Ultramicroscopy 40 (1992) 240–246
North-Holland

ultramicroscopy

Molecular dynamics simulations of 45° [100] twist plus tilt grain boundaries in aluminum

J D Weinberg [a], M Shamsuzzoha [b] and P A Deymier [a]

[a] *Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, USA*
[b] *School of Mines and Energy Development, University of Alabama, Tuscaloosa, AL 35487, USA*

Received 3 January 1991, at Editorial Office 16 July 1991

High-resolution electron microscopy has been used to study a [100] 45° twist/17 5° tilt grain boundary in aluminum This mixed-type aperiodic boundary is characterized by two fundamental structural units Each of these two units is a basic building block for the 45° twist/13 29° tilt and 45° twist/19 47° tilt grain boundaries, respectively Molecular dynamics simulations of bicrystals with the above two misorientations have been performed Interatomic forces between aluminum atoms have been modelled by the use of density-dependent pseudopotentials A new type of boundary condition has been used to allow for translational relaxation at the interface The results presented here show that the observed structural units are stable, with some relaxation occurring at the grain boundary core

1. Introduction

The study of grain boundaries is crucial to the determination of many physical properties of polycrystalline materials Recently, the atomic structure of a mixed-character grain boundary in aluminum was examined [1] The orientation relation between the two abutting crystals (1 and 2) could be described by a [100] 45° twist plus a 17 5° tilt about a common $\langle 100\rangle_1 \| \langle 110\rangle_2$ The grain boundary is parallel to $(010)_1$ for the lower crystal and $(49\bar{9})_2$ for the upper The authors concluded that this aperiodic boundary is best described by a structural unit model High-resolution electron microscopy (HREM) clearly shows the boundary to be composed of two basic structural units (fig 1a) Fig 1b gives a schematic representation of the boundary, with the two basic structural units labelled as X and Y If the tilt angle of the boundary is changed from $\theta = 17\,5°$ to $\theta = 13\,29°$, the boundary can be described with a single structural unit, X Similarly, if the tilt angle is $\theta = 19\,47°$, the boundary is completely characterized by a unit Y Thus, $\theta = 13\,29°$ and $\theta = 19\,47°$ are the delimiting boundaries of the $\theta = 17\,5°$ boundary, for example, the 17 5° boundary is composed of X and Y structural units in an approximate ratio of 1 4

The purpose of this note is to provide additional information on the 45° twist plus 17 5° tilt aluminum grain boundary, through the use of molecular dynamics computer simulations While HREM only provides a two-dimensional image of the grain boundary, computer simulations offer the advantage of being able to exactly specify three-dimensional structures Simulations also provide additional information such as energy It is because of this experimental shortcoming and the added benefit of simulation that the two delimiting cases of the above boundary are analyzed

2. Simulation specifications

The current simulations have all been performed using the technique of constant-stress, constant-temperature molecular dynamics [2] The interactions between the aluminum atoms are described by a density-dependent pair potential,

derived from pseudopotential theory [3–5] This interatomic potential includes seventh-nearest neighbors, but not eighth In order to avoid surface effects and simulate a system embedded in a bulk material, periodic boundary conditions (PBC) were used Because the system is aperiodic, however, modifications to the structure and the boundary conditions must be made In two

