Characterization of Selective Impurities Segregation in MgO Grain Boundaries using Atomic-resolution STEM-EDS Mapping

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Real materials including ceramics and minerals are, in general, of polycrystalline nature, and the presence of an internal interface between grains, i.e., a grain boundary (GB) often influences significantly their mechanical, electrical and physical properties. Furthermore, a GB can provide shortcut paths for mass transport and also act as nucleation sites for precipitation, corrosion, fracture and plastic deformation, suggesting that it serves as effective sinks for impurities or defects. Therefore, a GB structure characterization including impurities is essential to elucidate how impurities segregation may trigger structural transformation of GBs and consequently modify material properties. Besides, the recent advent of spherical aberration corrector for transmission electron microscopy (TEM) and scanning TEM (STEM) provides direct atomic-resolution imaging of buried interfaces and GBs. Magnesium oxide (MgO) is one of the best characterized crystalline materials including GBs and defects for such microscopic observations, and is often considered as a model oxide system owing to its simple rocksalt structure (with both the Mg and O atoms octahedrally coordinated). Moreover, it also represents a relevant oxide with a broad range of technological applications, e.g. as insulators, heat resistors, substrates, barriers in tunneling magneto resistive (TMR) devices and so forth.

In this work, we investigated the microstructures of MgO "Σ5" and "near-Σ5" (310)[001]GBs (Σ indicates the degree of geometrical coincidence at a GB) in order to understand how the misalignment of tilting angles from the exact Σ5 orientation relationship can modify GB structures at the atomic scale. Also it still remains unknown whether residual impurities are segregated to these coherent or incoherent GBs and how such a segregation can drive GB structure change and thus modify material properties. Here, we applied a bicrystal technique to fabricate symmetrical tilt Σ5 and near-Σ5 GBs with bonding-angles of 36.9° and 35.3°, respectively. STEM observations were performed by Cs-corrected STEM JEOL JEM-ARM300F (300kV, 160kV) and JEM-ARM200F (200kV) with Dual SDD EDS detectors.

The high-angular annular dark-field (HAADF) images and the atomic-resolution EDS mappings revealed formation of periodic array of structure units (SUs) at the GB and co-segregation of calcium (Ca) and titanium (Ti) impurities at the specific atomic sites of the SUs in both GBs. In the Σ5 MgO GB, a periodical super structure is self-organized at atomic scale through interaction between Ca, Ti impurities, vacancies, interstitials, charges, and the SUs. On the other hand, the near-Σ5 GB comprises alternating array of several normal Σ5 GB SUs and one deformed Σ17 GB SU. This kind of a high Σ GB structure can easily be described by two different kinds of low Σ GB SUs, i.e., Σ5 and Σ17 GB SUs. Furthermore, the Ca and Ti impurities strongly segregated to the Σ5 SUs, while they preferred not to segregate to the lattice sites in the Σ17 SU.