Impurity-Induced Structural Transformation of a MgO Grain Boundary

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A combination of atomic-resolution Z-contrast imaging and first-principles density-functional calculations are used to establish that Ca impurities segregating to particular atomic columns in MgO grain boundaries induce a structural transformation. The presence of Ca in the boundary structure is independently confirmed by electron energy loss spectroscopy. The calculated electronic structure indicates that stabilization of the new boundary structure by Ca is a mechanical rather than an electronic effect. [S0031-9007(98)07367-0]

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Small concentrations of impurities that segregate to the grain boundaries of a polycrystal can have a profound effect on the properties of the material. Perhaps the best example is the catastrophic brittle intergranular failure of metals (see, for example, Ref. [1]) that follows the diffusion of certain elements to the relatively open structures present at the boundary core. In most cases, the impurities segregate at substitutional or interstitial sites without significantly affecting the atomic configurations at the boundary. Much of the theoretical work on impurity segregation in grain boundaries is in fact based on such an assumption. A recent example is the prediction by Vitek *et al.* [2] that Bi segregates as a substitutional impurity in certain atomic columns of a grain boundary in Cu.

In some cases, segregated impurities form more complex structures such as glassy or ordered phases [3], induce relative shifts of adjacent grains [4], or induce changes to the dislocation arrays that form the core of the grain boundary [5]. There have also been suggestions and theoretical predictions that segregated impurities may induce a structural transformation of a grain boundary [4,6].

In this Letter we use a combination of experimental and theoretical techniques to conclude that Ca impurities segregating to particular atomic columns in a grain boundary in MgO cause a structural transformation. In particular, direct atomic-resolution Z-contrast imaging [7,8] reveals an atomic structure that is different from the widely accepted structure of the boundary [9], with certain columns appearing with extra brightness. Spatially resolved electron energy loss spectroscopy (EELS) [8,10] confirms that the boundary contains Ca impurities. Theoretical calculations find the normally accepted structure indeed has the lowest energy in the absence of impurities, but the observed structure has the lowest energy when Ca atoms replace Mg atoms in the extra-bright columns in the Z-contrast images.

Magnesium oxide was used in this investigation because it is a rather simple model ceramic material, well suited for both experimental observation and theoretical calculations. Nominally pure bicrystals containing a 24° tilt grain boundary were obtained from Shinkosha Ltd., Tokyo, Japan. The supplier indicated that three impurity elements, Al, Ca, and Fe, are present at concentrations in the parts per million range.

The high-resolution Z-contrast technique was used to form composition-sensitive images in a scanning transmission electron microscope (VG Microscopes HB603U STEM operated at 200 kV). Z-contrast images were formed by scanning a 0.126 nm probe across a specimen and recording the transmitted high-angle scattering with an annular detector (inner angle ~45 mrad). The Z-contrast image gives a directly interpretable, atomic-resolution map of the columnar scattering cross section in which the resolution is limited by the size of the electron probe [7]. Because the Z-contrast image does not reverse contrast, bright features can be directly interpreted as positions of atomic columns. High spatial resolution EELS was used to identify the impurities at the boundary. Spectra were collected using a VG Microscopes HB501UX STEM fitted with a high-sensitivity parallel EELS system.

Figure 1(a) shows the Z-contrast image of the 24° ⟨001⟩ tilt grain boundary in MgO as viewed along the

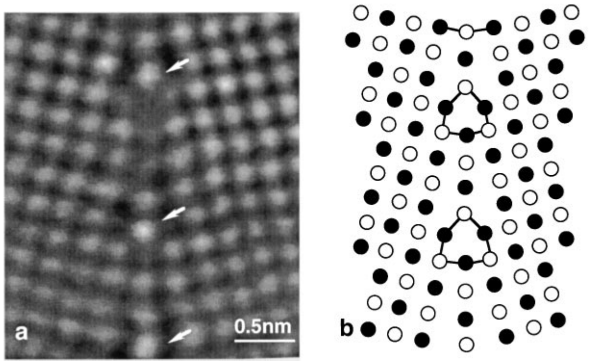

FIG. 1. (a) Z-contrast image of a symmetric 24° [001] tilt grain boundary in a MgO bicrystal. The white arrows highlight boundary columns with extra intensity. (b) Boundary structure model directly determined from the image. The open and closed circles indicate the location of the cations and anions on a single (001) plane.

tilt axis. The boundary between the two grains is seen to be symmetric and to contain an aperiodic sequence of two different atomic configurations, perfect crystal units, and defect structural units. Figure 1(b) is a schematic of the boundary structure directly obtained from the image. The relation between the adjacent crystals is the same as would be expected for a simple rotation of the grains about a common tilt axis. No rigid body translation parallel to the boundary or expansion perpendicular to the grain boundary was detected. Structural units in the grain boundary are indicated in the schematic by solid lines. The closure failure around each unit is found to be $\mathbf{a}\langle 100\rangle$.

