The Influence of Fields and Dopants on the Microstructural Evolution of Alumina

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Introduction

Alumina is one of the most widely studied ceramics. The manufacturing process, from green body preparation to dopant selection and sintering conditions, affect the microstructure and properties of sintered ceramics. Sintering serves the purpose of promoting densification through facilitated diffusion at high temperatures, which is also usually accompanied by grain growth.

Making the sintering process of ceramics more energy and time efficient has been a goal for well over a century. New methods employing the use of electric fields have garnered interest, with spark plasma sintering (SPS) seeing rapid development since the 90's[1]. In SPS, the powdered sample is simultaneously subjected to a uniaxial pressure and electrical current via a graphite die, either in vacuum or a protective atmosphere.

Flash sintering was discovered in 2010 by Cologna et al.[2]. In Flash sintering, the electric field is applied directly to the green body so that the current is forced to flow through the ceramic body. At a specific combination of furnace temperature and electric field, also referred to as the *onset*, the material densifies in an extremely short time, typically within minutes.

In alumina, due to its insulating nature, attempts to perform flash sintering saw the need to use higher voltages and/or dopants[3]. A voltage of 250 V/cm was not enough to reach the onset of flash sintering and a voltage of 1000 V/cm was required at a furnace temperature of more than 1000°C.

Jeong and Han studied the influence of an electric field on grain boundary (GB) migration[4]. By diffusion bonding large-grained alumina to small-grained alumina, they demonstrated that the GB migration rate into the small-grained region was accelerated when a negative bias was applied to the large-grained region, and impeded when a positive bias was applied.

Motivation

It has become apparent in recent years that there is a direct correlation between disconnection motion and GB mobility. It is known that dopants adsorbed to grain boundaries can alter the GB mobility, likely via interaction with disconnections. In a similar way, external electromagnetic fields may alter the activation energy to form disconnections and/or the kinetics of disconnection motion, and thus affect the GB mobility.

Defect chemistry is of significant importance when talking about the way dopants alter GB mobility. For alumina, Mg is known to hinder grain growth while Ca has the opposite effect. The presence of impurities results in compensating defects that are characterized by local charges and the application of external electromagnetic fields may help shed light on their role.

The ***goal*** of this study is to observe the influence of external electromagnetic fields on GB mobility in alumina by measuring the effective GB mobility of polycrystalline alumina, as well as that of *specific crystallographic planes*, as a function of fields and dopants.

Grain growth can be described by:

$$\overline{G_t}^2 - \overline{G_0}^2 = 4M_{GB}\gamma_{GB}t = kt$$

where $\overline{G_t}^2$ and $\overline{G_0}^2$ are the squared average grain sizes at times t and t = 0 respectively, M_{GB} is the GB mobility, γ_{GB} is the GB energy and k is the rate constant.

Experimental Setup

Figure 1: Disks were cut from sintered, undoped alumina, covered with Pt paste and thermally treated to form densified platinum layers on each electrode.

Figure 2: The platinum wire was placed against the already present platinum and coated with another layer of platinum paste to ensure constant contact during the annealing treatments.

Figure 3: After annealing at 300°C for 0.5 hour, followed by annealing at 900°C for 1 hour.

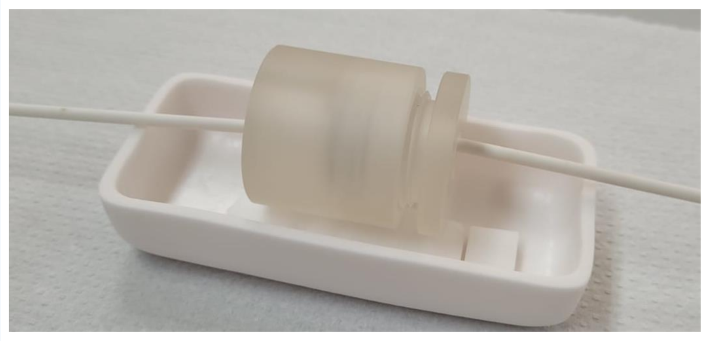

Figure 4: Dense undoped alumina, ~2.8mm in width, was placed between the electrodes in a threaded die made of sapphire.

Figure 5: The sapphire die with the sample, the electrodes, the platinum wires and thin alumina tubes was placed in the middle of a tube furnace and connected to the power supply.

Samples were annealed at 1600°C.
A field was applied upon reaching 1600°C and turned off at the end of the dwell time at 1600°C.

Figure 6: Density measurements were carried out via the Archimedes method prior to annealing. After the annealing treatments, samples were cut and polished for SEM observations to measure the grain size, relative to the distance from the electrodes.

