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Nucleation and reaction rates controlled by local reaction volume and reaction-induced stress - spinel layer growth as an example

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We observed the growth of spinel *sensu stricto* ($MgAl_2O_4$) between periclase (MgO) and corundum (Al_2O_3) in thin films deposited by the pulsed laser deposition method on crystallographically oriented single crystal substrates. The starting samples consisted of cut and ultra polished single crystals of either corundum (parallel (0001)) or periclase (parallel (111)) and an amorphous source layer of the respective reactant that in the very first stages of the experiments became polycrystalline. The cutting direction in the substrate minerals ensures that the substrate phases start to react along their close-packed hexagonal oxygen layers which allows topotactical growth of the newly formed spinel. The entire layer setup on the substrate crystals was only a few 100 nm thick. The growth of these spinel product layers was monitored in-situ using a heating attachment and synchrotron X-ray diffraction. From the reacted samples we took electron transparent foils by the focused ion beam method and analysed them ex-situ by TEM.

At 1000°C we found a difference in spinel growth rate between one and two orders of magnitude between the two substrates, all other parameters held constant. At 900 and 1000 °C spinel had formed after one hour by 0.004 nm/s (900°C) and 0.034 nm/s (1000°C) on corundum substrate, while on periclase substrate the reaction had gone completely through the Al_2O_3 source layer transforming it to spinel by at least 15-30 times higher reaction rates (boundary values) and probably even faster. At 800°C no reaction occurred between periclase layers and corundum single crystals, whereas spinel crystallized at a (linearized) rate of 46 nm/h on periclase single crystals.

We explain our findings by the local reaction volume at the periclase-corundum interface. Many studies (including this one) have established that spinel grows by cation exchange in a rather immobile oxygen sublattice. This mechanism implies a negative volume change at the Sp-Per interface (by -13 %) and a positive volume change at the Sp-Cor interface (by +17 %). We observed in TEM images formation of porosity at the Sp-Per substrate interface and lattice strain in the polycrystalline corundum substrate at the Sp-Cor substrate interface, both observations being fully in line with the respective local volume changes. We infer that the local stress field between the growing reaction layer and the rigid single crystal substrate is responsible for the dramatic effect on both the nucleation and reaction rates. With respect to minerals growing at dry conditions in the Earth's crust (granulite facies) we infer that rates of reactions might strongly depend on local volume changes at interfaces, that reactions are impeded by compressive reaction-induced stress applied to rigid neighboring grains, and that nucleation of thermodynamically stable phases on grain boundaries might be suppressed by a positive reaction volume.