

Formation of rutile nuclei at anatase {112} twin interfaces and the phase transformation mechanism in nanocrystalline titania

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ABSTRACT

In nanocrystalline anatase coarsened under hydrothermal conditions (250 °C, P_{sat}), the anatase-to-rutile phase transformation is nucleated at anatase {112} twin boundaries formed by oriented attachment. The anatase twin boundary is constructed from structural elements common to rutile. Specifically, rutile nucleation involves displacement of only one half the titanium cations within the twin slab. Subsequent transformation of bulk anatase involves rupture of 7 of the 24 Ti-O bonds per unit cell and cooperative displacement of Ti and O. As the transformation advances into the bulk material, adjacent slabs of anatase octahedra are destabilized, resulting in rapid progression of the transformation of bulk anatase to rutile. The implied chain reaction, scarcity of partly reacted crystals, absence of multiply twinned rutile, and the importance of nucleation at anatase twins indicate a rate law based on slow nucleation and rapid growth. The displacements are comparable to those proposed previously for macroscopic anatase at much higher temperatures, indicating the atomic mechanism is not modified by particle size or temperature, despite the rapid kinetics in finely crystalline aggregates. In addition to the formation of twins, clusters with rutile-like character may occur at some fraction of random anatase-anatase particle contacts. Such interfaces should result in decreased activation barriers for rutile nucleation and, thus, contribute significantly to the observed faster transformation rates in nanocrystalline compared to coarsely crystalline materials.