Results & Discussion

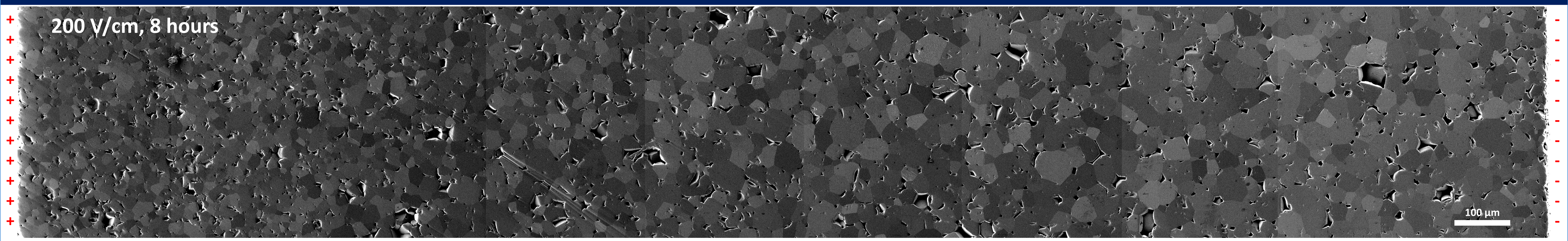

Figure 7: Montage of secondary electron SEM micrographs of undoped alumina annealed for 8 hours in air under an external field of 200 V/cm. The left and right sides mark the positive and negative electrodes, respectively. An increase in grain size is observed closer to the anode (-). The overly motivated graduate student resulted in pull-outs during polishing.

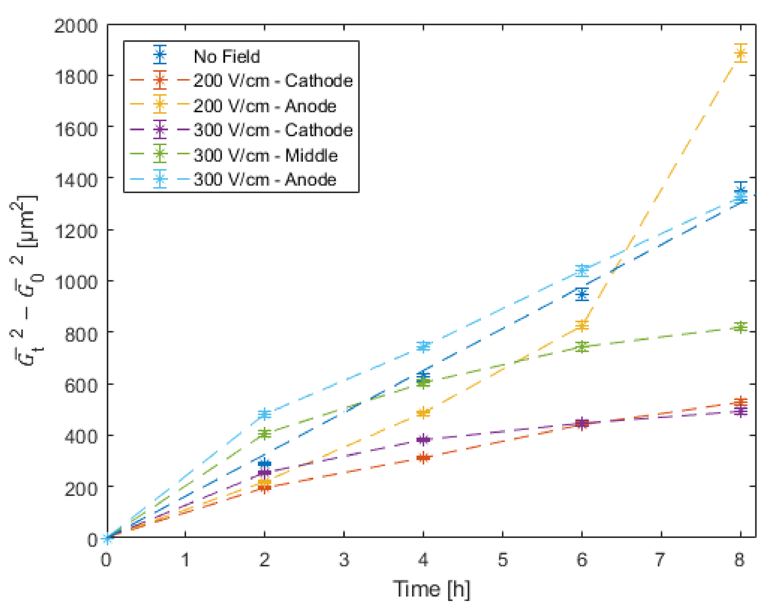

Figure 8: Average grain size versus time for undoped alumina annealed in air without a field, and under external fields of 200 and 300 V/cm.

