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Investigation of Y-doping in Alumina Grain Boundaries Using STEM

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The addition of small amounts of selected impurities has long been known to control the mechanical and/or electrical properties of certain metals and ceramics. For example, Bi is known to lead to embrittlement of Cu, and Pr is known to substantially increase the varistor effect in ZnO. In both cases, the segregation of the impurities to the grain boundary has been found to be the origin of the improved properties. Yet, only recently have atomic models of impurity segregation to grain been investigated experimentally [1]. In this study we use Z-contrast imaging in the STEM to yield fundamental data for developing a model of rare earth impurity segregation in Al2O3 grain boundaries. In particular, the addition of Y_2O_3 has been shown to substantially improve the creep resistance of grain boundaries in alumina [2].

To understand the changes of the grain boundaries properties from an atomic perspective, a pair of Σ31 bicrystals was made using the diffusion bonding technique. One bicrystal was made of pure alumina, and the other had a layer of Y_2O_3 in aqueous solution deposited on the bonding surface before joining. After successful joining of the bicrystal pair, TEM specimens were fabricated using standard mechanical polishing followed by ion beam thinning. High resolution Z-contrast imaging in the STEM was performed to acquire detailed atomic structural information for both bicrystals. Results show that both bicrystals were joined smoothly across the interface. Images show nearly identical structural units along both grain boundaries (figures 1a and 1b), suggesting that Y segregation is simply substitutional. For the Y-doped bicrystal, atomic columns that contained sites of preferential Y segregation appeared much brighter than the neighboring columns due to the image intensity of in Z-contrast imaging is approximately proportional to the atomic number squared. From the image Y can be seen to be segregated to specific atomic sites along the grain boundary plane.

Finally, static lattice calculations were performed to investigate the energetics of Y doping along the grain boundary. These calculations used a Buckingham type ionic potential. As the images suggested that the Y doping is simply a substitution on the cation sublattice, calculations were done to find the lowest energy state of the undoped grain boundary first. The minimum energy structure showed good agreement with the Z-contrast image (figure 2). Using the undoped grain boundary structure, the energetics of Y substitution on various sites. Results show that for the Σ13 grain boundary specific sites occupying a large open space are strongly preferred to facilitate Y substitution in comparison to other sites (figure 3). These sites coincide with the sites that were found experimentally. A qualitative model for the increase in creep resistance will be discussed.

[1] G. Duscher, M.F. Chisholm, U. Alber, M. Ruhle, "Bismuth-induced embrittlement of copper grain boundaries," *Nature Materials* **3** 621-626 (2004)

[2] K. Matsunaga, H. Nishimura, H. Muto, T. Yamamoto, Y. Ikuhara, "Direct measurements of grain boundary sliding in yttrium-doped alumina bicrystals," *Appl. Phys. Lett.* **82** 1179-1181 (2003)

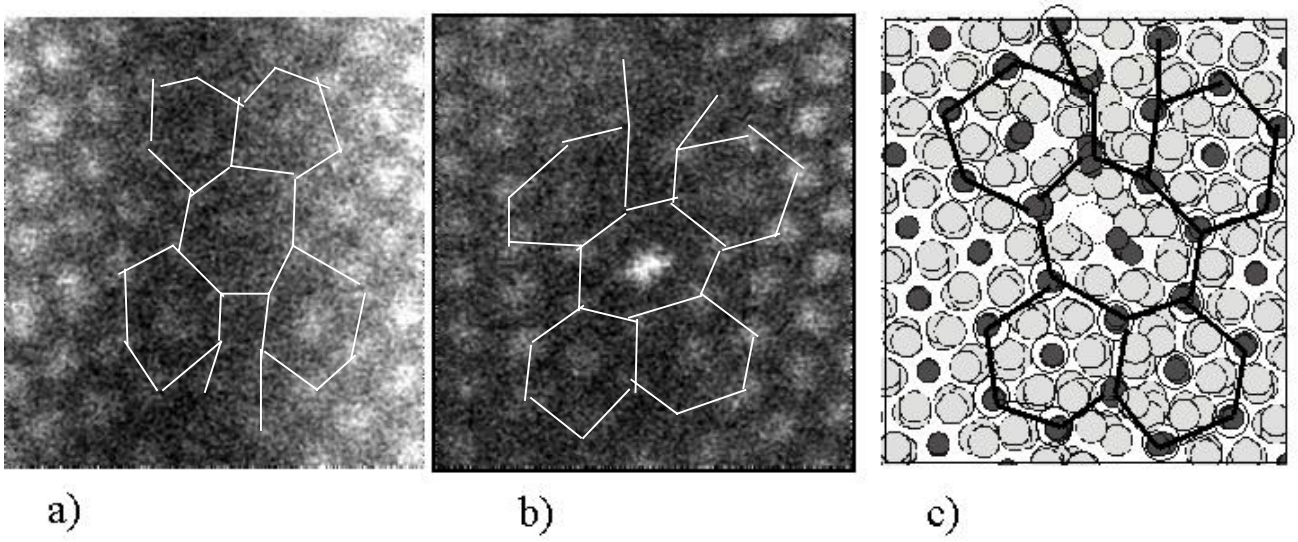

Figure 1: Z-contrast STEM images of a) pure Σ13 grain boundary in alumina, b) Y-doped Σ13 grain boundary, and c) schematic of the lowest energy grain boundary structure obtained by static lattice calculations for pure alumina. The grain boundary structure of both the pure and Y-doped have the same columnar arrangement suggesting that Y exists at the grain boundary by replacing Al ions on the cation sublattice. The heavy Y appears very bright in the Z-contrast image allowing easy recognition of the Y containing atomic columns.

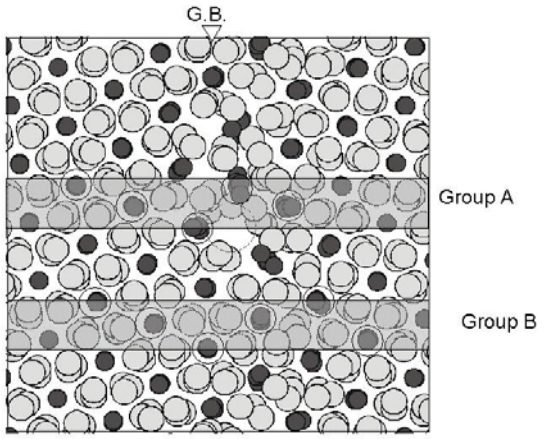

Figure 2: Schematic of showing the location of the various grain boundary cation sites used to calculate the substitution of Y for Al.

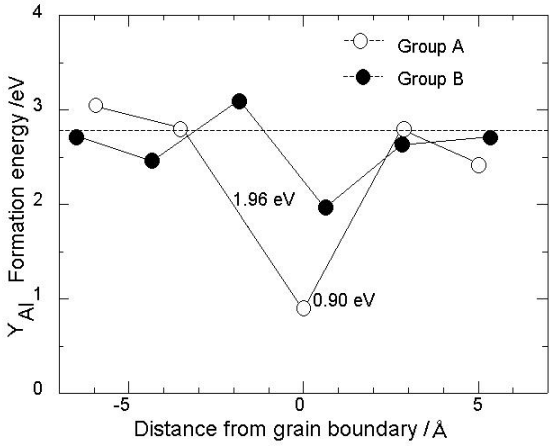

Figure 3: Results for the static lattice calculations showing the formation energies of Y substitution on Al sites for the different sites shown in figure 2.

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