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The Atomic Structure of a $\Sigma = 5$ [001]/(310) Grain-Boundary in an Al-5% Mg Alloy by High-Resolution Electron Microscopy

M. SHAMSUZZOHA
School of Mines & Energy Development, and Department of Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, AL 35487

I. VAZQUEZ AND P.A. DEYMIER
Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721

DAVID J. SMITH
Center for Solid State Science and Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287

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Abstract. A symmetrical tilt $\Sigma = 5$ [001]/(310) grain-boundary and its surrounding matrix in an Al-5% Mg alloy, as prepared by cold rolling and annealing, have been studied by conventional transmission electron microscopy, high-resolution electron microscopy, and analytical electron microscopy. EDS measurements of the Mg concentration in the bulk and at grain boundaries indicate variations of Mg content ranging between 4 to 11 atomic percent. This variation is attributed to local ordering of Mg atoms in the alloy. HREM images show that the boundary runs parallel to the median of (310) and contains segments primarily composed of two types of structural unit. One unit contains seven atomic sites, while the other contains eight. In both types of unit, the grain-boundary coincident site lattice is continuous across the interface and exhibits periodicity in its core structure. The core structure, which is characterized by "kite-like" structural units containing seven atoms, conforms well with the structure of $\Sigma = 5$ grain boundaries in pure FCC materials. The presence of atomic-scale ordering of Mg atoms along [001] of the boundary core is associated with the existence of the structural unit possessing eight atomic sites.

Keywords: grain boundary, atomic structure, high-resolution images, Al-5% Mg alloy

Introduction

Experimental observations in metallic and semiconductor systems show a strong dependence of grain-boundary structure and morphology on grain-boundary solute content. Some examples include the impurity-induced grain-boundary faceting of Zn [1] and the stabilization of grain-boundary faceting in Fe induced by Te segregation [2]. Morphological changes of Si symmetrical-tilt grain-boundaries in Sr-doped Si have been reported [3], and an Sb-enriched $\Sigma = 3$ grain-boundary in a Cu-1.5% Sb sample has also been observed [4]. In addition, microscopic observations of dislocations in pure Fe, when compared with Fe-rich Fe-Au alloy small-angle [001] twist boundaries, indicate a change in dislocation content caused by Au segregation [5]. This change in dislocation structure of the grain-boundary was proposed as evidence for a grain-boundary structural transformation induced by solute segregation.

In recent years, the atomic structure of impurity-free grain boundaries in chemically pure metals has been

investigated [6–10]. In many cases, the concepts of coincident site lattice (CSL) [11], displacement shift complete (DSC) lattice [12–14], and the O-lattice model [11], based on geometrical construction of adjoining crystals forming boundaries, have been successfully used for structural characterization. The present investigation was undertaken with the aim of understanding atomic structure of grain boundaries present in typical solid-solution alloys. This paper presents a high-resolution electron microscopy (HREM) study of the core structure of a $\Sigma = 5$ [001]/(310) symmetrical tilt boundary in an Al-5% Mg alloy. The boundary structure obtained from experimental HREM images is described within the framework of geometrical models based on the CSL and DSC lattice concept, and then compared to the corresponding structure found in pure FCC materials. Clear differences in structure are interpreted as microscopic evidence for a structural modification induced by the presence of Mg atoms at the boundary core.

Experimental Procedures

The Al-5% Mg alloy sample was prepared by Mg evaporation onto on Al melt, using commercial high-purity elements (Al 99.999% and Mg 99.98%). Details of the alloy preparation procedure have been given elsewhere [15]. The alloy composition was determined through the use of a Scanning Electron Microscope (JEOL JSM-840A) equipped with an Energy Dispersive Spectrometer (SEM/EDS). Concentration measurements were performed at different locations on a cross-section of the casting alloy. The average concentration measured was 5.15 at.% with a standard deviation of 0.51%.

