

Transient Dopant Segregation and Precipitation in Yttrium-doped Alumina

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Yttrium segregation at the grain boundaries (GBs) of polycrystalline alumina was quantified previously as a function of the Y-content by different research groups [1-4]. With increasing Y-doping, the GB excess rises through a maximum and is expected to be stable when the activity is pinned by the presence of precipitates. However, there is a surprisingly wide variation in the reported average levels of excess Y ($\Gamma_Y = 3.0\text{--}7.0$ Y-atoms/nm²) at the GBs at solute saturation [3-5]. This investigation seeks to understand the reasons behind the inconsistencies in the reported excess yttrium values.

Ultra-pure $\alpha\text{-Al}_2\text{O}_3$ powders doped with 2000 - 3000 ppm ($\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$) Y were pressed and then sintered between the temperatures 1500°C and 1650°C for 2 to 12 hours [4]. The excess Y adsorption levels at the GBs, the local atomic and electronic structure of the precipitates and the bulk $\alpha\text{-Al}_2\text{O}_3$ and the chemical compositions were measured utilizing a dedicated scanning transmission electron microscope (STEM) VG HB 501 UX (spatial resolution of 0.6 nm), equipped with a cold-field-emission gun, an energy dispersive x-ray spectrometer (EDS), and a parallel electron energy loss spectrometer (EELS). Precipitates in the microstructure were investigated using EDS and electron-loss near-edge structure (ELNES) analysis [6] and GB chemistries determined as reported previously [4]. The absorption corrected experimental $k_{(\text{Y}/\text{Al})}$ -factor was determined using reference standards of YAP (YAlO_3) and YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$). For this STEM operating at 100 keV, the $k_{(\text{Y}/\text{Al})}$ -factor approximated to zero-thickness was 1.12 ± 0.02 . For all EDS spectra, specimen thicknesses were measured using EELS and the Y/Al ratios are corrected for absorption and beam broadening.

Two different types of yttrium aluminate precipitates were observed in these samples; these differed in terms of crystallography and also the size and the shape of the particles. FIG. 1 shows annular dark-field (ADF) STEM images of these two types. The isometric (Type I) precipitates are YAP, unexpectedly present as a metastable phase, with a typical grain size of 200 nm or less. Precipitates of the second type (Type II) are irregularly shaped having up to four times larger grain sizes than the Type I precipitates. The type II precipitates are YAG and found near YAP precipitates in the samples heat-treated at higher temperatures or for longer durations. GB excess measurements of Y segregation revealed that GBs contain on average 5.5 ± 0.9 Y-atoms/nm² when only YAP is present in the samples. GBs in the samples having both YAG and YAP precipitates contain an average excess Y of 4.2 ± 1.2 Y-atom/nm² (Figure 2). In the microstructure of a saturated polycrystal, the solute atoms can be distributed in the bulk, at the GBs and on the free surfaces or they can precipitate out as second phase particles. The partitioning of the dopants is governed by their activities in these respective features. Thus, the chemical equilibrium between a precipitate and the segregant level is connected to the precipitate chemistry. The variation of the type of the precipitates could locally modify the amount of the segregated dopant at the GBs. At equilibrium YAG is the stable precipitate. Different groups reported precipitation of YAG previously [3-5], but it is uncertain that careful identification was always done to preclude the presence of YAP. Thus, a sample that contains YAP or both types of precipitates (YAP+YAG) is believed to be in a transient state. It is possible that equilibrated samples with only YAG precipitates have a GB excess Y-concentration that is even lower than measured in this study. In retrospect, this study shows that all the values reported in the previous literature may be correct depending on the type of precipitates they contain. The present work has shown that two different precipitate types can –even if only transiently – co-exist in Y-doped $\alpha\text{-Al}_2\text{O}_3$. The associated differences in boundary chemistry could of course have further implications on properties.

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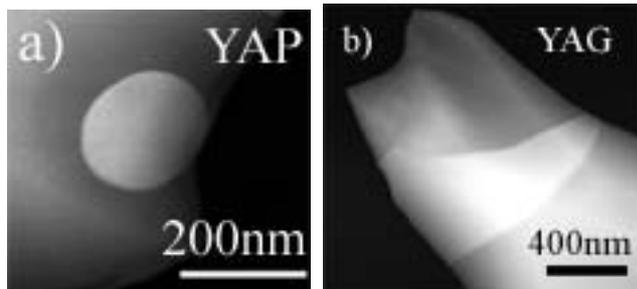


FIG. 1. ADF-STEM images of (a) YAP, and (b) YAG precipitates.

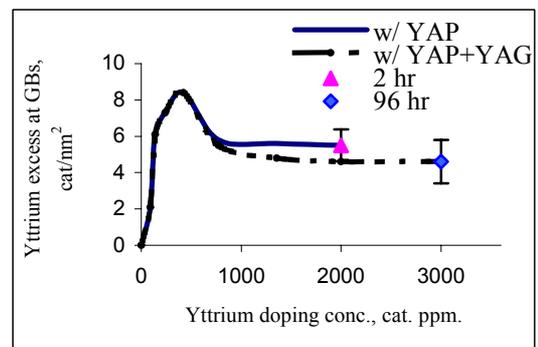


FIG. 2. Saturation Γ_Y with YAP and YAP+YAG