The Solubility Limit of SiO_2 in α-Alumina at 1600°C

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Introduction

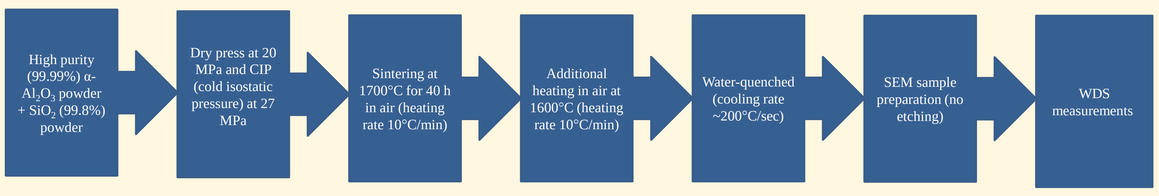
Polycrystalline alumina (Al_2O_3) is widely used as a structural ceramic material mainly due to its high hardness and fracture strength, creep and corrosion resistance, low density, and mechanical strength at high temperatures. These macroscopic properties of mass-produced alumina strongly depend on the composition of the powder used for the sintering process, and the microstructure of the sintered body, where dopants and impurities are known to affect sintering rates and grain growth. It has been shown that MgO promotes sintering and normal grain growth, whereas Si results in secondary phases and abnormal grain growth [1]. There are conflicting reports in the literature whether Si is detrimental to sintering of alumina when it is in solution, since the solubility limit of Si in alumina at the sintering temperature has not been determined [2]. In this study, the solubility limit of Si in Al_2O_3 is investigated using WDS from samples quenched from 1600°C in order to further understand the effect of impurities on the microstructural evolution of alumina.

Methodology

In order to determine the solubility limit of Si in alumina, a sample was prepared with an amount of SiO_2 powder that, once sintered, would result in the presence of only mullite ($3Al_2O_3 \cdot 2SiO_2$) and alumina. In addition, sintering conditions were chosen to achieve large alumina grains to facilitate the measurement of Si in solution, and to provide sufficient time for diffusion of Si to reach equilibrium. This ensured that the alumina grains were indeed saturated with Si, and the amount of Si measured in the grains represents the solubility limit. Finally, the sample was quenched (in water) from 1600°C, and the Si content of the alumina grains was determined using fully standardized wavelength dispersive spectroscopy (WDS) following the technique demonstrated in [3-5].

Experimental Methods

Sample Preparation



Wavelength Dispersive Spectroscopy (WDS)

WDS measurements were acquired at a working distance of 11 mm, a magnification ≥10,000x, a spot size resulting in a probe current of at least 40 nA, and a measurement time of 20 sec per data point. An accelerating voltage of 25kV was used to optimize between high signal intensity and low background intensity. The following equations were used for the concentration measurement and to determine the limit of detection for the measurement.

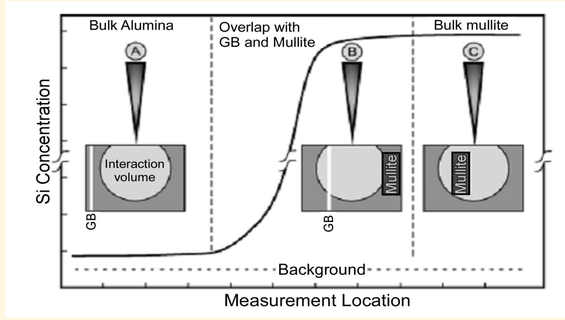


Fig. 1: Schematic drawing of the Si concentration distribution versus WDS measurement location.

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

C_{spec} – Concentration of element

k – Ratio of intensity of characteristic X- ray radiation measured from an unknown specimen to that measured from a selected standad

g_{ZAF} – Correction factor for atomic number, absorption and fluorescence

C_{std} – Element concentration within the standad

$$C_{\lim,0.975} = g_{ZAF} \cdot C_{std} \cdot \frac{2\sqrt{2I_{Bgd}}}{\sqrt{m\tau I_{Std}}}$$