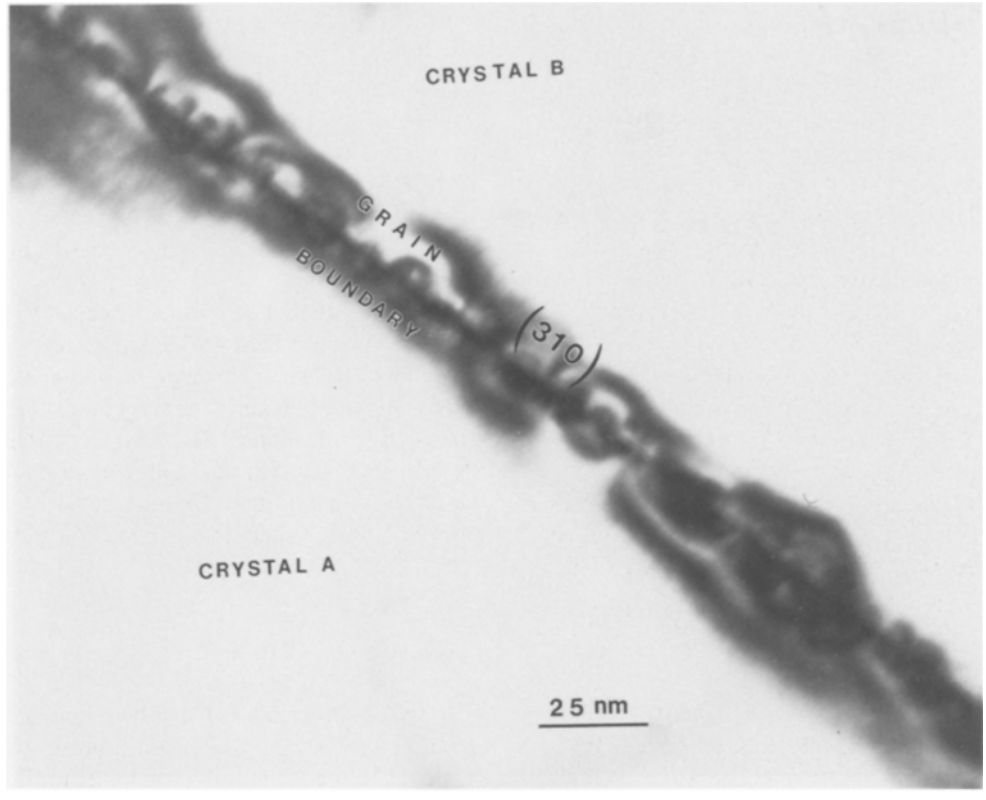
The cast alloy was cold-rolled to produce a 0.25 mm thick plate. The cold-rolling was repeated along the same direction in 10% increments up to 90% total reduction from the initial thickness. The heavily deformed plate was annealed at 400°C for an hour to promote recrystallization. At this temperature the solid solubility of Mg in Al is almost at a maximum (~13 wt.% Mg). Spark cutting was used to produce specimens, in the form of 3 mm diameter discs, from the recrystallized sample. The discs were further annealed for two hours at the same temperature to ensure chemical equilibrium, and then furnace-cooled.

In order to obtain thin foils for Transmission Electron Microscopy (TEM), the discs were single-jet electropolished at room temperature, at a voltage of 60 V in a solution of 73% methanol, 25% nitric acid and 2% hydrochloric acid. The polishing was halted when perforation occurred. The thin foils, thus prepared, were also ion-mill-thinned at room temperature to eliminate any surface contamination. These thin foils were then examined with a TEM (Hitachi H-8000) equipped with EDS facilities to determine the relative Mg concentration at the grain-boundary and in the bulk near the grain-boundary. A 5 nm probe was used in the analysis.

High-resolution electron microscopy (HREM) was performed with a JEM 4000EX electron microscope operated at 400 keV. The high-resolution electron micrographs were obtained near optimum defocus at a typical magnification of 500,000 times. Under these experimental conditions, atomic columns appeared black and images could be interpreted intuitively in terms of atomic column position to within 0.3 Å [16].

Results and Discussion

The specimens exhibited a rather imperfect ⟨100⟩/{100} cubic texture. Neighboring {100} grains often possessed large-angle misorientations resulting in the presence of large-angle boundaries. Figure 1a shows a bright-field image of such a boundary. A nanoprobe composite diffraction pattern (Fig. 1b) taken at this boundary establishes that it is a $\Sigma = 5$ [001]/(310) symmetric tilt grain-boundary. The diffraction pattern exhibits diffraction spots characteristic of the periodicity of the $\Sigma 5$ boundary. In Fig. 1b, the spots associated with the grain-boundary are marked by arrows. These spots lie within the square net (outlined) of FCC spots 200, 020 and 220. The boundary cell parameter obtained from the diffraction pattern indicates that the unit cell of the boundary structure is five times larger than that of either grain. Within the square bounded by FCC spots in Fig. 1b, five diffraction spots belonging to the $\Sigma 5$ unit cell are present. These include the four diffraction spots lying inside the square, as indicated by arrows, and the spot that shares the corner of the square net. This relationship, when transformed to real space, yields an ideal $\Sigma 5$ CSL relationship, i.e., the $\Sigma 5$ unit cell consists of five unit cells of the participating crystals. However, the periodicity of the $\Sigma 5$ coincident lattice is not really evident in the bright-field image. The boundary neither reveals any periodic strain nor shows pendullosung fringes marking any periodic extinction of the transmitted beam.



