



## Structure of reaction interfaces and their migration during diffusive phase transformations

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The structure of crystalline interfaces plays an important role in solid-state reactions. The relatively simple system of metal oxides  $\text{Al}_2\text{O}_3/\text{MgAl}_2\text{O}_4/\text{MgO}$ , i.e. corundum/spinel/periclase, provides an ideal model system for investigating the mechanisms underlying the migration of interfaces during diffusive phase transformations. Spinel reaction rims have been formed in between the corundum and periclase reactants with controlled crystallographic orientation at  $1350^\circ\text{C}$ , dry atmosphere and under uniaxial load (Jeřábek et al. 2014). The atomic structure at both corundum/spinel and periclase/spinel interfaces has been characterized using aberration-corrected scanning transmission electron microscopy (STEM). The growing spinel is topotactic to both the corundum and the periclase reactant crystals and shows a semicoherent lattice contacts between trigonal corundum and cubic spinel, and between cubic spinel and cubic periclase. At the corundum/spinel interfaces the oxygen sublattice transforms from hexagonal close-packed (hcp) stacking in corundum to cubic close-packed (ccp) stacking in spinel. Partial dislocations associated with steps along two close-packed oxygen layers are observed at the interface. Progression of the corundum/spinel interface into corundum is accomplished by the glide of these partial dislocations at the interface accompanied by the exchange of  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  cations (Li et al. in rev.). The periclase/spinel interface represents the ccp/ccp contact characterized by similar lattice spacing of the two compounds. STEM atomic images show that the periclase/spinel interface has a periodic configuration consisting of curved segments (convex towards periclase) joined by regularly spaced misfit dislocations occurring every  $\sim 4.5$  nm ( $\sim 23$  atomic planes). This configuration observed in periclase/spinel interface sections along two perpendicular  $\langle 100 \rangle$  directions indicates that the 3D geometry of the interface is a grid of convex protrusions of spinel into periclase with each minimum between the protrusions occupied by a misfit dislocation (Li et al. 2016). This geometry results from the coupling between long-range diffusion, which supplies  $\text{Al}^{3+}$  to and removes  $\text{Mg}^{2+}$  from the reaction interface, and interface reaction, in which climb of the misfit dislocations is the rate-limiting process. The extra oxygen atoms required for dislocation climb were likely derived from the reactant MgO, leaving behind oxygen vacancies that eventually form pores at the interface. The glide dominated propagation of the corundum/spinel interface, which is a conservative mechanism with respect to the oxygen sublattice, contrasts with the non-conservative climb dominated propagation of periclase/spinel interface. This implies relatively high mobility for the first, and a relatively low mobility for the latter interface, explaining the systematic deviations from equilibrium Al/Mg partitioning between the phases at the two interfaces (Abart et al. 2016).

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