Diffusion in yttrium aluminium garnet at the nanometer-scale: Insight into the effective grain boundary width

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ABSTRACT

Atomic diffusion along grain boundaries in solids is a key process in many geological environments and in ceramics research. It is closely related to the grain boundary width, which is an important parameter in numerous equations describing diffusional or rheological processes, including plastic deformation of polycrystals, intergranular failure, and recrystallization. Here, we studied diffusion along a single well-characterized, near Σ5 grain boundary in yttrium aluminium garnet (YAG) using different transmission electron microscopy methods at atomic resolution. For the diffusion experiment, YAG thin-films containing Yb as diffusant were deposited perpendicular to the grain boundary on the bicrystal. We investigated the grain boundary using a focal series in combination with multislice calculations that yield the electron exit wave. This, coupled with chemically sensitive Z-contrast images, as well as the Yb distribution over the grain boundary measured using electron energy loss spectroscopy, show the zone of enhanced Yb diffusion parallel to the grain boundary. This zone of enhanced diffusion is often considered as the effective grain boundary width.

Profiles from the boundary into the crystal volume suggest a highly permeable zone of about 18 nm, which we assume to be the effective grain boundary width for diffusional processes. The effective width strongly differs from the structural grain boundary width of about 2 nm in the present study. Furthermore, it is much shorter compared to the calculated volume diffusion profile. We conclude that the combination of small samples and transmission electron microscopy at atomic resolution are excellent tools to study varying processes, such as diffusion, deformation, or reactions at the atomic scale.

Keywords: Grain boundary, diffusion, width, grain boundary width, deformation, rheology, recrystallization

INTRODUCTION

Individual mineral grains in Earth’s interior are separated by phase or grain boundaries. Their structure and interface chemistry impact the bulk properties of rocks and thus play a pivotal role in numerous geological disciplines (Fyfe et al. 1978). Diffusional or rheological processes are described using several equations, which include the effective grain boundary width, δ (Dillon and Harmer 2007; Farver and Yund 1991), as an imperative parameter (Kaur et al. 1995).

The effective grain boundary width is defined as the zone of enhanced diffusion around a grain boundary (White 1973) and results from strain induced by misfit of the adjacent crystal lattices. In ionic crystals, the effective grain boundary can be accompanied by a space-charge layer (Kingery 1974; Kliwer and Koehler 1965; Lebovec 1953). The structural (or physical) grain boundary width, in contrast, is defined as the distance between two adjacent crystal lattices.

Chemical segregation refers to the accumulation of certain elements at grain and interphase boundaries, which usually extends over a restricted width along the grain boundary (Hiraga et al. 2003, 2004; Kaneko et al. 2000; Wirth 1996). Both the effective grain boundary width and the width of segregation are affected by: (1) lattice misfit of the adjacent grains, (2) misfit lattice strain due to the difference between the size of a solute ion and that of the ideal strain-free lattice site (Hiraga et al. 2007; Hiraga and Kohlstedt 2007), and (3) in ionic crystals a space charge layer can be present. Because both widths result from the same phenomena, it stands to reason that both show a similar extent. On the other hand, chemical segregation during grain boundary diffusion is considered as an additional factor in different solutions to the diffusion equation (e.g., the equilibrium segregation factor, s, Mishin and Herzig 1999). Furthermore, if the solute atom has the same diameter as the ideal occupant of the crystal lattice, it will not introduce additional strain. Therefore, the present scenario is ideal to study the effective grain boundary width; Y and Yb have the same valence state (3+) and comparable ionic radii (~3% difference, Shannon 1976). Every solute atom that is considerably smaller or bigger might cause subtle changes in the grain boundary width and its structure. Element concentration contours, i.e., the concentration distribution in two dimensions, resulting from diffusion experiments can be measured on a nanometer scale (as in principle shown here). From these data s, δ, the volume diffusion coefficient (D), and the grain boundary diffusion coefficient (D_e) can be principally determined simultaneously from one experiment (Dohmen and Milke 2010).