I_{Bgd} – Background intensity

I_{Std} – The intensity from a standard

m – Number of measurements

τ – Single measurment time

Results and Discussion

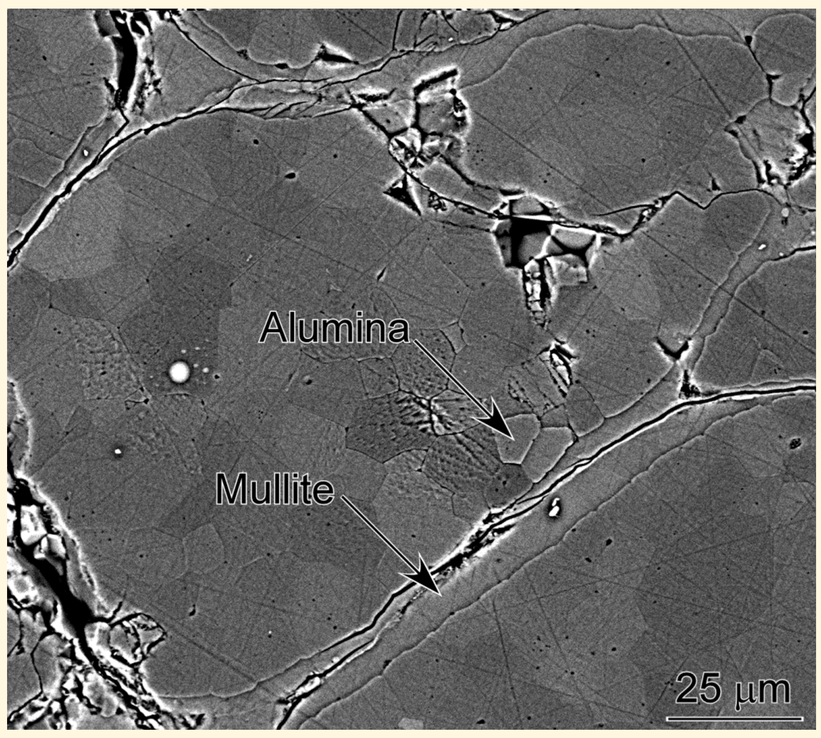


Fig. 2: Backscattered electron (BSE) SEM micrograph of an alumina sample doped with SiO_2, which underwent liquid phase sintering until the SiO_2 reacted with alumina to form crystalline mullite.

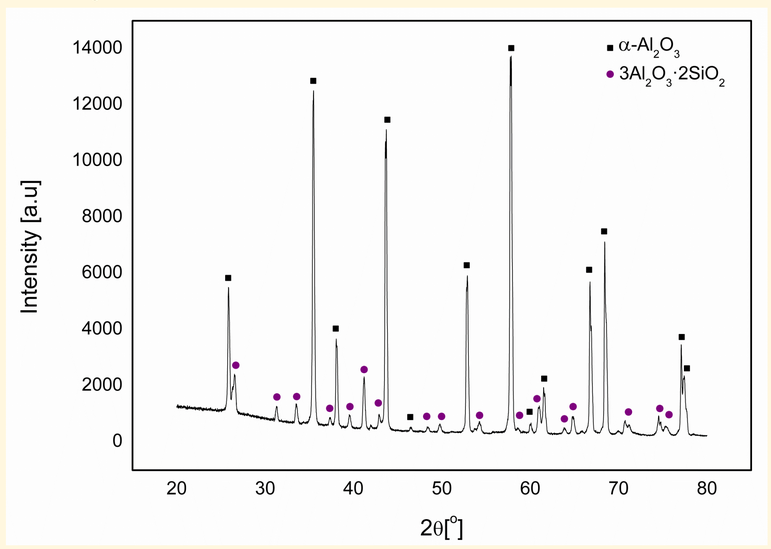


Fig. 3: X-ray diffraction (XRD) pattern confirming the presence of only mullite ($3Al_2O_3 \cdot 2SiO_2$) and alumina, thus ensuring saturation of the alumina grains with Si. XRD measurements were acquired using a conventional X-ray powder diffractometer (Rigaku MiniFlex X-Ray diffractometer) with a CuKα tube.

300 WDS measurements were conducted. The measurement frequency versus Si concentration shows two regions; a higher concentration regime ranging from 400 up to 1000 ppm which correlates to a region where the electron probe sampled both bulk mullite and alumina grains, and a lower concentration ranging from 70 up to 400 ppm, shown as a histogram in Figure 4. The lower region can also be divided into two regions after fitting to a Gaussian distribution where the peak at 226±5 ppm corresponds to interaction volumes containing both alumina grains and grain boundaries. The peak at 188±7 ppm corresponds to the Si concentration within alumina grains, which is thus the solubility limit of Si in alumina at 1600°C [8].