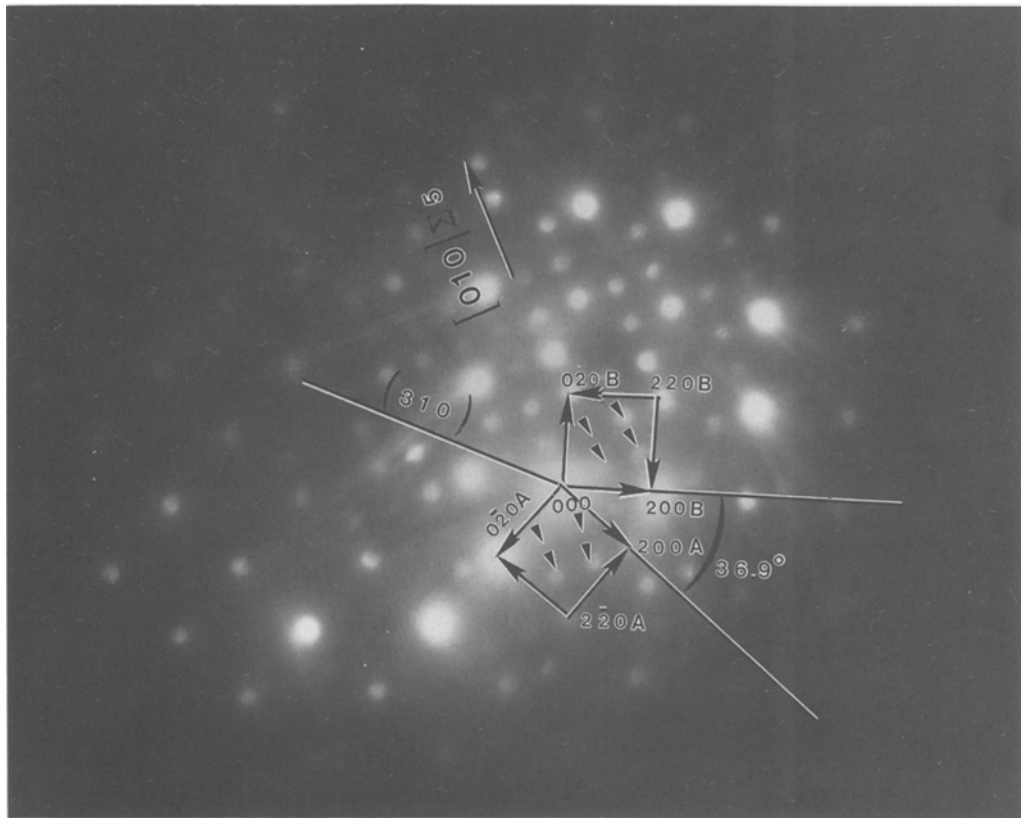
(a)

Figure 1. TEM micrographs of Al-5% Mg alloy. (a) Bright field image showing $\Sigma = 5$ [001]/(310) grain-boundary. (b) Microdiffraction pattern taken at grain-boundary of (a). Incident electron beam is parallel to [001] of bicrystal (*Continued on next page*).

The structure of a $\Sigma = 5$ [001]/(310) grain-boundary can be described theoretically within geometrical models based on CSL, DSC lattice and the O-lattice theories. Figure 2a illustrates the expected rigid unit structure for the $\Sigma = 5$ [001]/(310) grain-boundary constructed on the basis of geometrical models. The "kite-like" structure delineates the grain-boundary periodicity. The individual kite-like unit designated as Y contains eight atoms, of which two are located at the center of the unit. However, because of the close proximity of the two sites, this structural unit has been previously identified as highly unstable [17, 18]. Molecular Dynamic Simulations (MDS) in pure FCC metals such as Au, Ni, Al and non-metallic FCC systems, Ar [17–20] have demonstrated that the structural stability of a $\Sigma 5$ [001]/(310) boundary is maintained only when the kite-like structural unit, representing the boundary periodicity, contains one atom at its center, as shown by unit X in Fig. 2b. HREM images of the pure Au $\Sigma = 5$ [001]/(310) boundary [8], also reveal the occurrence of the structural unit X at the boundary.

