Anisotropic Grain Boundary Mobility in Undoped and Ca Doped α-Alumina

Ran Akiva and Wayne D. Kaplan

Department of Materials Science & Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel

Introduction

The equilibrium phase of alumina (α−Al_2O_3) has a variety of applications, such as in bio-medical implants, diffusion barriers for high temperature applications, and applications requiring good wear resistance. The mechanical and functional properties of polycrystalline alumina strongly depend on the microstructure, which in part depends on grain growth during sintering.

At this point it is accepted that dopant segregation to grain boundaries results in a solute drag effect, reducing the mobility and the rate of grain growth. However, recent studies[1,2] of various systems have shown that dopants segregating to grain boundaries actually increase the grain boundary mobility, although it is not clear if the samples were doped below the solubility limit.

In order to achieve a better understanding of the microstructural evolution during sintering, the influence of Ca on grain growth in alumina was studied at dopant levels below the solubility limit.

Grain Boundary Mobility

Grain growth is a process in which grain boundary (GB) migration occurs in order to decrease the total GB area and thus the total free energy of a system.

The movement of a GB is a short term diffusion process whereby the atoms or ions move across the boundary and adopt the orientation of the growing grain.

The driving force is the difference in curvature (difference in pressure) between adjacent grains.

$$\Delta P = \frac{\alpha \cdot \gamma_{GB}}{G} = F_{GB}$$

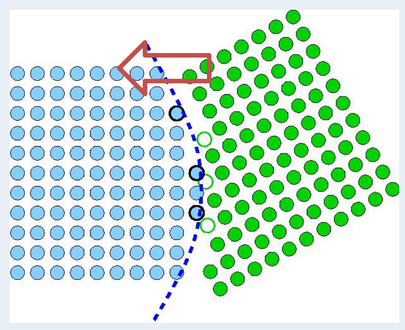
where:

ΔP = *Difference in pressure between adjancent grains*

α = *Geometric factor*

γ_{GB} = *Grain boundary energy*

G = *Grain size*



Convex →concave

V_{GB} depends on F_{GB}, and thus it is convenient to normalize V_{GB} and consider the boundary mobility M_{GB}:

$$M_{GB} = \frac{V_{GB}}{F_{GB}}$$

Experimental Methods

High purity (99.99%) α-Al_2O_3 powder

↓

H_2O (HPLC Grade) and HCl

↓

For Ca doped 20 ppm of ($Ca(NO_3)2{\cdot}4H_2O$)

↓

Pressure filtration at 5 MPa

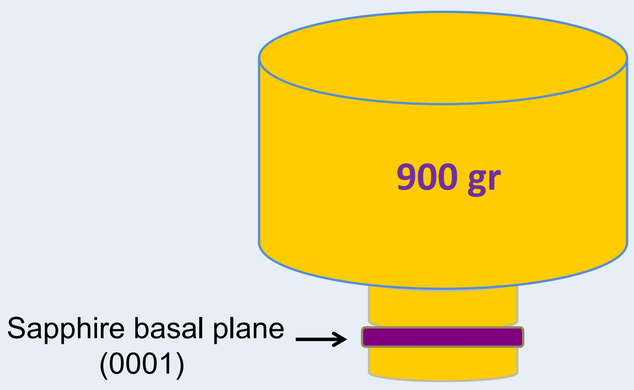
↓

Drying and Sintering at 1600°C for 2 hr

↓

Polished using a diamond suspension down to 0.25 μm

Diffusion Bonding



- Undoped alumina specimens were annealed at 1600˚C, 1650˚C and 1700˚C for 36, 48, 60 hours.
- Ca doped alumina samples were annealed at 1600°C for 5, 10, 25, 30,40,50 and 60 hr
- The microstructure was investigated by scanning electron microscopy (SEM – FEI Quanta 200).
- The grain size was measured using the linear intercept method.
- The density of the specimens was measured using the Archimedes' method.

Measurement Methods

The most common method is to extract an average M_{GB} by measuring the kinetics of normal grain growth in a dense compact.

