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Geoffrey H. Campbell
S.M. Foiles
W.E. King
W.L. Wien

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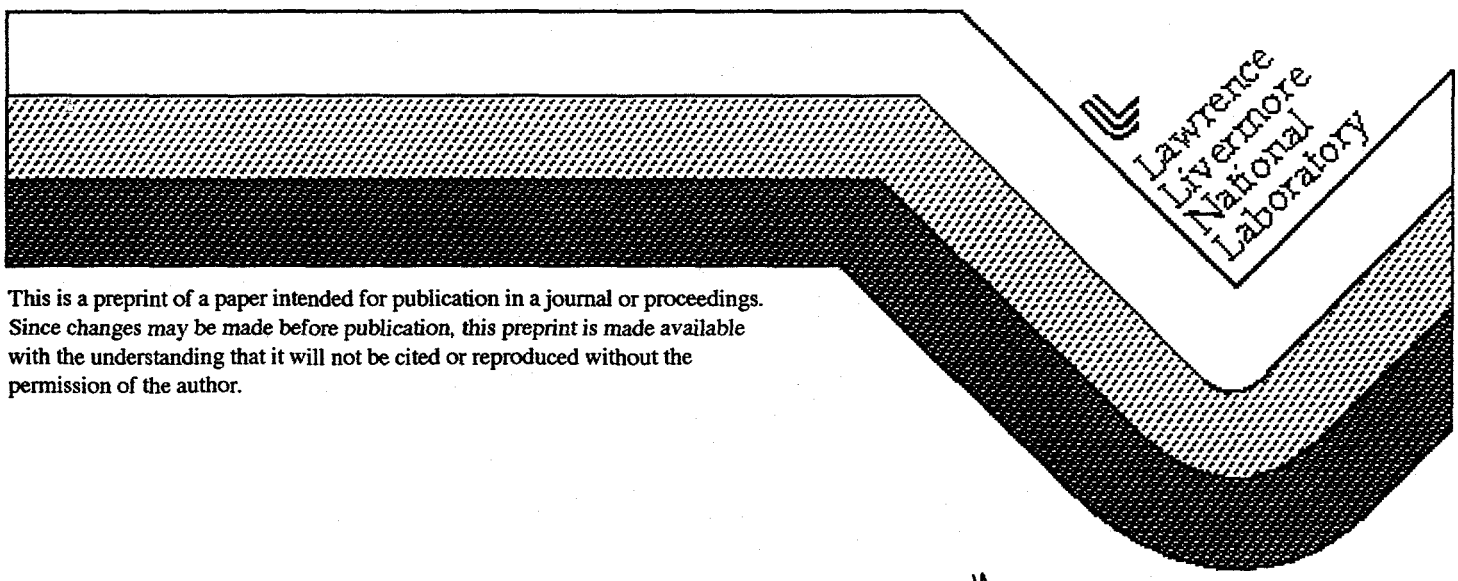

A HIGH RESOLUTION ELECTRON MICROSCOPY STUDY OF THE Σ11 (113)/[1$\bar{1}$0] SYMMETRIC TILT GRAIN BOUNDARY IN PURE Al AND Al - 1.5 wt.% Cu

G.H. CAMPBELL,* S.M. FOILES,** W.E. KING,* AND W.L. WIEN*

*Chemistry and Materials Science Directorate, University of California, Lawrence Livermore National Laboratory, Livermore, CA 94550

**Computational Materials Science Department, Sandia National Laboratories, Livermore, CA 94550

ABSTRACT

Identical bicrystals of pure Al and Al - 1.5 wt.% Cu were prepared by diffusion bonding in ultra-high vacuum. The boundary chosen was the Σ11 (113)/[1$\bar{1}$0] symmetric tilt grain boundary. Characterization of the atomic structure of and segregation to the boundary was performed by high resolution transmission electron microscopy along the common [110]. The stable sites for Cu segregation were probed using electronic structure calculations. Boundary atomic structures were simulated using embedded atom potentials. The Cu was found to segregate to this boundary by occupying sites removed from the mirror plane boundary by one (113) plane. This prediction was compared to experimental micrographs through high resolution image simulation. The experimental results are consistent with the predictions of the theoretical calculations.