The structure of the MgO grain boundary revealed by the Z-contrast image (Fig. 1) is *not* consistent with what has been deduced by theory and experiments in the last two decades [9,11–13]. We will make the case that the structure seen in Fig. 1 is in fact induced by the segregated impurities.

Figure 1(a) reveals that certain columns in the boundary (as indicated by arrows) are brighter than their neighbors. The extra brightness is an indication that impurity elements with atomic numbers greater than that of Mg ($Z = 12$) are segregated to these sites. The bright spots are consistently seen in extended regions of the boundary. While a few sites adjacent to the boundary also appear bright, they are sparsely and randomly distributed. Figure 2 shows the EELS spectrum acquired from a 2 nm $\times$ 3 nm region containing the boundary [8,14]. The spectrum obtained at the boundary clearly shows the presence of Ca in the boundary. No Ca was detected in bulk regions away from the grain boundary. Using the intensity ratio between Ca $L_{2,3}$ and oxygen K edges, the density of Ca atoms is calculated to be about 4 atoms/nm^2 boundary area (equivalent to 0.2–0.3 monolayer) [15]. Combining this information with the Z-contrast image, we estimate that the concentration of Ca in the specific segregation column is $\leq$ 40% of the cation sites. No other impurities were detected at the boundary. It is important to note that Ca segregates to particular columns in the boundary structural units.

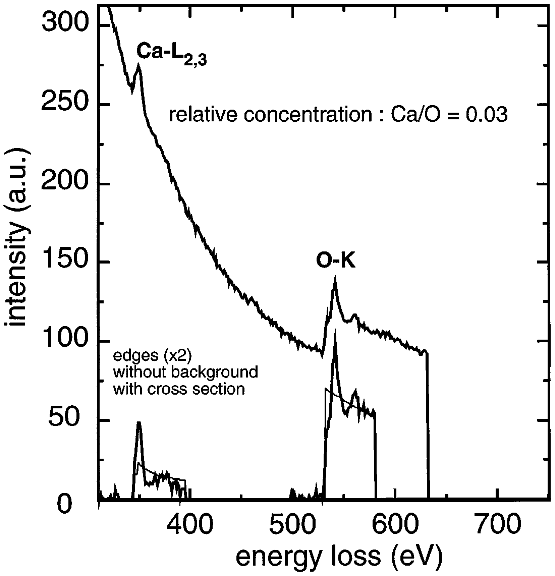

FIG. 2. EELS spectrum from an energy loss range containing both the oxygen K edge and the Ca $L_{2,3}$ edges showing the presence of Ca in the grain boundary region. Calcium is not detected away from the boundary. Also included are spectra with the background subtracted that determine the relative concentration of Ca to O in the boundary region is 0.03.

Kingery [16] first proposed the structure shown in Fig. 3(a) for the 37° symmetric $\langle 001\rangle$ tilt boundary [$\Sigma = 5$ (310) $\langle 001\rangle$] in NaCl-type metal oxides. Subsequent static-lattice simulations [11] found that Kingery's structure is unstable and that the alternative structure shown in Fig. 3(b) is energetically favorable. This structure is made up of arrays of a single structural unit combined with perfect-crystal spacer units. This structural unit appears to be relatively open when compared with that in Kingery's model. We will, therefore, refer to the two structures as *open* and *dense*, respectively. In 1996, Kizuka *et al.* [13] reported phase contrast high-resolution electron microscopy (HREM) observations that are consistent with the *open* structure found by the simulations.

We used first-principles calculations to examine the effect of Ca impurities on the energies of these two grain boundary structures. One complication arose because the 24° tilt boundary studied experimentally is aperiodic (the number of perfect crystal spacer units between each defect structural unit is not constant) so that a finite supercell cannot be constructed. However, one expects that the same structural unit present in the aperiodic 24° boundary may also be present in all $\langle 001\rangle$ tilt boundaries with misorientations between 0° and 37° [11,17]. Calculations were, therefore, performed using a misorientation of 37° which yields the smallest period. The supercells have a periodicity of 0.4211 nm in the $\langle 001\rangle$ direction and 0.664 nm in the direction perpendicular to the $\langle 001\rangle$ axis and along the

