

Chemical mass transfer in polycrystals and polyphase aggregates

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Chemical mass transport may be rate limiting in mineral reactions, in particular when a fluid or melt phase is absent. Whereas volume diffusion coefficients of major and trace elements have been determined for a variety of minerals, attempts to assess chemical mass transport along grain- and phase boundaries are comparatively scarce. Here we present three experiments that address chemical mass transfer (1) along an isolated grain boundary, (2) in a polycrystal, and (3) at a migrating reaction front.

In a first example yttrium/ytterbium interdiffusion is investigated in a synthetic Yttrium Aluminum Garnet bicrystal (YAG, $Y_3Al_5O_{12}$). Bicrystals with near $\Sigma 5$ (210)/[100] grain boundaries were synthesized by direct bonding. HRTEM indicates a structural grain boundary width of 1 to 2 nm. The bicrystals were coated with 100 to 200 nm thick thin-films with an $Yb_{1.065}Y_{1.578}Al_{5.357}O_{12}$ composition using Pulsed Laser Deposition and annealed at 1350 to 1450°C for up to 24 h. Element concentrations were analyzed using TEM-EDX applied to 20 by 40 nm scanning areas on lamellae of about 100 nm thickness. This revealed preferential penetration of Yb into the bicrystal along the grain boundary as compared to the volume of the YAG crystal. During annealing the thin film diffusant source gradually crystallizes and within two hours changes from amorphous to homoepitactic. The associated change in the transport properties of the thin film complicates the extraction of diffusion coefficients. The influence of successive crystallization of the thin film on the evolution of concentration profiles is assessed by numerical modeling, and diffusion coefficients of $D_{gb} = 10^{-18} \text{ m}^2/\text{s}$ and $D_v = 10^{-21} \text{ m}^2/\text{s}$ are obtained for the interdiffusion of yttrium and ytterbium along the grain boundary and in the volume of the YAG bicrystal, respectively.

In the second example growth of polycrystalline spinel reaction rims at the interface between periclase and corundum at 1350°C and ambient pressure with uniaxial load corresponding to compressive stresses of 3 to 30 MPa is investigated. Rim growth occurs by interdiffusion of Mg^{2+} and Al^{3+} through the spinel-layer. The position of the original periclase-corundum interface is readily discerned from a change in the internal microstructure/texture of the spinel layer as identified by crystal orientation imaging and is compatible with fluxes of 3 Mg^{2+} versus 2 Al^{3+} . When single crystal starting materials are used, a pronounced increase in rim thickness with increasing load is observed. Such an effect is, however, absent, if polycrystalline corundum is used as a starting material. This is due to the fact that, depending on the load, spinel reaction rims that grow from single crystal starting materials obtain different textures, whereas spinel that grows from a corundum polycrystal always shows the same type of texture, irrespective of the stress. In single crystal experiments at low load, spinel grows epitaxially on corundum with [111] spinel parallel to [0001] corundum and with a strong prevalence of $\Sigma 3$ 60°@[111] twin boundaries. In contrast, spinel shows a successively stronger epitactic relation to periclase at higher load and large angle grain boundaries become dominant. The rim growth rate increases by a factor of about 4, corresponding to a change in effective bulk component diffusivities from $8 \cdot 10^{-16}$ to $2 \cdot 10^{-14}$

m^2/s with this change in grain boundary character distribution indicating that diffusivities are substantially higher in large angle grain boundaries than in the densely packed $\Sigma 3$ (111) twin boundaries. This effect outweighs the often-propagated influence of grain size on the transport properties of polycrystals.

In the third example chemical mass transport along a migrating reaction front is considered in the context of symplectite formation. Typically symplectitic replacement occurs at a sharp reaction front, producing a vermicular or lamellar intergrowth with a characteristic wavelength. We present an example of symplectite synthesis in the system CaO-MgO-SiO_2 , where at 900°C and 1.2 GPa, monticellite with a8 mole% forsterite component decomposes into a symplectite comprised of more pure monticellite and forsterite and into a merwinite - forsterite symplectite. The 3D geometry of the resulting microstructures is reconstructed from FIB serial sectioning. An irreversible thermodynamic model is developed that provides quantitative relations among the thermodynamic driving force (reaction overstepping), the characteristic dimension of the symplectite microstructure (wavelength), the interfacial energy, and component mobility.