INTRODUCTION

Aluminum - copper alloys have demonstrated superior performance versus pure Al in microelectronics applications. The presence of Cu in the proportion of order 1 wt. % ameliorates problems stemming from electromigration.[1] It is thought that Cu segregates to grain boundaries in the Al and acts to block them as fast migration paths for Al.[2] However, beyond these general ideas, the physical process in action is not well understood. A deeper understanding of the physics behind the beneficial effects of Cu solute in Al requires analysis at the atomic level. Atomistic simulations offer one such opportunity.

Application of atomistic simulation methods to the complex situation of electromigration requires that they be first validated under simpler conditions. High resolution transmission electron microscopy (HRTEM) is a useful technique for determining the atomic structure of defects in materials. It has served to validate atomistic models of interatomic interactions in several instances.[3, 4] The validated models can then be applied with higher confidence to situations that are not as readily accessible to experimental confirmation. HRTEM has been used less frequently for examining segregation, but there are successful examples.[5] We will report here on a comparison of identical boundaries in pure Al and Al(Cu) alloy. The results of the HRTEM analysis are compared to the predictions of atomistic simulations and electronic structure calculations.

EXPERIMENT

Acquisition of high quality single crystals of Al(Cu) alloy proved problematic. The best crystals were grown at Ames Laboratory, IA and this source was used for both the pure Al and the Al - 1.5 wt.% Cu. The crystals were grown by the Bridgeman technique. The quality of the alloy crystal degraded as its growth progressed. Only a limited volume of the crystal near the seed end was found to be useful for diffusion bonding. The crystals were oriented, cut, and polished to create cylinders 19 mm dia. by 13 mm height with faces parallel to (113). Special flat-polishing procedures have been developed which achieve a polished surface that is flat to less than 100 nm and parallel to the desired crystal plane to <0.1°.[6]

The bicrystals were prepared by ultra-high vacuum (UHV) diffusion bonding.[7] The sur-

faces of the prepared crystals are cleaned by ion sputtering to remove impurities. The crystals are then heated to approximately 450°C for an hour to out-gas the sides and bottom surfaces which are not polished. The polished faces are briefly ion milled again immediately prior to bonding and the surface composition monitored by Auger electron spectroscopy to confirm that they are free of contamination. These surfaces remain clean in the UHV environment for many hours.

The cleaned surfaces are brought together in preparation for bonding, but they are not allowed to touch. Any contact of the clean surfaces results in immediate bonding. They are oriented to form the desired boundary first and then brought into contact. A small load of 0.5 MPa is maintained throughout the bonding cycle (larger loads produce levels of creep that cause unacceptable amounts of crystal rotation and hence loss of precise orientation). The crystal pairs are heated to .94 T_m (600°C for pure Al and 540°C for Al - 1.5 wt.% Cu) and held for 4 h to form the bicrystal.

Slices of the bicrystal 300 μm thick normal to the common [110] were taken by electric discharge machining (EDM) with a wire attachment. Disks 3 mm in diameter were then cut by EDM with the grain boundary in the center. A dimple was ground on each side of the disk directly over the grain boundary to leave approximately 100 μm thickness. The dimpled disks were electropolished in a solution of 10 vol.% perchloric acid, 20 vol.% butyl cellusolve, balance methanol at -25°C and 22 V until perforation. Finally, the specimens were ion milled with 6 keV Ar^+ at 13° glancing angle until the hole intersected the grain boundary. High resolution microscopy was performed in a JEOL JEM - 4000EX with spherical aberration coefficient of 1.0 mm operated at 400 keV with an illumination semi-angle of convergence of 0.91 mrad. Images were acquired on film (Kodak SO-163) at electro-optical magnification of 800 kX and exposure times of 1 s.

High resolution image simulations were performed with the EMS[8] software package. The multi-slice formalism was used with slice thicknesses of 0.285 nm in the [110] direction. Grain boundary simulations were performed on cell sizes of 8.60 nm normal to the boundary and 0.946 nm along the boundary. A simulation array size with effective dimensions of 1024 by 113 pixels was used with periodic boundary conditions.