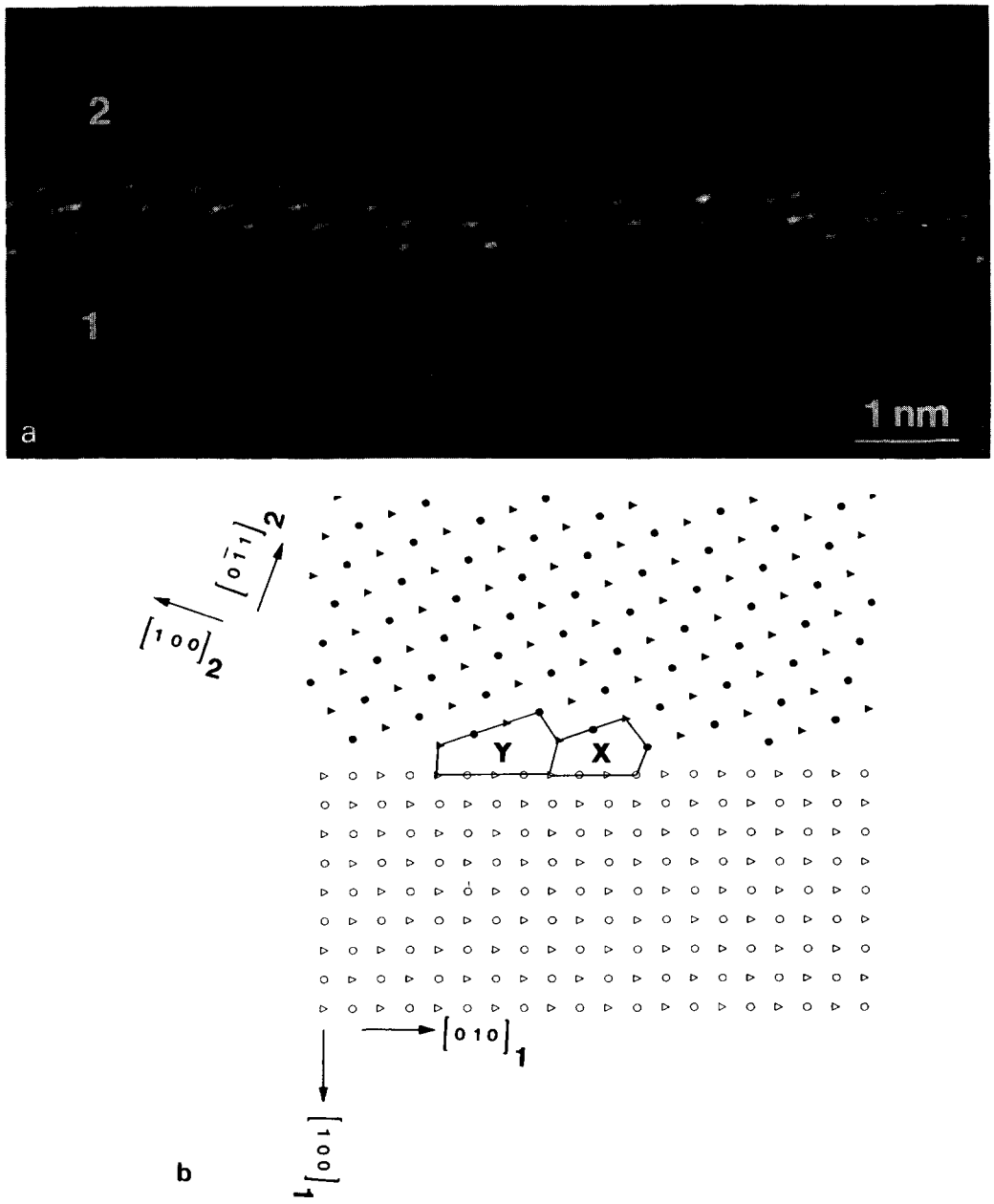

Fig 1 (a) High-resolution electron micrograph showing [100] 45° twist plus $\theta = 17.5°$ tilt grain boundary in aluminum Incident electron beam is parallel to $[001]_1$ and $[011]_2$ (b) Schematic representation of bicrystal showing two basic structural units labelled X and Y The triangles and circles represent successive atomic planes parallel to $[001]_1$ and $[011]_2$

directions, the bicrystal is quasiperiodic, and has been compressed to be periodic In the third direction, normal to the grain boundary plane, a second boundary is introduced due to PBC This artifact exists for all bicrystals simulated with PBC Because the second boundary may not behave the same as the central one, all properties of the central boundary have been calculated within a slab, defined as the central half of the simulation cell

