Atomic structure and formation mechanism of (301) rutile twins from Diamantina (Brazil)

NINA DANEU,1,* HERBERT SCHMID,2 ALEKSANDER REČNIK,1 AND WERNER MADER2

1Department for Nanostructured Materials, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
2Institut für Anorganische Chemie, Universität Bonn, Römerstrasse 164, D-53117 Bonn, Germany

ABSTRACT

Rutile (TiO2) twins from Diamantina in Brazil were investigated using analytical transmission electron microscopy methods. High-resolution transmission electron microscopy (HRTEM) imaging of (301) twinned rutile revealed the existence of a coherent interlayer at the twin boundary. The interface lamella, with a lateral width of a few nanometers, consists of ilmenite (FeTiO3) containing some Al. The orientation relationship between the ilmenite lamella and the epitaxial rutile crystals is (01T0) || (0001)I || (301) || (010)R. The ilmenite-rutile interfaces are atomically sharp and devoid of misfit dislocations that would compensate for the lattice mismatch between the two structures. The Ti/Fe concentration ratios, as measured in the twin lamella by means of the variable-beam-diameter energy-dispersive spectroscopy (VBD/EDS) technique, correspond to ilmenite. The valence-sensitive features in electron energy-loss spectra (EELS) revealed that the Fe in the twin lamella adopts a divalent oxidation state (Fe2+), which is characteristic of ilmenite. The lattice mismatch between the ilmenite and rutile appears to be compensated by the incorporation of Al into the ilmenite. The presence of goethite-related reflections and the existence of nanotwins in the ilmenite lamella imply that it formed via a thermally induced dehydration process from an oxyhydroxide precursor mineral with a tivanite-type structure. This lamella subsequently served as a nucleation site for the epitaxial growth of rutile domains in a (301) twin configuration.

Keywords: Rutile, ilmenite, corundum, hematite, epitaxy, twinning

INTRODUCTION

Rutile is a rare but widespread mineral, being found as of small grains in various igneous rocks or as an accessory mineral in metamorphic rocks. Due to its high resistance to weathering it is also quite common in sediments and sedimentary rocks. Larger rutile crystals are usually found in granite pegmatites and hydrothermal quartz veins.

Diamantina in Brazil is one of the most famous localities where well-developed single crystals as well as {101} and {301} twins of rutile can be found. Because of the variety of twin-plane combinations, multiple-twinned aggregates of rutile are relatively common (reticulated twinning; sagenite). Characteristic of this locality are large twins with equally developed twin domains having a straight twin contact plane without any macroscopically visible secondary phase in between. According to Force et al. (1996), these features indicate that the crystals formed by growth and not by epitactic/topotactic exsolution of rutile from ilmenite or other hexagonal precursors. Besides naturally grown twins, twinned rutile crystals can also be produced synthetically. For example, the crystallization of TiO2 nanocrystals from solutions (Li et al. 1999) or microemulsions (Wang and Li 2003) results in the formation of rutile twins of both types in co-existence with elongated prismatic single crystals.

One of the most common explanations for the formation of growth twins is based on the assumption of accidental nucleation during the initial stages of crystal growth (Buerger 1945). Penn and Banfield (1998) found that the coarsening of TiO2 nanoparticles under hydrothermal conditions results in the oriented attachment of defect-free nanocrystals and suggested that this would be the major mechanism of twinning and polytypism in macroscopic crystals. However, such an oriented attachment of atoms or clusters of atoms would result in the formation of dopant-free boundaries, which, on the other hand, are characteristic of deformation twins (Suzuki et al. 1991; Lee et al. 1993). Recent investigations of growth faults (such as twin boundaries) in various synthetic materials revealed that such special boundaries not only possess a special crystallographic setting, but also may contain small amounts of foreign atoms that trigger the formation of such polytypic/polysonic faults (Rečnik et al. 2001a).

The formation of growth defects is thus chemically induced, and can be described as an epitaxial chemical reaction between the major phase and the dopant along well-defined crystal planes of the crystal under specific chemical and thermodynamic conditions. After nucleation, crystals with such chemically induced planar faults grow exaggeratedly along the fault direction and always grow to a larger size than the fault-free (normal) crystals. According to this theory, a change in local chemistry across the contact twin boundaries in rutile would be expected, as indirectly predicted by Armbruster (1981), who first proposed that the formation of twinned rutile is a result of oriented overgrowths on structurally related minerals possessing a corundum- or spinel-type structure.

* E-mail: nina.daneu@ijs.si