THEORY

The atomic structure of the Al boundary was computed using the embedded atom method (EAM)[9] with potentials for Al developed by Ercolessi and Adams.[10] In addition, density functional electronic structure calculations were used to confirm the structure predicted by the embedded atom method and to study the energetics of Cu impurities at the boundary. The electronic structure code uses pseudopotentials and a mixed plane - wave and local orbital basis set to solve for the electronic structure in the local density approximation.

RESULTS

Experiment

A high resolution image of the grain boundary in pure Al is shown in Figure 1. Long, straight, and atomically flat segments of the boundary separated by steps are observed everywhere along the boundary, indicating facetting. High resolution image simulation showed the imaging conditions to correspond to "white - atom" contrast.

A high resolution image of the boundary in Al(Cu) alloy is shown in Fig. 2. Again, grain boundary facetting is observed. A row of noticeably bright spots is seen to lie in one (113) plane off of the mirror plane of the boundary. The presence of these brighter spots is highlighted by the glancing angle perspective view along the boundary presented in Figure 3. These bright spots were not present at all values of thickness and focus. They are, however, reproducibly encountered under certain imaging conditions for the Al(Cu) alloy, but they were never observed in the case of pure Al.

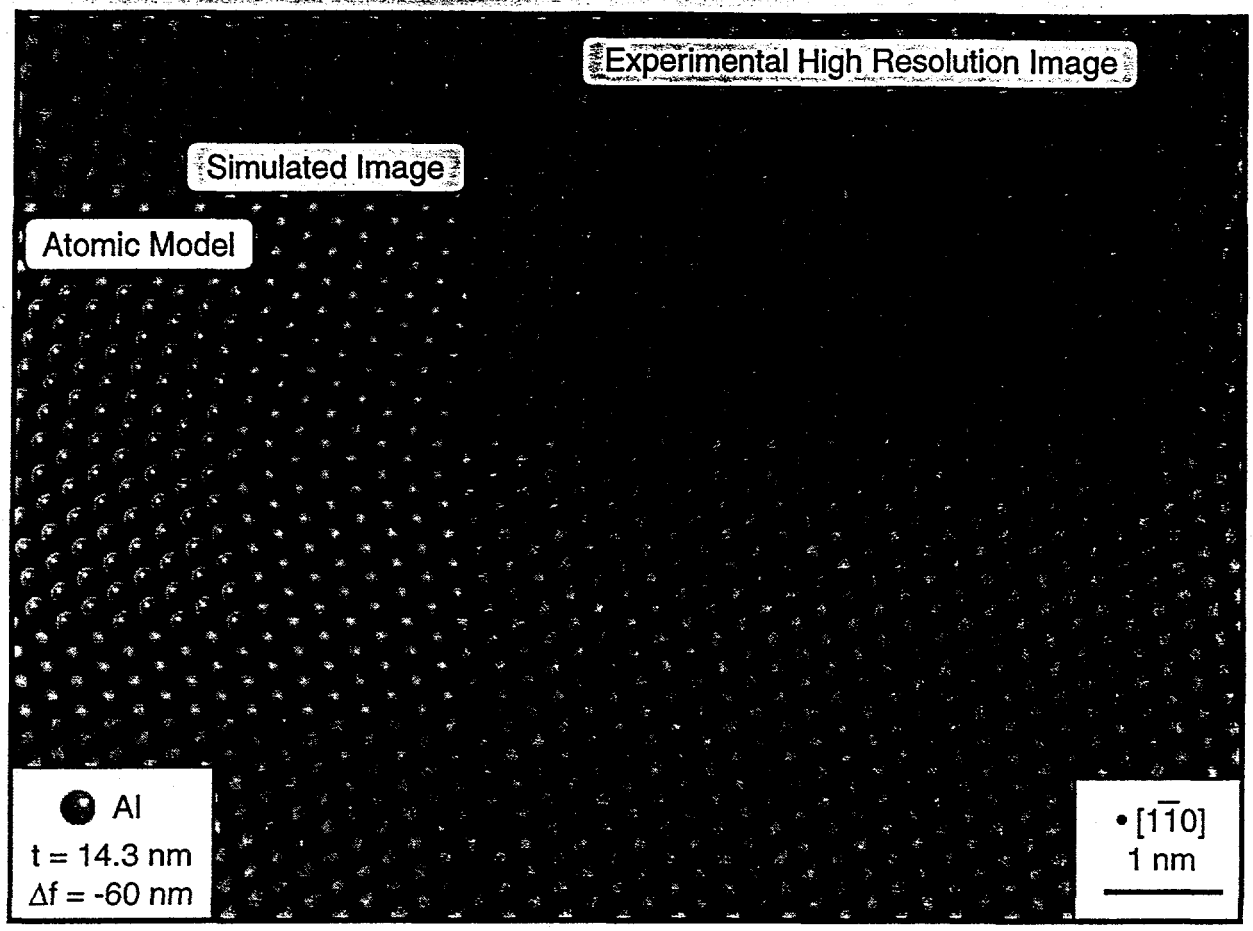

Figure 1: High resolution micrograph of a Σ11 (113)/[1$\bar{1}$0] symmetric tilt grain boundary in pure Al. Atomic model and high resolution image simulation are shown as inserts. Conditions for the simulation are indicated.

