow and joule heating in zirconia, a suppression of grain growth with electric fields of up to 40 V/mm was found [1,16,17]. The authors explained the observations by a reduction of

the grain boundary entropy and energy by local joule heating of the interfaces and local point defect creation. These point defects are believed to segregate and to cause a solute drag-like [18] effect on boundary motion.

Two similar studies have investigated grain growth in barium titanate in an electric field of 20 V/mm at different dopant concentrations and atmospheres [19,20]. The authors report diverse growth gradients across the samples depending on dopant concentration and atmosphere. Several complex grain growth effects seem to be coupled, for example a change of the boundary potential from positive (acceptor doped and undoped) to negative (donor doped) and a field induced wetting transition. Wetting is assumed to increase the boundary mobility drastically. The authors explain all growth effects observed in the samples by the grain boundary potential and its interaction with local defect concentrations, which are graded across the sample due to the electric field. However, the composition of the second phase, joule heating, a possible change in faceting and its impact of grain growth [21–24] are not considered.

At these fields, joule heating is expected due to the high conductivity of these materials at high temperature. Accordingly, the present study focuses on grain growth in the no-current case with insulating alumina plates to separate the electrodes from the samples. The seeded polycrystal method was used, in which a single crystal is joined to a polycrystalline matrix [25,26]. This method allows evaluating the grain boundary mobility continuously across the sample and highlighting gradients induced by the electric field.
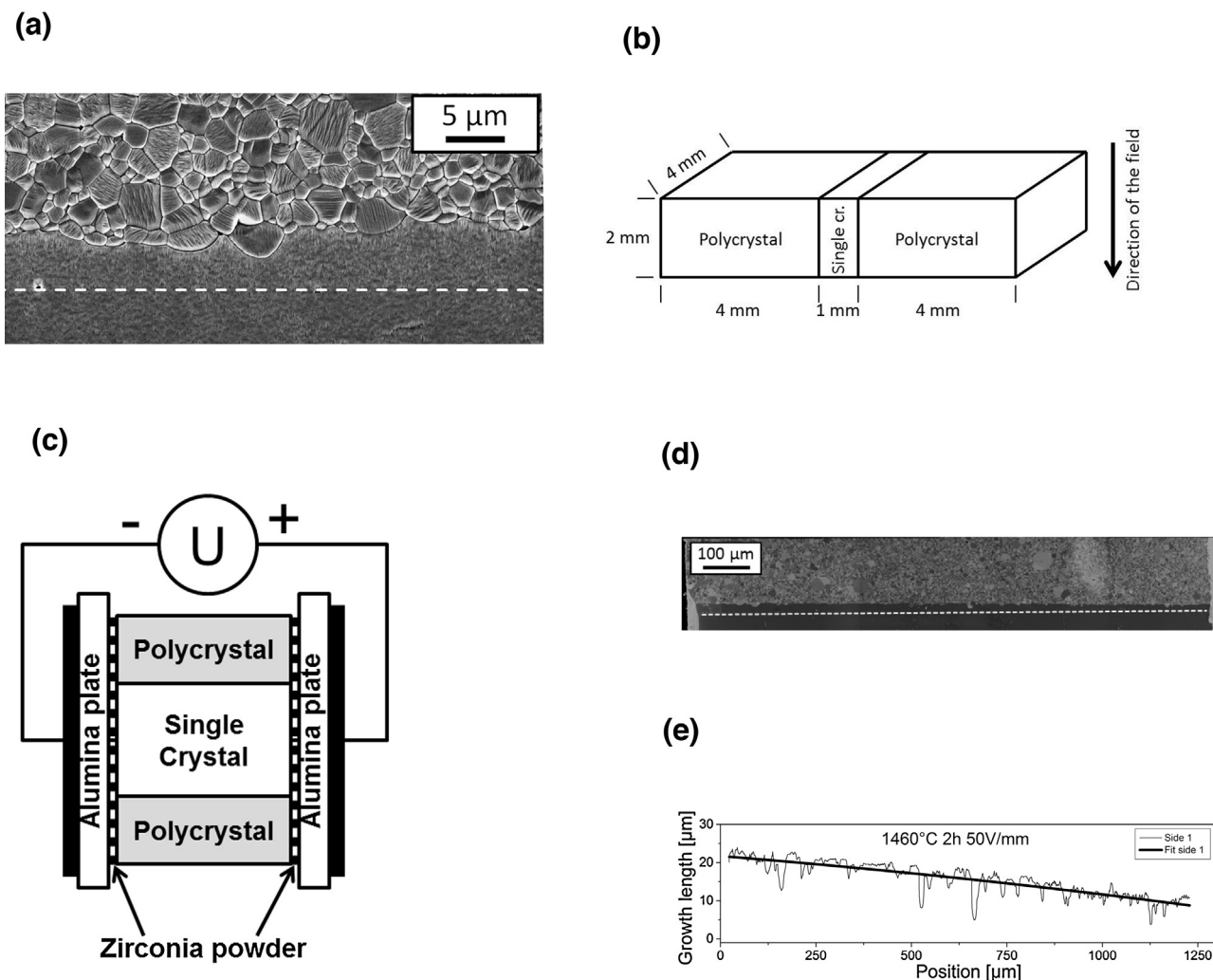
Fig. 1. Microstructure of a seeded polycrystal after diffusion bonding (a). The initial position of the interface prior to bonding is marked by a row of small pores (white broken line). Sample dimensions as used for all experiments (b). Sketch of the experimental setup with seeded polycrystal, insulating alumina plates and voltage source (c). Microstructure across a sample from negative (left side) to positive electrode (right side) after 2 h at 1460 °C and 50 V/mm (d). The initial position of the interface prior to bonding is marked by a row of small pores (white broken line). The growth length between the initial and actual position is shown in d with respect to the position in the sample (e).