The presence of a second boundary can also create a stress field within the bicrystal, preventing full relaxation of the atoms To address this problem, the boundary conditions have been modified based on a concept introduced by Lutsko et al , known as the t-vector [6] The t-vector is a new dynamical variable which introduces another degree of freedom into the Lagrangian Its purpose is to minimize forces across the borders of the simulation cell by adjusting the pair potential of particles near the cell borders By doing this, the particles at the core of the central grain boundary are able to relax, free of any extraneous influences imposed by PBC This new boundary condition is only applied to the borders where PBC creates an extra grain boundary It allows decoupling of the simulation cell from the periodic image cells

All bicrystal systems have been simulated with both types of boundary conditions (PBC and decoupled t-vector) Simulations were run for several thousand time steps at a temperature of 300 K and a pressure of 1 atm The isothermal condition has been maintained using a momentum rescaling method The equations of motion for the particles were calculated using a finite difference scheme, with an integration time step of $2\,53 \times 10^{-15}$ s All distances and dimensions are expressed in units of Bohr radii (1 Bohr radius $\approx 0\,529$ Å)

3. Bicrystal construction

The initial structure of the 45° twist plus 13 29° tilt is characterized by a boundary composed of

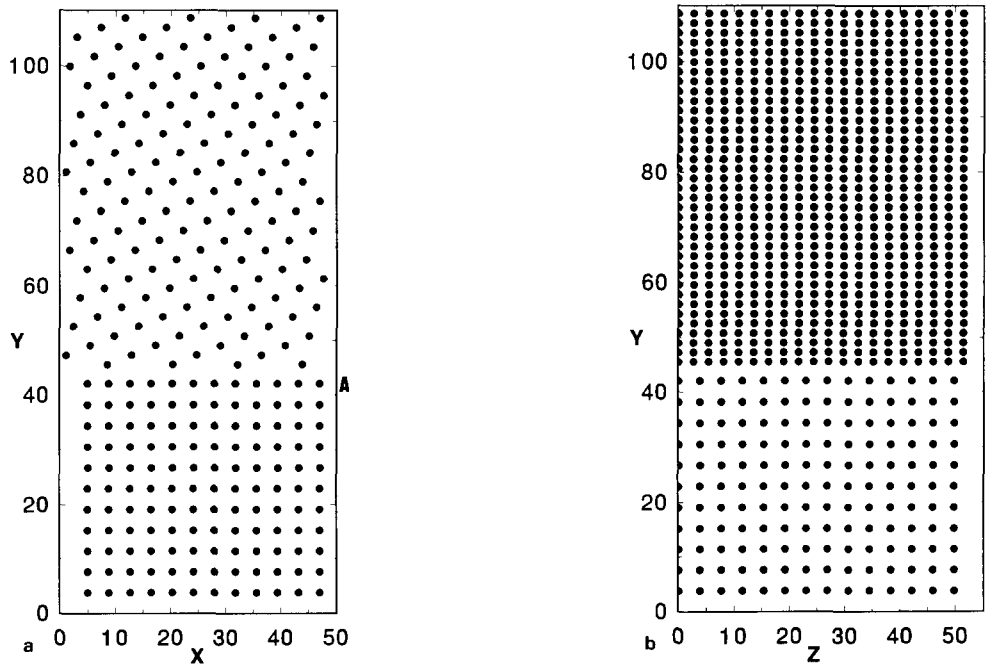

Fig 2 (a) XY projection of initial structure of $\theta = 13\,29°$ bicrystal (b) ZY projection of initial structure of $\theta = 13\,29°$ bicrystal

four X structural units (see fig 2a) Looking along the boundary in the x direction, there is only one true coincidence point (A), and three pseudo-coincidence points The pseudo-coincidence points are represented by atoms belonging to the lower crystal, whose positions are very close to the atomic sites of an extended upper crystal

Because of the misorientation between the two crystals, they are incommensurate Thus, periodic boundary conditions (PBC) cannot be employed without some constraints A further complication in the x direction is that the choice of a simulation cell to match the upper crystal results in a plane mismatch for the lower crystal Thus, a yz (001) plane in the lower crystal has been removed, while the remaining planes have been proportionally spaced to fill the void