Theory

The predicted structure of the grain boundary in pure Al is shown in Figure 4. This structure was predicted using EAM calculations and subsequently verified to be a local minimum using the electronic structure calculations. The energetics of Cu interactions with the boundary were computed using the electronic structure calculations by placing Cu atoms at the boundary and in the bulk of the crystal. These calculations require periodic boundary conditions, so actually a [110] row of Al atoms is replaced by a [110] row of Cu atoms. In the present results, the atomic positions are assumed to be the same as the pure Al boundary. (Relaxation of the atomic positions is in progress.) It is found that the energy is increased by 0.13 eV/Cu atom if the Cu atoms are placed in the mirror symmetric site of the grain boundary compared to their energy in the bulk site. However, the energy is lowered by 0.03 eV/Cu atom if the Cu is placed in a site one plane away from the mirror plane, suggesting that this is the equilibrium site for the Cu atoms. The nature of the interactions between Cu atoms at various sites near the boundary is under investigation to determine the reason the Cu all lie on one side of the boundary.

Image Simulation

The theoretically predicted grain-boundary structures are compared to the experimental high resolution images by high resolution image simulation. The atomic coordinates in the model grain boundary structures are used to determine the projected potentials in the multislice calculation. The simulated image for the case of the pure Al boundary is shown as an insert in Fig. 1. Simulated and experimental images are in qualitative agreement.