In alumina [27] and sodium chloride [28], the general impact of electrostatic forces on grain boundary migration parallel to electric fields was documented. Thus in the present experiments the growth direction of single crystalline seeds was orthogonal to the electric field to prevent possible effects. The perovskite model system strontium titanate was chosen, since its grain growth behavior is well-known in relation to defect chemical parameters (but in the absence of electric fields). For example a grain growth transition was documented resulting in strongly decreasing grain growth rates with increasing temperature [29–31]. Information on grain boundary energy [32,33] and mobility anisotropy [25,26] as well as grain boundary faceting [34–36] and atomic structure [37] are available. The impact of stoichiometry on grain growth was thoroughly examined [31,38,39] and the bulk defect chemistry is well-known [40,41].

2. Experimental procedure

Stoichiometric strontium titanate powder was prepared by the mixed oxide/carbonate route based on high purity raw materials ($SrCO_3$ and TiO_2, both 99.9 +%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany). The green bodies were sintered at 1425 °C

for 1 h in oxygen to a relative density of 99.5 ± 0.2%. Further details of the powder synthesis are published elsewhere [42]. 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. These pore channels mark the original position of the interface during growth experiments (cf. white broken line in Fig. 1a and d [26,33]).

The seeded polycrystal technique was used to evaluate the impact of an electric field on grain growth. A single crystalline disc (chemical-mechanical polished, impurity content: <10 ppm Si, <2 ppm Ba, <1 ppm Ca, SurfaceNet GmbH, Rheine, Germany) was placed between two polycrystalline discs and joined by a diffusion bonding process (1430 °C, 20 min in air, 1 MPa). A typical microstructure of a seeded polycrystal is shown in Fig. 1a (initial microstructure) and c (after 2 h at 1460 °C and 50 V/mm). The single crystal grows into the polycrystal. The driving force for this growth is the interface area of the polycrystal consumed by the growing single crystal. Further details on this experimental setup are published elsewhere [26,33].

Samples were again cut perpendicular to the single crystal in slices of a thickness of about 2 mm (Fig. 1b). As shown in Fig. 1c, samples were placed between two high purity alumina plates