Y segregation behavior controlled by the transient precipitation in saturated Y-doped alumina

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The two orders of magnitude improvement in creep resistance of Y-doped polycrystalline alumina is believed to be related to the segregation of large Y ions to the grain-boundary core structure [1]. The effect of Y-segregation was recently evaluated by theoretical studies, which confirmed that in contrast to undoped alumina, Y-segregation increased the bond strength at the grain-boundary core and consequently, the resistance to creep [2]. Therefore, controlling the Y segregation levels at grain boundaries could have a significant impact on the grain boundary strength and on the final mechanical properties of the whole ceramic bulk. Several investigations showed that in high-purity alumina doped with Y, the initial Y grain-boundary excess concentration increased monotonically to the point where the grain boundaries were saturated with a critical amount of Y. Above this level Y−Al−O precipitates were formed and the excess concentration of Y at the grain boundaries levelled off at a constant value. A further increase in the amount of Y-dopants only resulted in an increased volume of precipitates. Until recently this postulates were widely accepted in the scientific community implying that in the saturated Y-doped alumina the amount of Y that can segregate to the grain boundary is a fixed value. However, our recent results obtained in investigations of saturated Y-doped alumina suggest that newly discovered transient precipitation behaviour can be applied to control the amount of Y at grain boundaries [3].

For that case ultra-pure α-Al_2O_3 powders doped with different amounts of Y were pressed and then sintered at temperatures between 1350°C – 1650°C for 2 to 12 hours. The excess Y adsorption levels at the grain boundaries, the local atomic and electronic structure of the precipitates and the bulk alumina were measured utilizing a field-emission transmission electron microscope (TEM) JEM-2010F UHR, Cs=0.5nm, equipped with an energy dispersive x-ray spectrometer (EDXS), and a parallel electron energy loss spectrometer (EELS). To determine the precipitate types an ELNES analysis was performed by means of a finger-printing method with reference standards of pure α-alumina and three different Y-Al-O phases with a known structure and composition: YAM ($Y_4Al_2O_9$), YAP ($YAlO_3$) and YAG ($Y_3Al_5O_{12}$). The excess Y segregation levels at grain boundaries were measured by applying the spatial difference box method.

To verify the connection between the transient precipitation in Y-doped alumina and the amount of segregated Y to the grain boundary core two extreme cases are presented in this work. Namely, Y-doped alumina samples where either only YAP or YAG precipitates were observed. In the case of 4 at.% Y-excess alumina sintered at 1450°C for 2h only YAP ($YAlO_3$) precipitates were found in the microstructure although the binary equilibrium phase diagram between Al_2O_3 and Y_2O_3 predicted $Y_3Al_5O_{12}$ (YAG) phase. A TEM image of three neighboring alumina grains with the YAP precipitate located at the grain boundary is shown in Fig. 1(a). On the contrary, YAGs were the only precipitates observed in Y-doped (10 at.%) alumina sintered at 1500°C for 10h [Fig. 1(b)]. Background-subtracted EEL spectra taken from the described precipitates and corresponding standard phases are shown in Fig. 2. The

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YAP precipitates were isometric in shape with a typical size of 200 nm or less, whereas YAG precipitates were more irregularly shaped and were generally up to four times larger than YAPs. The Y-excess grain boundary concentrations (Γ_Y) were measured on marked grain boundaries in the vicinity of precipitates (Fig. 1,2). The average Γ_Y values measured at grain boundaries associated with the YAP were 8.5±0.8 at./nm2, which is significantly higher than the Γ_Y value of 2.8±0.8 at./nm2 measured on grain boundaries close to YAG precipitate.

Grain boundary measurements performed in this study clearly show that Γ_Y, which is fixed by the activity of the precipitate, even only in the transient state, is related to the precipitate chemistry. In general, the precipitate, which is richer with Y will equilibrate the Y segregation levels at grain boundaries towards higher values. That might have further implications on designing special grain boundaries with controlled grain boundary bond strength.

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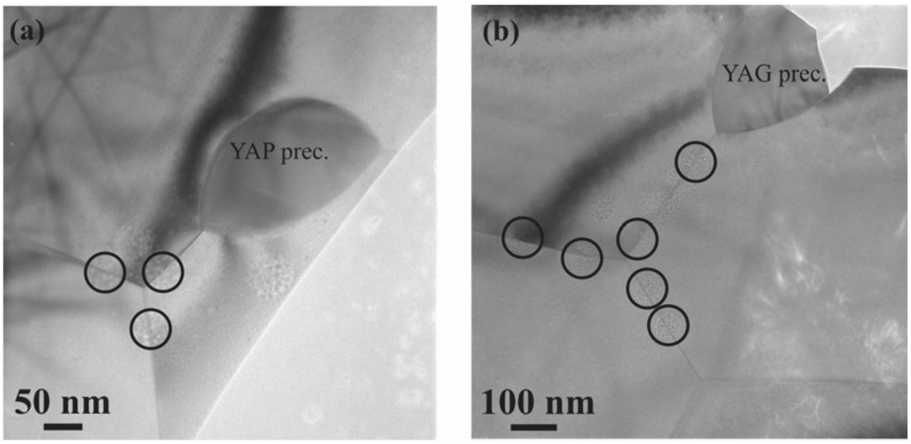

Figure 1. TEM images of neighbouring alumina grain with (a) YAP and (b) YAG precipitate. The Γ_Y values were obtained from the grain boundary regions marked by circles.

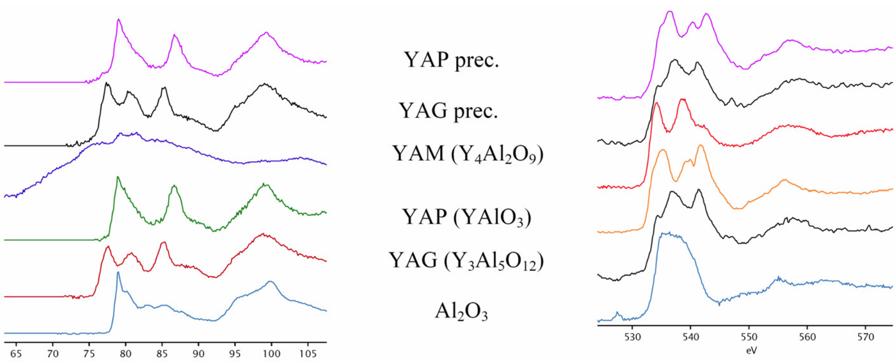

Figure 2. (a) Al-L_{23} and (b) O-K ELNES of precipitates and related Y-Al-O standard phases.

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