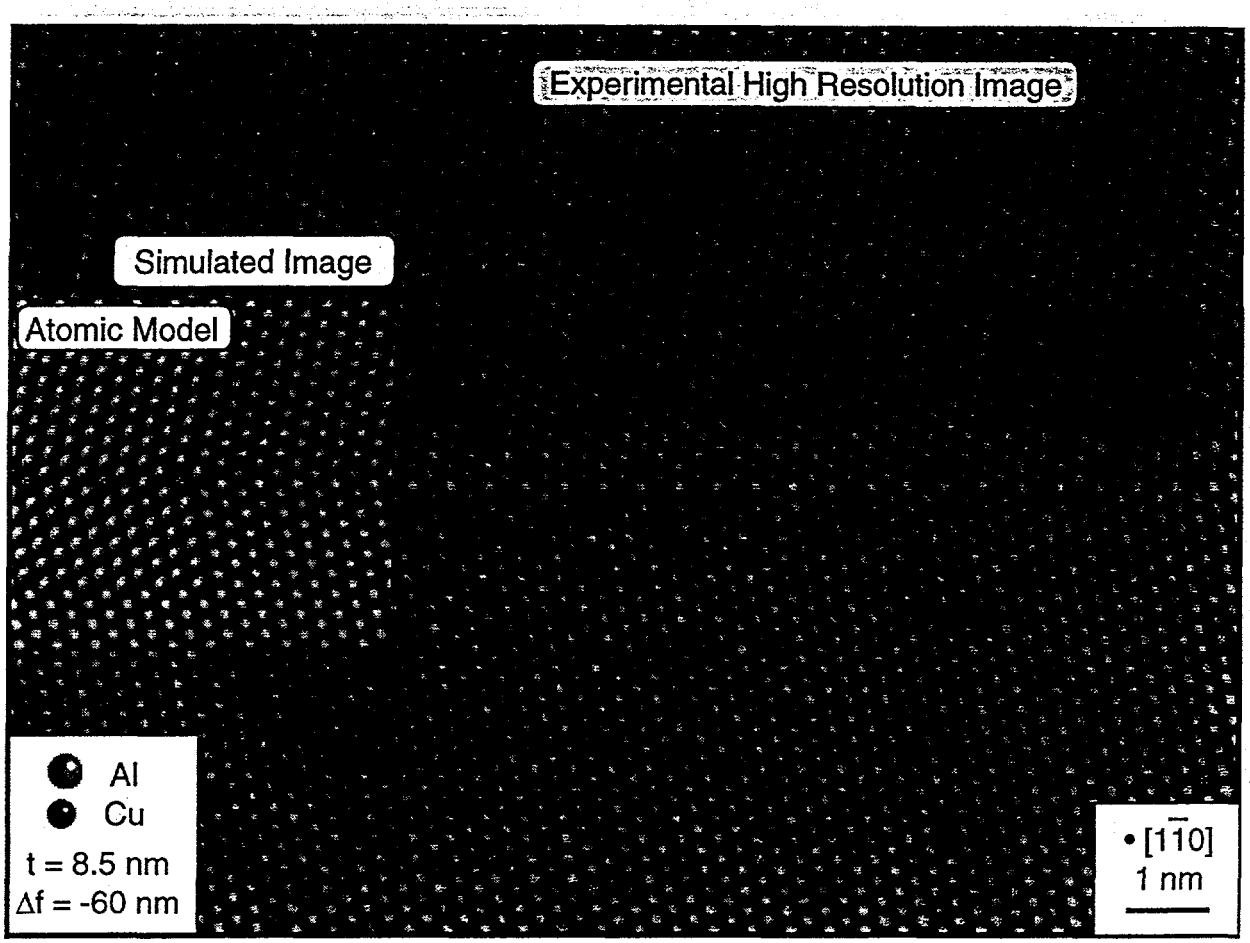

Figure 2: High resolution micrograph of a Σ11 (113)/[1$\bar{1}$0] symmetric tilt grain boundary in Al(Cu) alloy. Atomic model and high resolution image simulation are shown as inserts. Conditions for the simulation are indicated.

The results of the electronic structure calculations indicate a site preference of the Cu solute atoms near the interface. Taking this result as guidance, half the atoms on these sites in the model of the pure Al boundary were arbitrarily replaced by Cu atoms (Figure 5). Image simulations based on this proposed model for Al(Cu) are compared to the experimental image of the Al(Cu) alloy as an insert in Fig 2. The bright spots over the atomic columns containing Cu atoms matches well with the experimentally observed contrast.

Many other simulations were attempted using the model for pure Al. All available parameters of the simulation, e.g., specimen tilt, beam tilt, and aperture shift, were varied in an attempt to reproduce the experimentally observed contrast in Al(Cu). Every attempt was unsuccessful. The

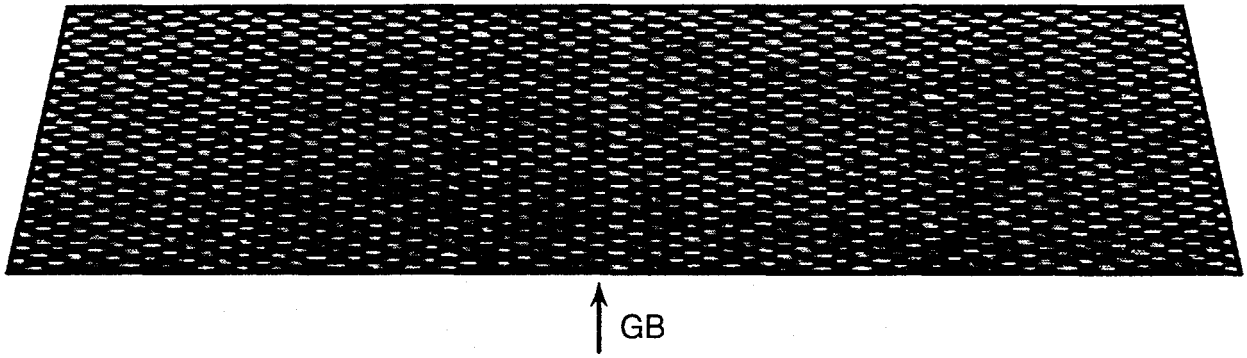

Figure 3: Glancing angle perspective view of the grain boundary shown in Fig. 2. The row of bright spots is accentuated in this view.

