Electron-Loss Near-Edge Structure Analysis of Precipitates in Yttria-doped Alumina

Sašo Šturm[1*], Mehmet Ali Gülgün[2], Rowland M. Cannon[3] and Manfred Rühle[4]

[1]Jozef Stefan Institute, Jamova 39, SI-100 Ljubljana, SLOVENIA
[2]Sabanci University, FENS, Tuzla, Istanbul 81474, TURKEY
[3]Evans Hall (MC 1760), Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
[4]Max-Planck-Institute für Metallforschung, 70569 Stuttgart, GERMANY
*Correspondence: saso.sturm@ijs.si

Yttria-doped alumina (α-Al_2O_3) is being known to have up to two orders of magnitude better creep resistance than pure undoped polycrystalline α-alumina [1]. The improved creep resistance is mainly attributed to the segregation of large yttrium cations to the grain boundary core structure, which leads to the reduced grain-boundary diffusion in comparison to pure alumina. However, owing the very limited solid solubility in alumina matrix (~ 10 ppm), excess yttrium not only segregates at the grain boundaries, but also forms Y-Al-O precipitates. It is generally believed, that the precipitation in the yttria-doped alumina is conducted through the formation of aluminium richest phase, YAG ($Y_3Al_5O_{12}$) [2]. Conversely, our recent studies showed that YAG is not the only Al-Y-O phase, which actually precipitates in this system. The aim of this study was, therefore, a systematic characterization of various precipitates, which were found embedded in the alumina grains and at the grain boundaries.

For this study, ultra-pure α-alumina powder was doped with yttria (3000 ppm Y/Al), pressed and sintered at 1550°C for 12 hours [3]. In order to characterize the local atomic and electronic structure of precipitates with the average size less than 200 nm, a dedicated scanning transmission electron microscope (STEM) VG HB 501 UX (spatial resolution of 0.6 nm), equipped with a cold-field-emission gun and a Gatan Enfina System was employed. An electron-loss near-edge structure (ELNES) analysis was performed by means of finger printing method, i.e. comparing the features in spectra obtained from precipitates with the features in spectra obtained from 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 ($Y_3Al_5O_{12}$). Spectra were typically recorded at relative thicknesses (t/λ) smaller than 0.4. All spectra were corrected for the dark current and channel-to-channel gain variation of the CCD detector. Full width at half maximum (FWHM) of the zero loss was 0.7 eV.

FIG. 1(a) shows an annular dark-field (ADF) STEM image of two types of precipitates, which can be considered representative among twenty-five investigated particles in this specimen. Precipitates of the first type (Type I) were isometric in shape, with a typical grain size of 200 nm. They were found to be located both at the grain boundaries and inside the α-alumina grains. Precipitates of the second type (Type II) were observed only in few cases. These irregularly shaped particles were found mainly at triple junctions of α-alumina grains and had up to four times larger grain size than the Type I precipitates. FIG. 1(b,c) shows background subtracted reference spectra taken from related standards superimposed with spectra taken from the precipitates of both types. Each standard spectrum for Al-L_{23} and O-K edge is showing a unique fine structure, which allows distinguishing them easily. The comparison of ELNES spectra features from Type I and Type II precipitates revealed their belonging to two chemically different species. Furthermore, Al-L_{23} and O-K spectra from the Type I precipitate matched perfectly with the reference spectra taken from YAP standard, while the spectra taken from the Type II precipitate agreed with the spectra taken from YAG standard.

In this work we showed that different precipitate types can co-exist in yttria-doped α-alumina. Furthermore, contrary to previous studies, YAP was the predominant secondary phase in the investigated system. Since the chemical equilibrium between the precipitate and the amount of segregant is connected to the precipitate type, the variation of the latter could locally modify the amount of the segregated dopant at the grain boundaries. As a consequence, non-uniform excess concentration of yttria at grain boundaries could have a significant impact on final creep behaviour of the whole ceramic body.

[1] J. Cho et al, *Acta Mater.*, 47 (1999) 4197
[2] C. M. Wang et al, *Acta Mater.*, 48 (2000) 2579
[3] M. A. Gülgün et al, *Interface Sci.,* 10 (2002) 99

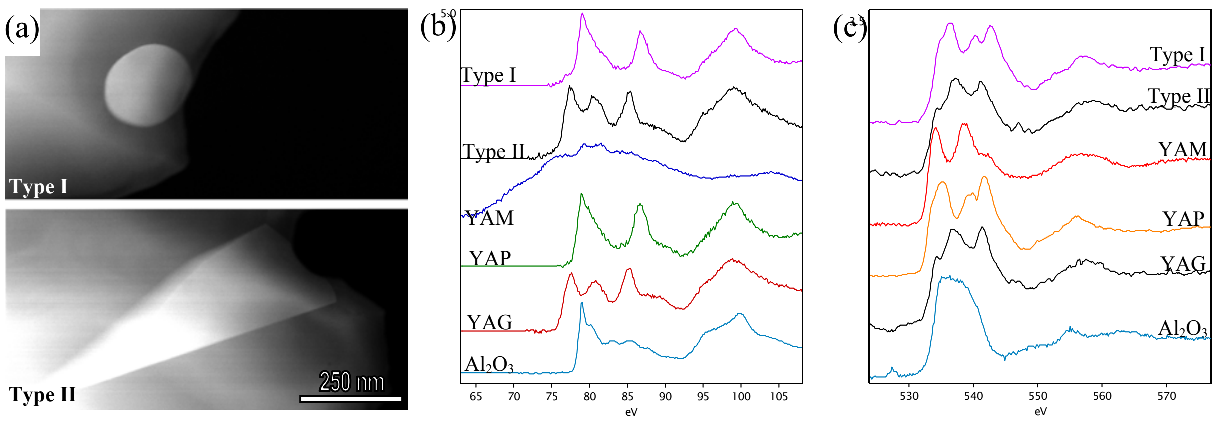

FIG. 1. (a) ADF-STEM images of Type I and Type II precipitates representative in the investigated yttria-doped α-alumina specimen: corresponding (b) Al-L_{23} and (c) O-K ELNES of precipitates (Type I and II) and Y-Al-O related standard phases.