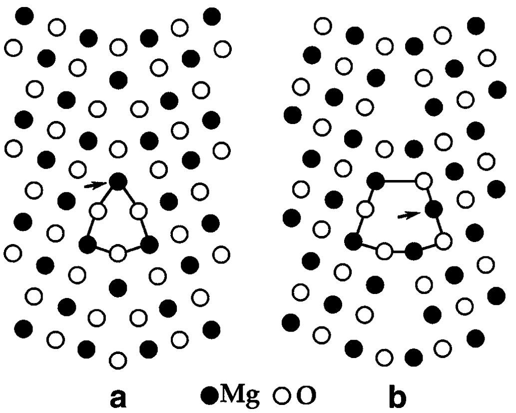

FIG. 3. Grain boundary structure models for a $\Sigma = 5$ $\{310\}$ $\langle 001\rangle$ tilt boundary in NaCl-type ceramics (a) proposed by Kingery [16] (b) calculated by Duffy and Tasker [11], and Harris *et al.* [9] for NiO and MgO, respectively. The site with the largest calcium segregation energy for both structures is indicated with a black arrow.

boundary. We used periodic supercells that contain two oppositely oriented grain boundaries separated by 1.33 nm, twice the distance between neighboring structural units in the boundary, in order to minimize the elastic interactions between boundaries. Each cell contains 40 magnesium and 40 oxygen atoms. A previous study has shown that such a supercell is large enough to adequately eliminate the interactions of the strain fields of the two boundaries [9].

The calculations were performed using density functional theory with the exchange correlation treated in the local density approximation [18,19]. The atomic cores are represented by nonlocal, norm-conserving pseudopotentials of the Kerker type [20] in a separable Kleinmann-Bylander form [21], and defined on a real-space grid [22]. The Ca pseudopotential includes the $3p$ states as valence electrons. The wave functions were expanded in a plane wave basis set with an energy cutoff of 600 eV and the integration over the Brillouin zone was performed using three special k points chosen according to the Monkhorst-Pack scheme [23]. Larger energy cutoffs and more k points were used in test calculations on bulk MgO to confirm that these parameters are adequate. For each atomic structure, the electronic wave functions were relaxed by the conjugate gradient scheme of Payne *et al.* [24]. A force tolerance of 0.1 eV/Å was used for the atomic relaxations. The cell dimension perpendicular to the boundary plane was varied to produce the minimum energy structure. The expansion associated with each boundary was calculated to be only 0.02 nm, a value that would be undetectable with our experimental technique.

The excess energy associated with the pure $\langle 001 \rangle$ tilt boundary with the *open* structure is calculated to be $1.73\ \mathrm{J\,m^{-2}}$ ($10.8\ \mathrm{eV\,nm^{-2}}$); the *dense* boundary structure has a higher boundary energy of $1.88\ \mathrm{J\,m^{-2}}$ ($11.8\ \mathrm{eV\,nm^{-2}}$). Therefore, our calculations indicate that the equilibrium structure of pure MgO $\langle 001 \rangle$ tilt boundaries is the *open* structure of Fig. 3(b), as was first concluded by Duffy and Tasker [11] for NiO, confirmed for MgO by Harris *et al.* [9], and observed in pure thin film MgO boundaries by Kizuka *et al.* using HREM phase contrast imaging [13]. However, while calculations based on empirical potentials [9,11] found the *dense* boundary structure was unstable in pure NaCl-type oxides, the present first-principles calculations show that it is a metastable structure. This result may explain previous observations of *dense* structures in NiO grain boundaries [25], although, as will be shown below, impurity segregation can also stabilize the *dense* structure.

We repeated the calculations for the two grain boundary structures with individual Mg-O columns replaced by Ca-O columns. In both structures, Ca prefers boundary columns where it has the longest nearest neighbor distances. The preferred segregation columns in the *dense* structure match those observed in the Z-contrast images [Fig. 1(a)].

