Atomic structure analysis of MgO Near-Sigma 5 (310)[001] Symmetrical Tilt Grain Boundary

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Real materials including ceramics and minerals are, in general, of polycrystalline nature, and the prevailing presence of internal interfaces between grains, *i.e.*, grain boundaries (GBs) often influences significantly their mechanical, electrical and physical properties. For example, GBs can provide shortcut paths for mass transport and also act as nucleation sites for precipitation, corrosion, fracture and plastic deformation. In addition, they can also serve as effective sinks for defects and impurities, which may trigger structural transformation of GBs and consequently modify material properties. Therefore, the ability to discover new materials and properties relies on a fundamental understanding of GBs and their associated impurity segregation. Magnesium oxide (MgO) is one of the best characterized oxide materials in terms of GBs and defects, 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. Furthermore, the recent advent of spherical aberration correction for a transmission electron microscopy (TEM) and scanning TEM (STEM) provide direct atomic-resolution imaging of buried interfaces and GBs. With this technique, we previously found that MgO Σ5 GBs (Σ indicates the degree of geometrical coincidence at a GB) can accommodate complex ordered defect superstructures composed of five different types of atomic defects and impurities that remarkably alter electronic and physical properties of GBs [1-2].

In this work, we investigated the microstructures of "near-Σ5" GB in MgO in order to understand how the misalignment of tilting angles from the exact Σ5 orientation can modify GB structures at the atomic scale. Also it remains unknown whether impurities are segregated to the near-Σ5 GB and how such segregation can drive GB structure change and thus modify material property.

Here, we apply a bicrystal technique to fabricate a symmetrical tilt near-Σ5 GB with a bonding-angle deviation of ~1.7±0.1° from the exact Σ5 orientation, *i.e.*, from the (310) plane. (S)TEM observations were performed by JEOL JEM-2010F (200 kV) and JEM-2100F (with Cs-corrector, 200 kV). Finally, we interpreted the GB local structure via mathematical approach based on O-lattice theory [3].

Fig. 1(a) is a dark-field (DF) image shows periodically aligned edge dislocations on the boundary in order to compensate lattice mismatch due to misalignment. The annular bright field (ABF) image in Fig. 1(b) and Fig. 2 reveals that the near-Σ5 GB comprises an alternating array of five ~ six normal Σ5 GB structural units and one deformed Σ17 GB structural unit, and importantly the Ca and Ti impurities are selectively segregated to the Σ5 units, while they are absent at the Σ17 units [4]. This near-Σ5 GB with tilting angle of 35.3° is mathematically equivalent to Σ533 GB on (22 7 0) plane. According to dissociation rule expected by O-lattice theory, this kind of GB with high Σ value can easily dissociate into two low Σ GB with

special structure units, *i.e.*, six Σ5 GB units and one Σ17 GB unit. This mathematical expectation is completely same as the obtained experimental result. The detailed will be reported.

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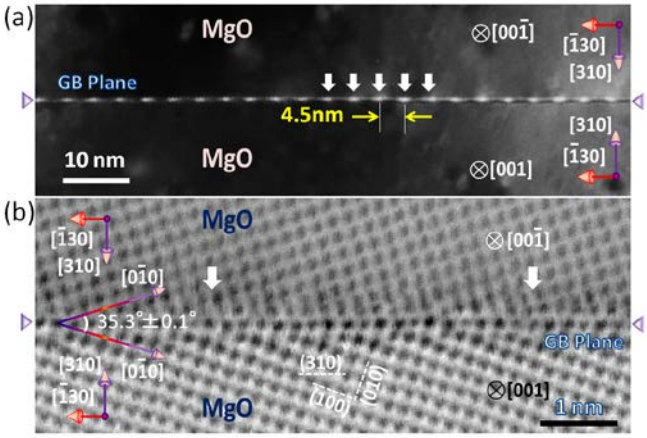

Fig. 1 (a) Dark-field TEM image and (b) ABF-STEM image of MgO bicrystal near-sigma 5 grain boundary.

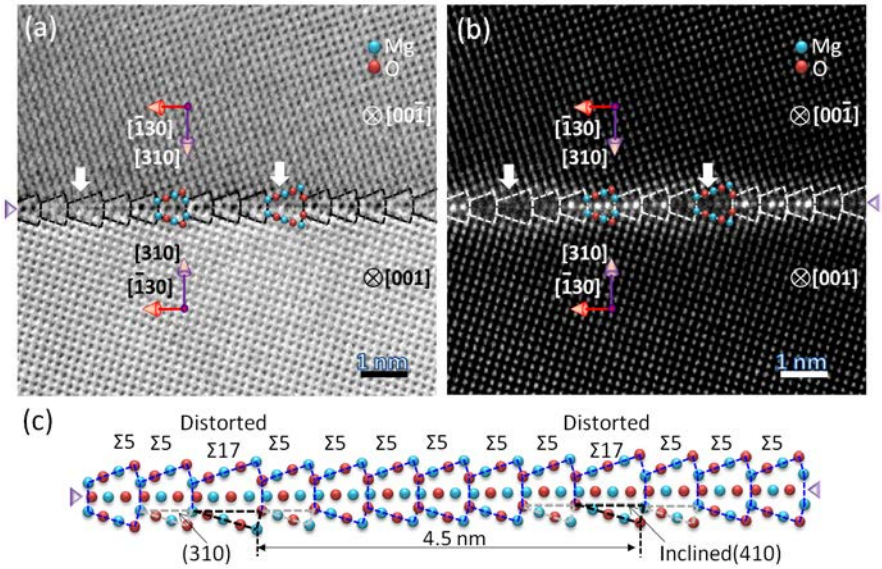

Fig. 2 (a) ABF-STEM image, (b) HAADF-STEM image, and (c) structure model of MgO near-sigma 5 boundary.