HREM observations of the $\Sigma 5$ boundary in the Al-5% Mg alloy indicate that the boundary is mostly defect-free in the sense that the two adjoining crystals always maintain a one-to-one lattice correspondence along ⟨100⟩ across the (310) interface. Figure 3 shows a high-resolution electron micrograph of a typical segment of the boundary. The boundary does not display an array of terminating lattice fringes that could result in the formation of periodic strain contrast. Instead, the boundary exhibits a perfect $\Sigma 5$ periodic structure with a continuous coincident site lattice indicated by arrows at the interface. This perfect $\Sigma 5$ coincidence existing at the boundary precludes any of the intrinsic dislocations that usually accommodate deviations from perfect coincidence.

When viewed at high magnification, the boundary shows some interesting features. Figure 4 shows an



(b)

Figure 1. (Continued.)

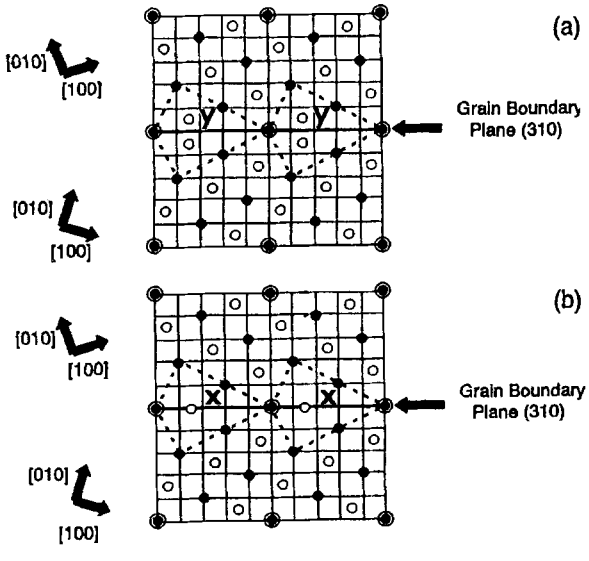


Figure 2. Grain-boundary atomic structure for $\Sigma = 5$ [001]/(310) grain-boundary. (a) Geometrically rigid and ideal structure. (b) Relaxed stable structure in pure FCC materials. Black and white atoms are located on successive planes along [001].

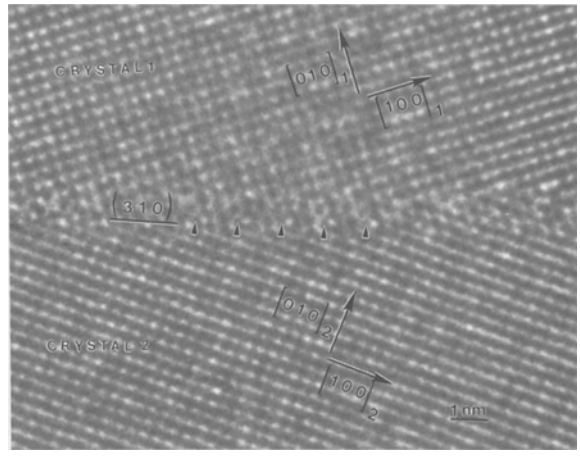


Figure 3. High resolution electron micrograph showing $\Sigma = 5$ [001]/(310) symmetric tilt grain-boundary in Al-5% Mg alloy. Incident electron beam is parallel to [001] of bicrystal.