We computed the segregation energy (at $T = 0$ K) of Ca impurities in both the dense and open structures and found it to be 0.4 and 0.35 eV/Ca atom, respectively. The segregation energy is defined as $E_{\mathrm{segr}} = \frac{1}{2}(E_i - E_{\mathrm{pure}} - 2E_{\mathrm{CaO/MgO}} + 2E_{\mathrm{MgO/MgO}})$, where E_i is the total energy of the Ca doped structure, E_{pure} is the total energy of the pure boundary structure, $E_{\mathrm{CaO/MgO}}$ is the energy of CaO in bulk MgO, and $E_{\mathrm{MgO/MgO}}$ is the energy of a MgO molecule in bulk MgO. This result confirms the experimental observation that Ca segregates to the grain boundary. A more important result, however, is the relative energy of the two structures with and without Ca. In pure MgO, the open structure is lower in energy by $0.9\ \mathrm{eV/nm^2}$. When Ca is present, the energy of the dense structure relative to that of the open structure is lower by $0.2\ \mathrm{eV/nm^2}$. This is a dramatic shift of $1.1\ \mathrm{eV/nm^2}$ with an uncertainty of about $0.1 \sim 0.2\ \mathrm{eV/nm^2}$. The prediction for a transformation, however, is within the range of uncertainty. Nevertheless, in combination with the experimental observation, the theoretical result strengthens the case that a structural transformation is in fact induced by Ca segregation.

There are reasons to believe the transformation energy is in fact somewhat larger than the calculated value. We find that, after full relaxation, the Ca-O column in the boundary is buckled (the O-Ca-O angle is $\sim 170°$ instead of 180°). The buckling occurs to increase the Ca to O separation, but the latter remains considerably smaller than the 0.24 nm separation in bulk CaO. This result suggests that larger segregation energies will result from reduced Ca occupancy in this column. This idea is consistent with the intensity of the bright boundary columns in the image [Fig. 1(a)], which is lower than expected for a full Ca-O column. Calculations with reduced Ca occupancy are not practical at this point, however, to test this possibility.

We calculated the electronic structure of bulk MgO, the pure *open* structure boundary, and the Ca-doped *dense* grain boundary. The band gap for bulk MgO is found to be 3.8 eV which, while considerably smaller than the experimental value of 7.8 eV, is consistent with previous local density approximation calculations [26]. The band gaps calculated for the supercells containing the grain boundaries are smaller (3.05 eV for the pure *open* structure and 2.55 eV for the *dense* structure). The smaller band gap associated with the grain boundary implies significant consequences for the electrical and optical properties of the material. Additional calculations, beyond the scope of this paper, are needed to explore these consequences. The addition of Ca to the *dense* structure did not affect its band gap.

To further understand the chemical interactions of Ca in the MgO grain boundary, charge-density differences were obtained by subtracting the charge density of the reference system (i.e., a grain boundary with the same atomic configurations but without Ca impurities) from the self-consistent charge density for the Ca-doped dense structure boundary. A plot of the electron density difference of the $\{001\}$ plane at the boundary, as seen in Fig. 4, indicates that Ca polarizes the nearest neighbor oxygen atoms.

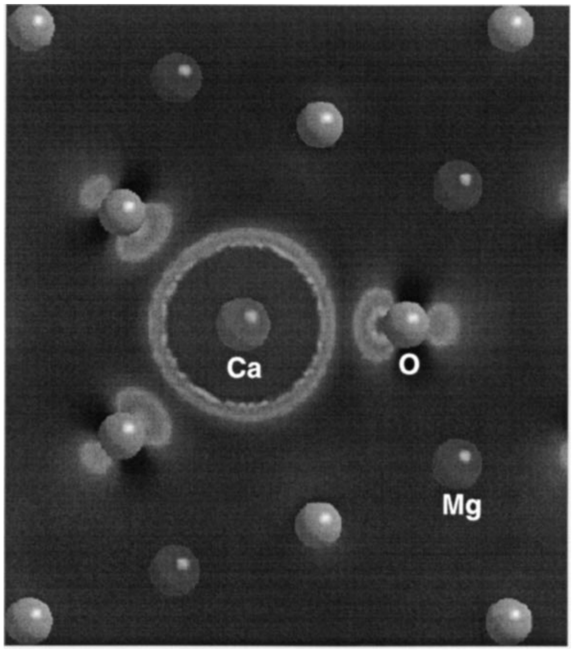

FIG. 4. Calculated charge density difference plot on a {001} plane perpendicular to the tilt axis showing the electron redistribution around the oxygen atom induced by the presence of Ca in the boundary.

The effect is quite small (a few percent) so that we do not attribute any significant electronic rebonding to the stabilization of this structure. We have performed calculations of Ca impurities in bulk MgO and verified that this effect is in fact quite general. Examination of the local bond lengths suggests that the segregation is purely a mechanical effect, i.e., the preferred segregation columns in the boundary provide sites with the longest bond lengths to the nearest neighbors.

In conclusion, experimental observations and theoretical calculations demonstrate that Ca impurities induce a structural transformation of a grain boundary in MgO. The effect is not caused by electronic rebonding but rather by elastic accommodation. This conclusion is consistent with that obtained in a recent experimental study of Ca on the MgO (001) surface [27].

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