$$V_{GB} = \frac{2M_{GB}\gamma_{GB}}{\overline{G}} \Rightarrow \frac{d\overline{G}}{dt} = \frac{2M_{GB}\gamma_{GB}}{\overline{G}}$$

$$\int_{G_0}^{G} \overline{G}\, d\overline{G} = \int_0^t 2M_{GB}\gamma_{GB} \Rightarrow \overline{G}^2 - \overline{G}_0^2 = \underbrace{4M_{GB}\gamma_{GB}}_{k} t = kt$$

$$M_{GB} = \frac{k}{4\gamma_{GB}}$$

where:

k = *Effective mobility*

Results

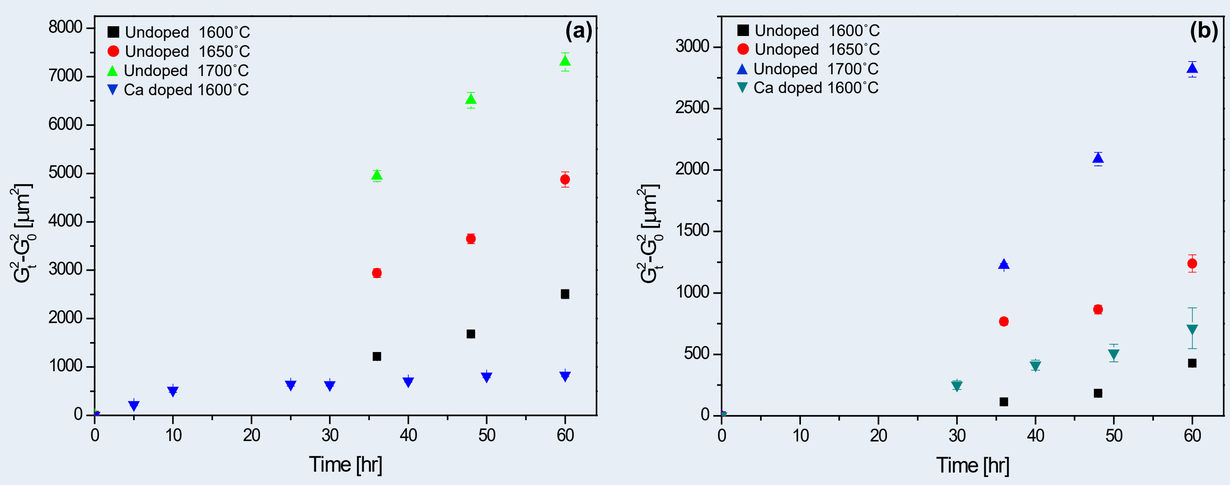


Figure 1: Grain size versus time for (a) undoped and 13 ppm Ca doped polycrystalline alumina, and (b) C-plane undoped and 13 ppm Ca doped diffusion bonded specimens.

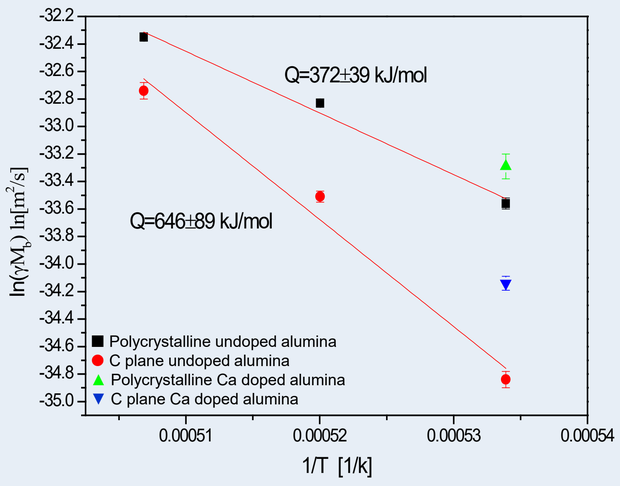


Figure 2: Effective grain boundary mobility versus inverse temperature for all specimens.

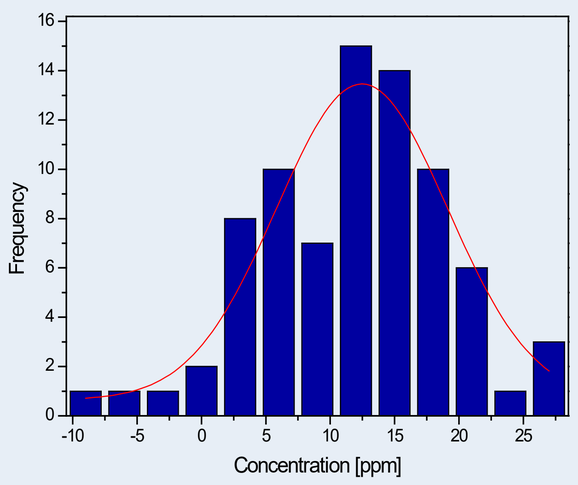


Figure 3: Histogram of the Ca concentration measurements from a Ca-doped specimen, indicating the Ca content.