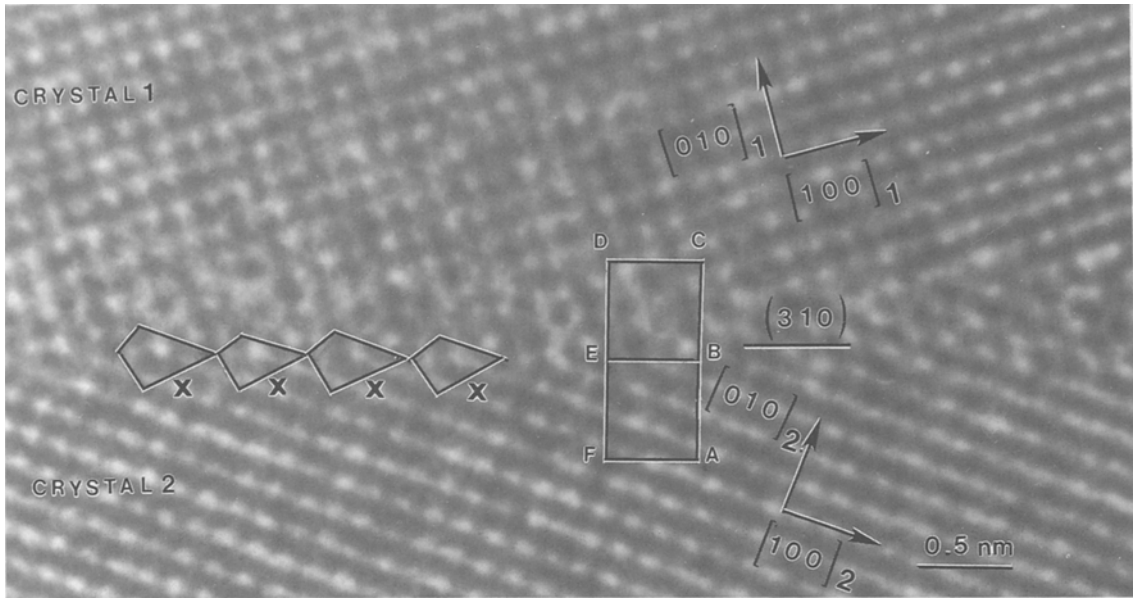


Figure 4. HREM image of $\Sigma = 5$ grain-boundary segment projected on (001) plane in Al-5% Mg alloy. Structural unit X is framed in some portion of boundary. The ABCDEF circuit, drawn in the image, typically outlines coincident site lattice pair across boundary.

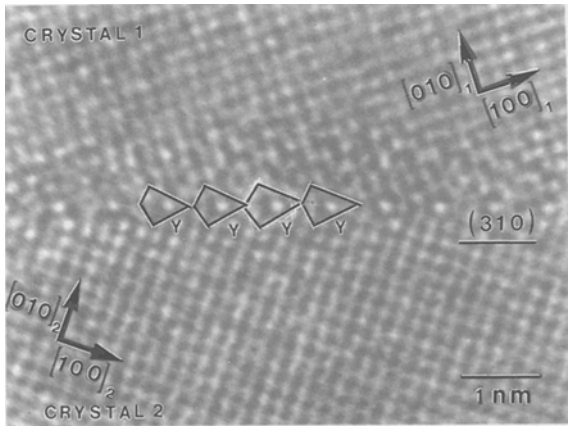


Figure 5. HREM image of a portion of $\Sigma = 5$ grain-boundary projected on (001) plane in Al-5% Mg alloy. Structural unit Y is framed in some portion of boundary.

enlarged view of a boundary segment. The structure of this segment can be described by the periodic occurrence of a kite-like structural unit, containing seven atoms. This structural unit contains only one atom at its center and has the width of the CSL as illustrated in the figure. The unit is designated as the X structural unit described earlier, because it has the characteristics of the stable structural unit usually found in pure metals and also predicated by computer simulation. Figure 5 also shows another high magnification view of the boundary from a different region. The boundary in this location exhibits a periodic arrangement of another structural unit consisting of eight atoms. This unit shows two atomic sites (periodic along the direction of electron beam) in close proximity at the center and has the same type of atomic arrangement described earlier for the unit Y that produces large instability in the pure system.

It is interesting to note that along [001], the $\Sigma = 5$ grain-boundary can have successive stacking of the X-structural unit, in which the central atom exhibits alternating anti-parallel displacement along [010]. HREM imaging on (001) projection of this boundary is likely to reveal a structural unit possessing two central atoms. The separation distance of the two central atoms, as observed in the HREM image, is dependent upon the magnitude of the anti-parallel displacement that the participating atoms undergo. On the basis of a three-dimensional description, such a structural unit is expected to exhibit no significant size difference by comparison with its counterpart containing undisplaced central atoms. The X and Y structural units observed in the experimental HREM images of the $\Sigma = 5$ grain-boundary show evidence for significant differences in their respective size. This feature is particularly evident in the HREM image of a boundary segment shown in Fig. 6. The boundary in this location can be described in terms of a mixture of the two

