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The Influence of Solutes on Grain Boundary Mobility in Alumina

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Introduction

The microstructure of a sintered body strongly depends on the composition of the powder used for the sintering process, where dopants and impurities are known to affect sintering rates and grain growth. In this study, the solute content was varied by doping alumina with different amounts of CaO, below the solubility limit. The Ca concentration was determined by conducting fully standardized wavelength dispersive spectroscopy (WDS) and the change in grain boundary mobility as a function of the amount of dopant was characterized by quantitative analysis of grain size as a function of annealing time, using scanning electron microscopy.

The goal of this study was to determine the grain boundary mobility of alumina under the influence of Ca at impurity levels that are below the solubility limit.



$$C_{spec} = K \cdot g_{ZAF} \cdot C_{std}$$

$$C_{spec} = C_{oncentration of element}$$

$$k = \text{Ratio of intensity of characteristic X- ray radiation}$$
measured from an unknown specimen to that measured
from a selected standad
$$I_{Bgd} = \text{Background intensity}$$

$$I_{Std} = -\text{The intensity from a standard}$$

$$g_{ZAF} = -\text{Correction factor for atomic number, absorption}$$

$$m = \text{Number of measurements}$$

$$\tau = \text{Single measurement time}$$

 C_{\perp} – Element concentration within the standad

$$\overline{G}_t^2 - \overline{G}_0^2 = 4M_{GB}\gamma_{GB}t = kt$$

 $M_{\alpha}\gamma_{\alpha}$ – Effective mobility





and fluor



Fig.1 Histograms of Ca concentration measurements from undoped and doped specimens sintered at 1600°C for 2 h in He: (a) trace (3±1 ppm) of Ca concentration in undoped alumina; (b) 9±1 ppm of Ca in doped alumina; (c) 15±2 ppm of Ca in doped alumina; (d) 47±1 ppm of Ca in doped alumina.





Fig.3 Effective grain boundary mobility of undoped alumina and alumina doped with 3, 9, 15 and 47 ppms of Ca, annealed at 1600°C.

Figure 3 presents the effective mobility of alumina grain boundaries under the influence of varying amounts of Ca and exhibits an increase in effective mobility as the Ca content is increased. It has been shown that Ca does segregate to the grain boundaries, and the presence of Ca at the grain boundaries has been confirmed. Thus, the results of this study contradict accepted solute drag theory, and Ca at grain boundaries does not reduce the grain boundary motion, but instead enhances it [4,5,6].

The increase in mobility is evident up to a Ca content of 47 ppm, where a sharp decrease in effective grain boundary mobility is observed. WDS measurements confirmed a mean Ca content below the solubility limit of Ca in alumina, which was determined to be 51 ppm of Ca at 1600°C by Akiva et. al. Figure 1 presents the Ca measurements. Given the wide distribution of Ca content in the sample containing 47 ppm of Ca (shown in figure 1(d)), it may be assumed that Ca precipitation occurred and Ca enriched particles caused a decrease in the effective grain boundary mobility, as described by Zener [7]. The decrease in effective mobility in a sample determined to be at an impurity content near the solubility limit emphasizes the importance in establishing the exact chemical content of a sample, and it's relation to the solubility limit, in order to investigate and understand all various types of influences impurities may have on the evolving microstructure.

5. W. D. Kaplan, H. Mxillejans, M. Rühle, J. Rödel, N. Claussen, Ca Segregation to Basal Surfaces in α-Alumina, Journal of the

Fig.2 Backscattered electron SEM micrographs (polished cross-section) of the microstructure of 9ppm Ca doped alumina annealed for (a) 1 minute; (b) 5 hours; and (d) 10 hours at 1600°C in He.

Summary & Conclusions

- Unlike segregating dopants which reduce grain boundary mobility by solute-drag, Ca *increases* the rate of alumina grain growth, and does not impose a solute drag force on grain boundaries.
- These results demonstrate an increase in mobility as a function of dopant concentration, at concentrations below the solubility limit.
- Speculation as why this cation does not comply with the solute drag theory are varied, and a full understanding of this phenomena has not been established.

References

- 1. R. Akiva, A. Berner, W. D. Kaplan, *The Solubility Limit of CaO in α-Alumina at 1600°C*, Journal of the American Ceramic Society, 96[10]:3258-3264, 2013.
- 2. R. Moshe, A. Berner, W. D. Kaplan, *The solubility limit of SiO2 in α-alumina at 1600°C*, *Scripta Materialia*, 86[0]:40-43, 2014.
- 3. J. D. Powers, A. M. Glaeser, Grain Boundary Migration in Ceramics, Interface Science, 6[1-2]:23-39, 1998.
- 6. J. W. Cahn. The Impurity-Drag Effect in Grain Boundary Motion. The Selected Works of John W. Cahn. John Wiley & Sons, Inc., 2013. p.115-116.

American Ceramic Society, 78[10]:2841-2844, 1995.

4. R. Akiva, A. Katsman, W. D. Kaplan, Anisotropic Grain Boundary Mobility in Undoped and Doped Alumina, Journal of the American 7. E. Nes, N. Ryum, O. Hunderi, On the Zener drag, Acta Metallurgica, 33[1]:11-22, 1985. Ceramic Society, 97[5]:1610-1618, 2014.