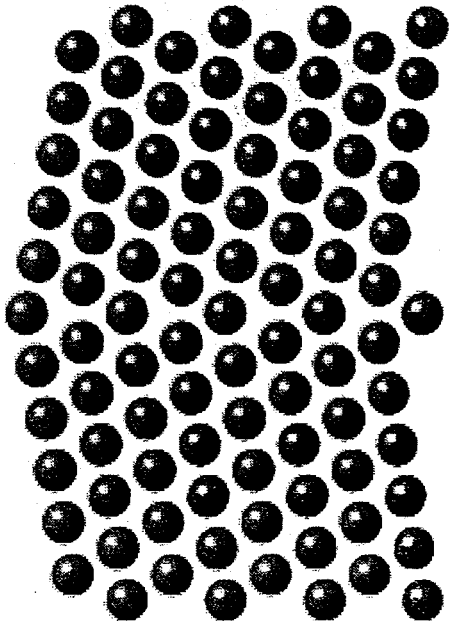

Figure 4: Calculated structure of the $\Sigma 11$ (113)/[0$\bar{1}$1] symmetric tilt grain boundary in pure Al.

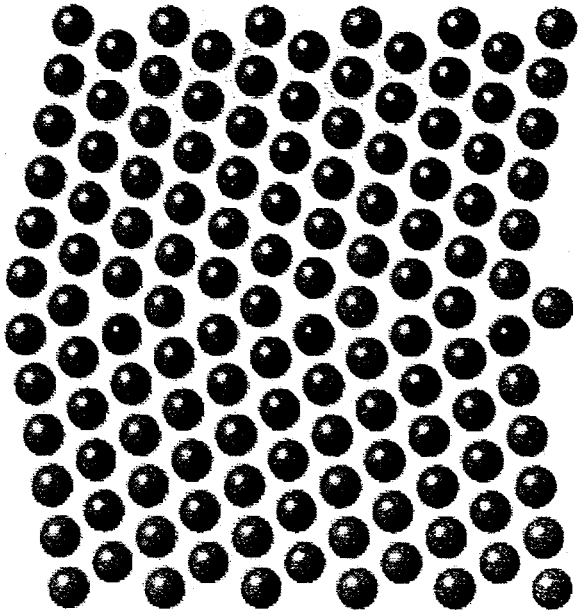

Figure 5: Model structure based on calculations for the $\Sigma 11$ (113)/[0$\bar{1}$1] boundary in Al(Cu) alloy

substitution of Cu was the only successful way to reproduce the contrast.

DISCUSSION

The preference of the Cu atoms for the site away from the mirror symmetric plane is consistent with the standard size effect. Cu has a smaller lattice constant than Al. The site in the mirror symmetric plane has expanded bond lengths compared to the bulk. Thus a smaller impurity would be expected to be less favored in that site. However, the site in the adjacent plane has contracted bond lengths compared to the bulk. Thus a smaller impurity would be expected to reside at that site. Similar calculations for a $\Sigma 3$ (310)/[001] tilt boundary in Al show Cu segregation sites also consistent with the size effect. The fact that all the Cu atoms sit on one side of the boundary is presumed to reflect the interactions between the Cu impurities at the boundary. The nature of these interactions is the subject of current work.

The $\Sigma 11$ (113)/[1$\bar{1}$0] symmetric tilt grain boundary is a low energy boundary compared to other boundaries differing by small variations away in crystal orientation or boundary plane orientation.[11] It lies in a cusp of the energy versus misorientation plot of symmetric tilt boundaries.[12] Therefore, it facets into atomically flat regions when exposed to high temperature during the diffusion bonding. Such regions of perfect interface are well suited to characterization by high resolution electron microscopy.[13] High quality images have been obtained for this boundary, which provides greater confidence in the analysis of the results.

The atomic structure of the $\Sigma 11$ (113)/[1$\bar{1}$0] symmetric tilt grain boundary in pure Al is well established. The boundary has been studied previously by Mills et al.[14] with EAM simulations, high resolution electron microscopy, and image simulations. Our results agree with those previously reported. Furthermore, we have compared the EAM results with predictions based on electronic structure calculations and found them to be also in good agreement.

