Replacement reactions are widespread in nature where minerals are often exposed to significant changes in physical (p, T) and geochemical conditions [1] . During progressive recrystallization, the precursor mineral is transformed into a more stable phase or mineral assemblage. Topotaxial reactions result in the formation of coherent structural intergrowths. During thermally induced oxidation of ilmenite (FeTiO$_3$), for example, the transformation products are structurally coherent rutile (TiO$_2$) and hematite (Fe$_2$O$_3$). Many samples of coherent rutile/hematite intergrowths are found in nature [2] and the transformation is also of high technological importance, for example in the production of titania from ilmenite [3]. In our work we studied atomic-scale mechanisms of ilmenite to rutile/hematite transformation on thermally treated natural single crystal of ilmenite from Zagi Mountain (Pakistan). The crystal was cut into oriented cuboids, which were heated at 600 to 1000°C in air for different periods of time (1, 12, 100 hours). The products were characterized by scanning and transmission electron microscopy (SEM and TEM) in two perpendicular zone axes ([0001]$_{ILM}$ and [10-10]$_{ILM}$).

After thermal treatment at 800°C and higher we observed progressive exsolution of rutile lamellae in three directions intersecting at 60° within the parent ilmenite. The formation of lamellae starts at the surface and proceeds into the interior of the single crystal. It is accompanied by the formation of cracks as a result of volume change and the formation of a hematite layer on the surface, indicating oxidation and diffusion of Fe ions to the crystal surface (Fig. 1a). The number of rutile lamellae and the thickness of the hematite layer increase with heating time and temperature (Fig. 1b). TEM analyses revealed that rutile and ilmenite are in a coherent orientation relationship: $<010>(100)_{RUT} || <0001>{11-20}_{ILM}$ (Fig. 2a,b). This confirms that the transformation is structurally controlled by ion diffusion though the common hcp oxygen sublattice. The suggested mechanism of transformation includes initial oxidation of Fe$^{2+}$ in ilmenite to Fe$^{3+}$ and its diffusion to the surface of the single crystal. The excess Ti ions exsolve within the parent ilmenite structure in the form of rutile lamellae. TEM analyses revealed the presence of an intermediate Ti-O phase prior to the formation of rutile and it is characterised by additional superstructure reflections, indicating that it is a crystallographic shear (CS) phase, possibly containing locally reduced Ti$^{3+}$ ions (Fig. 2c).

2. Armbruster, T., Neues Jahrbuch für Mineralogy, 1981. 7

Acknowledgement: The financial support of the Slovenian Ministry for Science under the projects PR-04364 and J1-4167 are gratefully acknowledged.
Fig. 1: (a) Progressive recrystallization of ilmenite after 12 hours at 800°C in air results in the formation of rutile lamellae intersecting at 60° and a hematite layer on the crystal surface. (b) At higher temperature, the thickness of rutile lamellae and the width of the surface hematite layer are increased.

Fig. 2: (a) TEM image of ilmenite with rutile lamellae (800°C/12h). (b) Diffraction pattern taken across a typical rutile/ilmenite contact reveals the \(<010> (100)_\text{RUT} || <0001> (11-20)_\text{ILM}\) orientation relationship. (c) Some rutile lamellae exhibit additional reflections, characteristic for a CS intermediate phase.