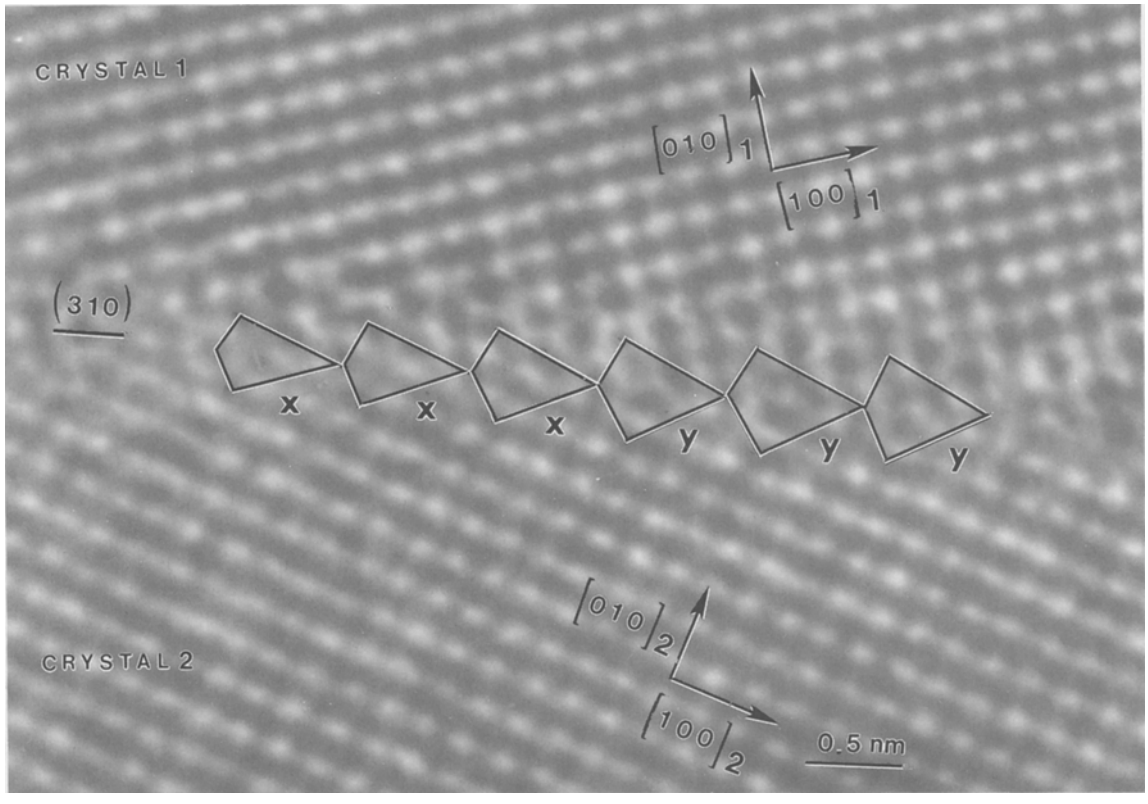


Figure 6. HREM image of $\Sigma = 5$ boundary segment projected on the (001) plane in Al-5% Mg alloy showing structural unit X and Y to be present in the boundary in mixed form. Note size difference between two types of unit.

types of structural unit. A visual inspection of this experimental image reveals that the neighboring X and Y structural units, although coexisting in the boundary with no associated structural defects, such as dislocations, faceting or stepping, still exhibit a marked difference in their size. The larger size of the Y structural unit no doubt results from the greater occupancy of atoms in the unit. These observations reject the antiparallel concept discussed earlier and support the idea that the Y structural unit, in fact, possesses two atoms in its center. Furthermore, there seems to be no plausible reason why, in its stacking along [001], the structural unit X should exhibit anti-parallel displacement for its central atom in successive units at some locations of the boundary, and no such displacement at other locations.