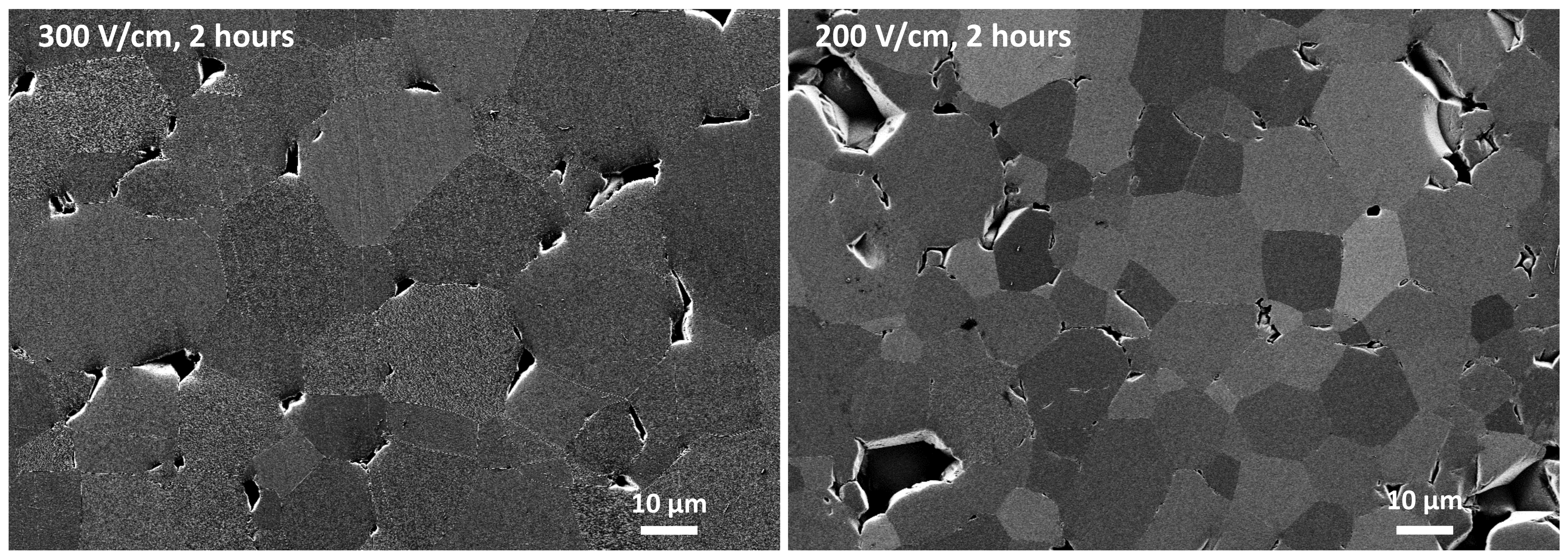

Figure 9: Secondary electron SEM micrographs of undoped alumina annealed for 2 hours in air under external fields of 300 and 200 V/cm. The micrographs were acquired ~100 µm away from the anode. No discernible difference could be seen between the grain size adjacent to the anode and the cathode at 200 V/cm after 2 hours at 1600°C under 300 V/cm, the average grain size near the anode is ***larger*** than near the cathode by ~7 microns.

Electric field → Larger grains near the negative electrode.

- The anode may attract positive defects (mainly oxygen vacancies $V_O^{\bullet\bullet}$).
- A time dependent increasing $V_O^{\bullet\bullet}$ concentration may activate additional disconnection motion mechanisms.
- The field may increase M_{GB} and/or γ_{GB}.

Calcium → Solute acceleration and/or more oxygen vacancies?

- Calcium is a common impurity that promotes grain growth below the solubility limit.
- Charge compensating oxygen vacancies are the most energetically preferable defects[5]:

$$Ca_{Ca}^{x}(s) \rightleftharpoons Ca'_{Al} + {}^{1}/_{2}\, V_O^{\bullet\bullet}$$

Table 1: Ca and Si concentrations measured in the sintered alumina by WDS. The detection limits are presented in brackets.

Ca [ppm]	Si [ppm]
7 ± 2 (3)	14 ± 3 (9)

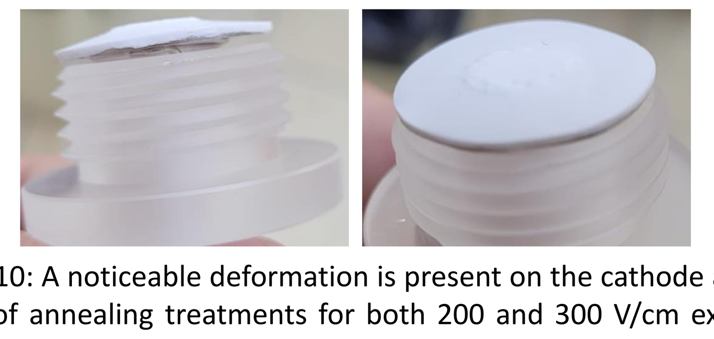

Figure 10: A noticeable deformation is present on the cathode after a series of annealing treatments for both 200 and 300 V/cm external fields. This deformation gradually increased with the use of the electrode and is accompanied by a mild dent in the inner face of the anode, where the samples are held.

Summary & Conclusions

- Since practically no current has passed through the alumina samples (a minimal voltage was measured throughout and no flash occurred), the altered grain growth can be attributed to the presence of the electric field. The change in the rate of grain growth ceases to be linear next to either of the two electrodes when applying an external field.
- The increasing rate of growth near the anode may be the result of an increase in either the grain boundary mobility, the grain boundary energy, or both.
- The electric field's potential influence on the local concentrations of oxygen vacancies may also lead to different local concentrations of impurities, such calcium or magnesium.

Future Research

- Additional data on grain size without a field is required for longer annealing times.
- Samples need to be annealed without a field inside the sapphire crucible with the electrodes to take into account the potential influence of platinum on grain growth.
- Calcium doped samples will be annealed.
- The local concentrations of dopants/impurities (mainly calcium) near the electrodes should be measured.
- Anisotropic grain boundary mobilities will be measured depending on the direction of the bias and orientation of the sapphire from sapphire diffusion bonded to undoped and calcium doped polycrystalline alumina.

References

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