For the $\theta = 19\,47°$ case, a good match can be made without removing or adding any planes The lower crystal yz (001) planes have a spacing of $\frac{1}{2}a$ (a is the lattice parameter) The pseudo-coincident points of the extended upper crystal have a linear x-direction spacing of $(\sqrt{18}/2)a$ This gives a spacing ratio along the boundary of $\sqrt{18}$ Since the ratio is not an integer, an exact match for PBC cannot be made in the x direction A good approximation, however, is to use thirty-four lower crystal yz (001) planes, yielding a near integer ratio of 0 9983 The resulting bicrystal is characterized by eight Y-type structural units (fig 3a) As with the 13 29° case, there is only one true coincident point (A), and several pseudo-coincident points along the boundary

In the z direction, the $\theta = 13\,29°$ and $\theta = 19\,47°$ cases are identical The ratio of plane spacings for the upper crystal (110) versus the lower crystal (100) planes is $\sqrt{2}/2$ Again, an exact match for PBC cannot be made A good approximation is obtained by using ten xy (110) planes in the upper crystal and seven xy (100) planes in the lower crystal This yields a near integer plane spacing ratio of 1 0101 (figs 2b, 3b)

The final consideration for bicrystal construction is the second boundary created by PBC at the y borders of the simulation cell To avoid direct interaction between the two boundaries, a minimum cell size of four times the range of interaction is required in the y direction With all of the above taken into account, the initial dimensions of the simulation cell for the 45° twist/13 29° tilt are $x = 47\,17$, $y = 108\,79$, and $z = 54\,1°$ Bohr radii The 45° twist/19 47° tilt dimensions are $x = 129\,85$, $y = 87\,99$ and $z =$

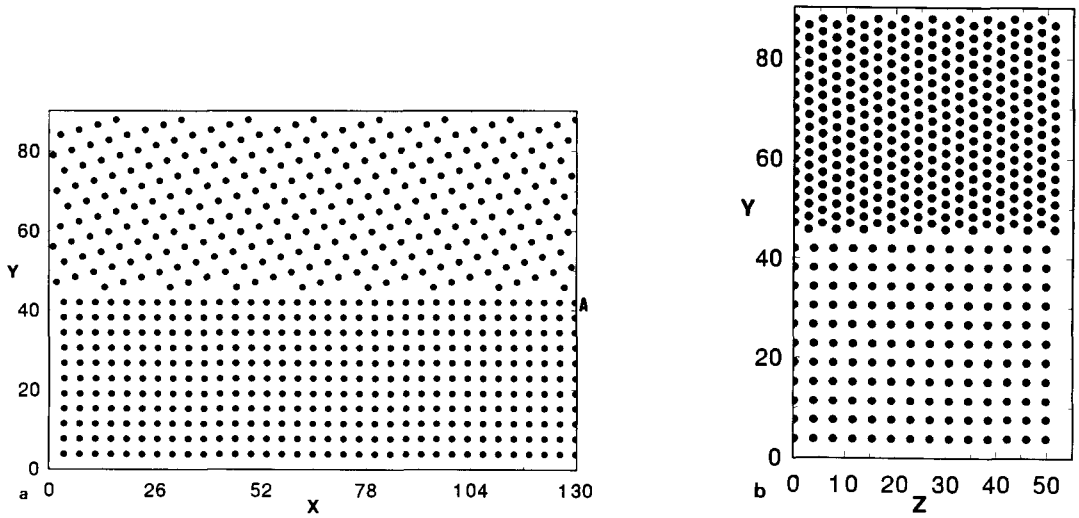

Fig 3 (a) XY projection of initial structure of $\theta = 19\,47°$ bicrystal (b) ZY projection of initial structure of $\theta = 19\,47°$ bicrystal

54 10 This yields 2404 and 5338 particles in the simulation cells of the $\theta = 13\ 29°$ and $\theta = 19\ 47°$ bicrystals, respectively