In the Al-5% Mg alloy Mg atoms usually occur substitutionally. This implies that a solubility of ~5% Mg in Al lattices is likely to allow one lattice site in every five unit cells (containing 20 lattice sites) of Al to be occupied by a Mg atom, and that the Mg atoms remain randomly arranged in the structure. In view of the fact that the participating atoms belong to two distinct atomic species, annealing of the alloy at 400°C for over three hours, followed by equilibrium cooling to room temperature, is likely to induce changes in the simple atomic structure of the alloy discussed above. Each atom in the alloy is unlikely to assume random occupancy in the lattice. Instead, some Mg atoms should co-exist with Al atoms in an ordered fashion by forming what are commonly described as clusters. Such Mg atom clusters found in Al-10% Mg alloys are reported [21] to exhibit successive planes of Al and Mg atoms along ⟨100⟩ of the Al matrix.

Selected-area electron diffraction patterns taken along ⟨100⟩ and ⟨110⟩ zone axes of the Al-matrix often revealed peak broadening in the diffraction spots along ⟨110⟩, suggesting that coherency strains are present along ⟨110⟩ of the matrix. Such coherency strains may result from a coherent misfitting of very small sized clusters present in the matrix. The same diffraction patterns taken after a long exposure (between 2

to 3 minutes) also revealed ⟨100⟩ satellite streaks at 200 and 220 FCC spots. This seems to indicate the existence of a tetragonal lattice dilation in some fraction of the Al-matrix. Such a tetragonal lattice dilation is likely to be caused by the presence of a successive layer of Al and Mg atom planes along ⟨100⟩ of the Mg atom clusters as observed previously [21]. Additionally, superlattice reflections present in these electron diffraction patterns showed a tetragonal structure consistent with successive stacking of Al and Mg atom planes along ⟨100⟩ [22]. Attempts to verify the existence of Mg atom ordering by identifying alternating atomic columns of Al and Mg atoms in HREM images were not successful. This is not unexpected since Al and Mg atoms are similar in size. However, EDS analyses revealed that the concentration of Mg in the matrix as well as grain boundaries varied between 4 to 11 atomic percent. Furthermore, Nanoprobe diffraction patterns of the high Mg content regions of the matrix only yielded recognizable ⟨110⟩ peak broadening in the diffraction spots. These observations support the idea that a significant fraction of Mg atoms assume ordering.

Grain boundaries in the alloy should not be immune to Mg atom ordering and are thus likely to possess a few ordered clusters. In this respect, the present $\Sigma 5$ [001]/(310) grain-boundary should possess a few correctly oriented Mg atom clusters at some terminating lattices of the constituent crystals. With such occurrences, it is expected that some Mg atom column or columns should be aligned along [001] of the boundary. According to the geometrical model of CSL, all terminal lattices (irrespective of being either Al or Mg) of constituent crystals should form the kite-like structural unit Y at the boundary. In boundary segments free of Mg atom clusters, the structural unit Y is formed by aluminum atoms. This unit is highly unstable and is likely to transform into the stable structural unit X. On the other hand, the boundary segments, formed at Mg atom cluster/clusters are also constituted by the same Y structural unit. The unit now possesses Al and Mg atoms in successive layers extending along [001]. Its two central atomic sites are occupied by two coplanar Mg atoms. Such atomic occupancy certainly brings different atomic interactions to the unit other than those found in the unit containing mainly Al atoms. Moreover, the bond energy of Al-Al and Mg-Mg atoms pair is 133(6) and 8.552(4) kJ mole^{-1} respectively [23]. The low bonding energy of Mg atoms indicates that the structural unit containing a Mg-Mg atom pair at the unit center is likely to experience weaker interactions and less instability than that which contains an Al-Al atom pair at the unit center. It is now believed that the destabilization brought about by such Mg-Mg atom pairs is weak enough to allow the structural unit of eight atoms to remain stable at the boundary, as observed presently.

Conclusion

The evidence presented in this paper suggests that:

(1) The symmetric tilt $\Sigma = 5$ [001]/(310) boundary present in the Al-5% Mg alloy possesses two types of structural units. One unit containing seven atoms in its structure has one atomic site at the center of the unit. All atomic sites in this unit are occupied primarily by Al atoms. The other unit possesses eight atoms and has two atomic sites at the unit center. The central atomic sites in this unit are believed to be occupied by a coplanar Mg-Mg pair, allowing the unit to be made up of Al and Mg atoms.

(2) The stacking of X and Y structural units along the direction of the electron beam implies that the Y unit containing Mg atoms has an ordered structure along [001].

(3) Mg appears to stabilize a structural arrangement which is otherwise considered unstable for pure Al grain-boundary, demonstrating a structural modification induced by the ordering of the impurity at the boundary.

Acknowledgments

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