The high resolution microscopy of the $\Sigma 11$ (113)/[1$\bar{1}$0] boundary in the Al(Cu) alloy shows a reproducible contrast feature of bright spots near the interface for certain values of thickness and defocus. Image simulations using a model atomic structure based on the predictions of electronic

structure calculations were able to reproduce this contrast feature. No combination of image simulation parameters were able to reproduce these contrast features for a pure Al grain boundary. These facts indicate that the contrast features are most likely due to columns of atoms near the boundary which are significantly enhanced in Cu concentration.

CONCLUSIONS

Identical $\Sigma 11$ (113)/[$1\bar{1}0$] symmetric tilt grain boundaries in pure Al and Al - 1.5 wt.% Cu alloy were produced by diffusion bonding in UHV. HRTEM was used to characterize the atomic structure of the grain boundaries. Images from the Al(Cu) alloy boundary demonstrated a distinct contrast feature near the boundary. The atomic structure of the grain boundaries were predicted with EAM and electronic structure calculations. High resolution image simulation using the predicted structure for Cu segregation to the grain boundary was able to reproduce the distinct contrast feature. Other image simulations using pure Al were unable to do so, even with a systematic variation of available free parameters in the simulation. These results are consistent with the high resolution images resolving the enrichment of Cu in particular columns of atoms near the grain boundary plane.

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REFERENCES

1. F. M. D'Heurle and R. Rosenberg in Physics of Thin Films, edited by G. Hass, M. H. Francombe and R. W. Hoffman (7, Academic Press, New York 1973) pp. 257 - 310.
2. M. B. Small, D. A. Smith and A. J. Garratt-Reed, Scripta Metall. Mater., **30**, pp. 1531 - 1534 (1994).
3. U. Dahmen, C. J. Hetherington, M. A. O'Keefe, K. H. Westmacott, M. J. Mills, M. S. Daw and V. Vitek, Philos. Mag. Lett., **62**, pp. 327 - 335 (1990).
4. G. H. Campbell, S. M. Foiles, P. Gumbsch, M. Rühle and W. E. King, Phys. Rev. Lett., **70**, pp. 449 - 452 (1993).
5. D. E. Luzzi, M. Yan, M. Sob and V. Vitek, Phys. Rev. Lett., **67**, pp. 1894 - 1897 (1991).
6. W. L. Wien, G. H. Campbell and W. E. King in Microstructural Science, edited by D. W. Stevens, E. A. Clark, D. C. Zipperian and E. D. Albrecht (Microstructural Science 23, ASM International, Materials Park, OH 1996) pp. in press; presented at 28th International Metallography Society Convention.
7. W. E. King, G. H. Campbell, A. W. Coombs, G. W. Johnson, B. E. Kelly, T. C. Reitz, S. L. Stoner, W. L. Wien and D. M. Wilson in Joining and Adhesion of Advanced Inorganic Materials, edited by A. H. Carim, D. S. Schwartz and R. S. Silberglitt (Mat. Res. Soc. Symp. Proc. 314, Materials Research Society, Pittsburgh, PA 1993) pp. 61-67.
8. P. A. Stadelmann, Ultramicroscopy, **21**, pp. 131 - 146 (1987).
9. M. S. Daw, S. M. Foiles and M. I. Baskes, Mat. Sci. Eng. D: Reports, **9**, pp. 251 (1992).
10. F. Ercolessi and J. B. Adams, Europhys. Lett., **26**, pp. 583 - 588 (1994).
11. D. Wolf, J. de Physique, **46-C4**, pp. 197 - 211 (1985).
12. D. Wolf, Acta Metall., **37**, pp. 2823 - 2833 (1989).
13. P. Pirouz and F. Ernst in Metal - Ceramic Interfaces, edited by M. Rühle, A. G. Evans, J. P. Hirth and M. F. Ashby (Pergamon Press, New York 1990) pp. 199 - 233.
14. M. J. Mills, M. S. Daw, G. J. Thomas and F. Cosandy, Ultramicroscopy, **40**, pp. 247 - 257 (1992).