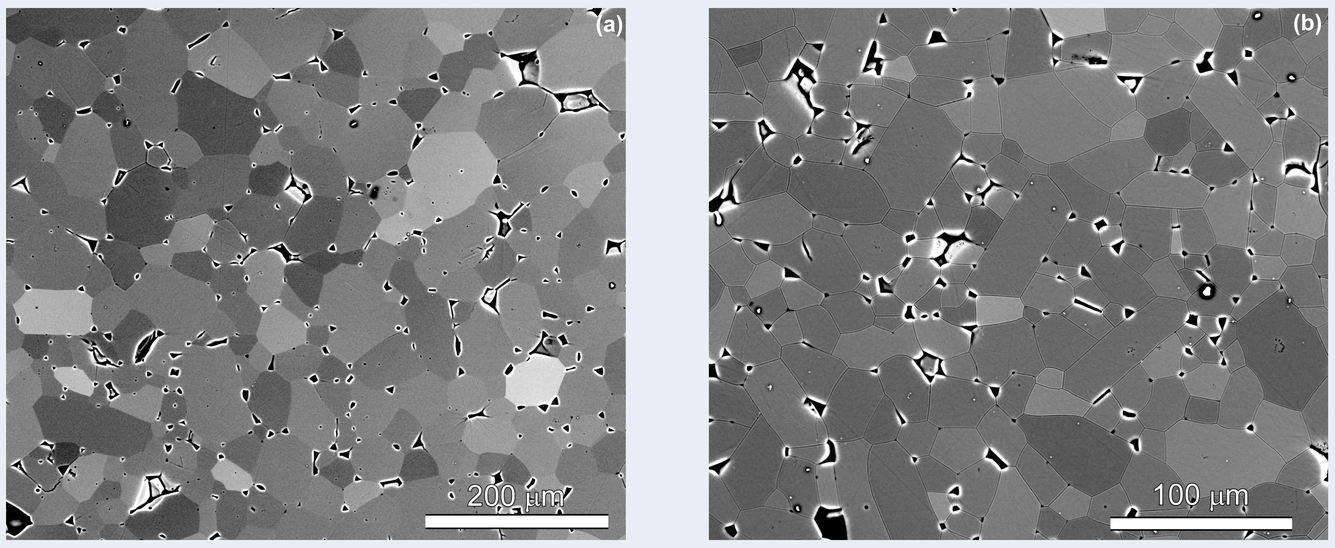


Figure 4: Grain size and morphology comparing (a) undoped alumina after 36 hr at 1700˚C and (b) 13 ppm Ca doped alumina after 50 hr at 1600˚C .

- Density measurements using Archimede's method result in 98.7%±0.6 of the theoretical density (3.97gr/cm^3)
- Although 20 ppm of Ca was add, WDS measurements showed 13 ppm Ca in the Ca-doped specimen, which is below the 51±1 ppm solubility limit of Ca in α-alumina at 1600˚C[3].
- As expected longer annealing times result in a larger grain size. The activation energies for the polycrystalline and basal plane (0001) specimens were determined from the effective mobility (Fig.2) to be 372±39 kJ/mol and 646±89 kJ/mol, respectively.
- The results show a clear trend of decreased grain growth for basal plane (0001) compared with polycrystalline specimens for both undoped and Ca doped alumina.
- An addition of 13 ppm Ca (below the solubility limit) results in enhanced grain growth compared to the undoped samples at earlier stages, and therefore a higher mobility. However after extended annealing times the grain growth rate decreased.

Conclusions

- The mobility of the basal plane (0001) is lower compared to the mean value for polycrystalline alumina, for both undoped and Ca-doped samples.
- Ca at levels below the solubility limit promotes grain growth with a plate-like morphology. While the mobility of the basal plane is reduced compared with the mean value of the polycrystalline sample, Ca is likely increasing the mobility of other (e.g. prismatic) planes, resulting in the final elongated microstructure.
- The activation energy for GB migration for polycrystalline alumina is 372±39 kJ/mol compared with 646±89 kJ/mol for the basal plane.

References

1. S. J. Dillon, M. P. Harmer and G. S. Rohrer, 'The Relative Energies of Normally and Abnormally Growing Grain Boundaries in Alumina Displaying Different Complexions,' J. Am. Ceram. Soc., 93[6] 1796-1802 (2010).
2. S. J. Dillon and M. P. Harmer, 'Relating Grain-Boundary Complexion to Grain-Boundary Kinetics I: Calcia-Doped Alumina,' J. Am. Ceram. Soc., 91[7] 2304-2313 (2008).
3. R. Akiva, Alex Berner and W.D. Kaplan, "The Solubility Limit of CaO in α-Alumina at 1600°C", submitted to Journal of the American Ceramic Society, March 2013.

M. Katz, D.Zinov and H.Gluska are acknowledged for assistance with the sample preparation and grain size measurements.