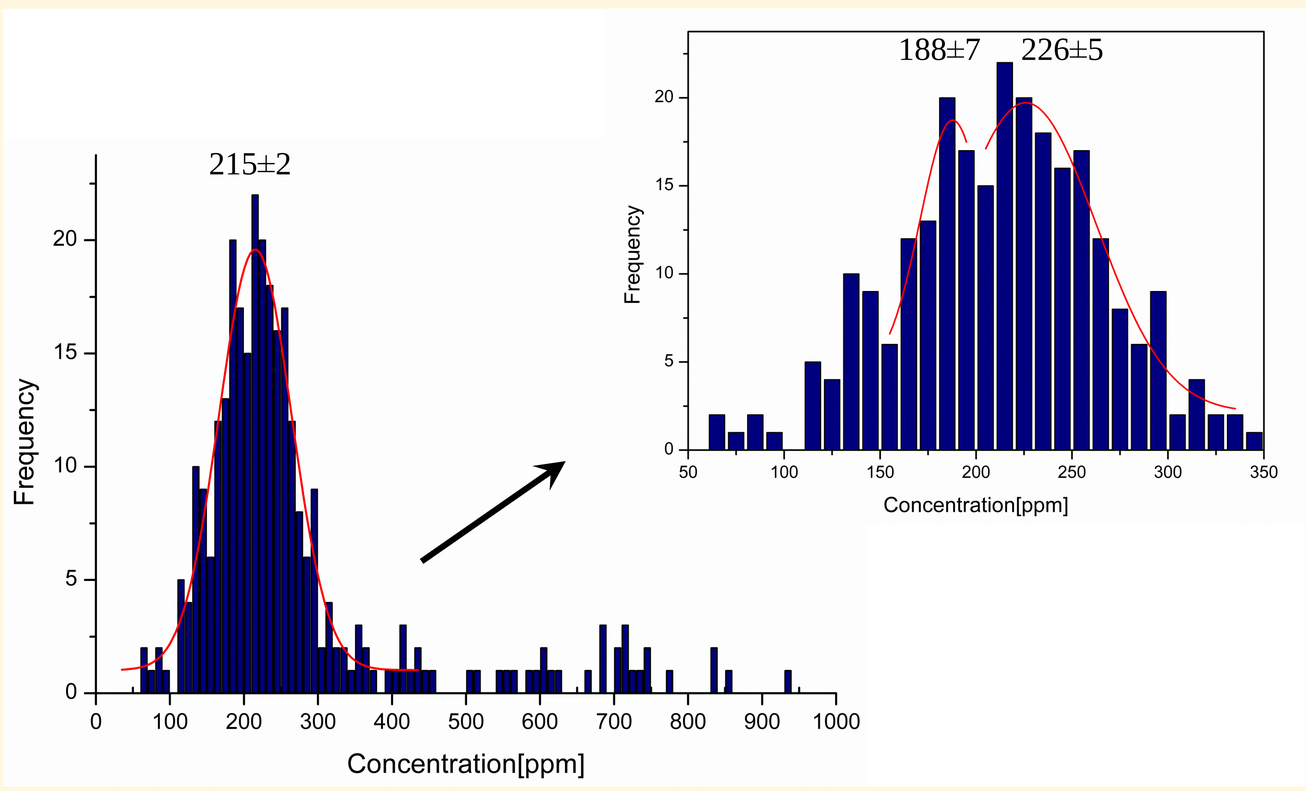


Fig. 4: Histogram analysis of 300 WDS Si measurements from the quenched sample. The peak at 215 ppm is the Si signal from alumina grains (188 ppm) and alumina grain boundaries (226 ppm). The experimentally determined detection limit for Si was determined to be 3 ppm. Thus the solubility limit of Si in α-Al_2O_3 at 1600°C is 188±7 ppm [8].

Table. 1 EDS measurement from a mullite grain detected in the quenched sample, confirming the XRD results that a two phase system had formed.

Element	Measured Concentration [at.%]	Stoichiometric Concentration [at.%]
O	68.83	69
Al	23.61	23.25
Si	7.56	7.75

- The solubility limit measured in this study gives rise to fundamental questions about the detrimental effect Si has on sintering. Bae and Baik correlated abnormal grain growth (AGG) with the formation of a liquid phase [6]. They determined that doping alumina with Si above 300 ppm will cause AGG to occur, and compared this with the solubility limit determined by Lee and Kröger [7] (by electrical conductivity measurements) which was the same value. ***Neither Bai and Baik or Lee and Kröger confirmed the actual Si content in their doped samples.***
- Dillon and Harmer correlated doping concentration with AGG and deduced that a complexion transition occurs in accord with a change in grain growth kinetics [2]. However, without knowledge of the solubility limit, one cannot distinguish whether segregation (correlated with complexions) or enrichment (above solubility limit) occurs. Furthermore, Dillon and Harmer stated Si concentrations according to the amount of Si added to the alumina slurry, and did not measure the actual Si content.
- Gavrilov et al. studied alumina doped with SiO_2 and MgO using HRSIMS[1]. Although this method is highly accurate, it provides concentration ratios for both grains and grain boundaries, and is not a direct measurement of the concentration in the alumina grains.

Conclusions

- The solubility limit of Si in α-Al_2O_3 at 1600°C is 188±7 ppm.
- The solubility limit of Si in alumina is higher than that of Mg in alumina(132±11ppm) and Ca in alumina (51±1ppm) at 1600°C [3,5].

Acknowledgments

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