4. Results

After adjusting the temperature to near 300 K the 45° twist/13 29° tilt was simulated with PBC at constant energy for a sequence of 7000 time steps The resulting equilibrium temperature was 301 K Because of its larger size, the $\theta = 19\ 47°$ case could only be run (at constant temperature) for 2000 time steps The average structures after equilibration are shown in figs 4 and 5, for the $\theta = 13\ 29°$ and 19 47° bicrystals, respectively Following the PBC simulations, both bicrystals were simulated using decoupled t-vector boundary conditions Under the constraint of constant temperature, the $\theta = 13\ 29°$ case was run for 3700 time steps, while the $\theta = 19\ 47°$ case was run for 2000 time steps

An examination of figs 4a and 5a demonstrates that the structural units of the boundaries remain intact There are no fundamental changes in the interfaces, such as disordering or restructuring Only local relaxation in the vicinity of the grain boundaries occurs Simulation with the t-vector has also shown no fundamental changes in the boundary structures While the t-vector allows translational relaxation of the boundary, none was observed This indicates that the quasiperiodic interfaces are in their lowest energy state with respect to translation parallel to the boundary

Using the bicrystal slab, energy calculations for the central interface indicate structural stability An average enthalpy per particle was calculated over the final 5000 and 1500 time steps, for the $\theta = 13\ 29°$ and 19 47° cases, respectively From these values, the enthalpy per particle of a (256 particle) perfect crystal was subtracted The remaining values were divided by the area of the grain boundary interface (i e , $X \times Z$, the area of the base plane of the simulation cell) The resulting values are the excess enthalpies of the interfaces, given by 711 mJ/m^2 for $\theta = 13\ 29°$, and 528 mJ/m^2 for $\theta = 19\ 47°$ These are reasonable values for grain boundaries in aluminum, and indicate their possible existence in real samples Furthermore, stability is determined by the free energy and not the enthalpy The addition of the negative term $(-T\Delta S_{\text{excess}})$ to the enthalpy will make the excess free energy lower Another factor making the excess free energy artificially high is the presence of elastic energy This arises due to the stress field imposed by PBC on an aperiodic system If this is accounted for, the excess

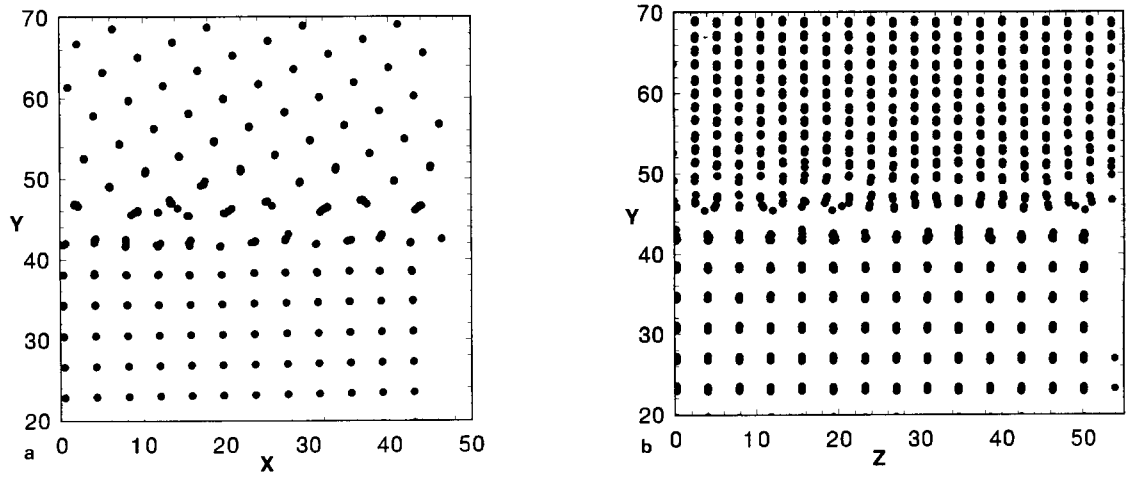

Fig 4 (a) XY projection of relaxed equilibrium grain boundary structure in $\theta = 13\ 29°$ bicrystal (b) ZY projection of relaxed equilibrium grain boundary structure in $\theta = 13\ 29°$ bicrystal

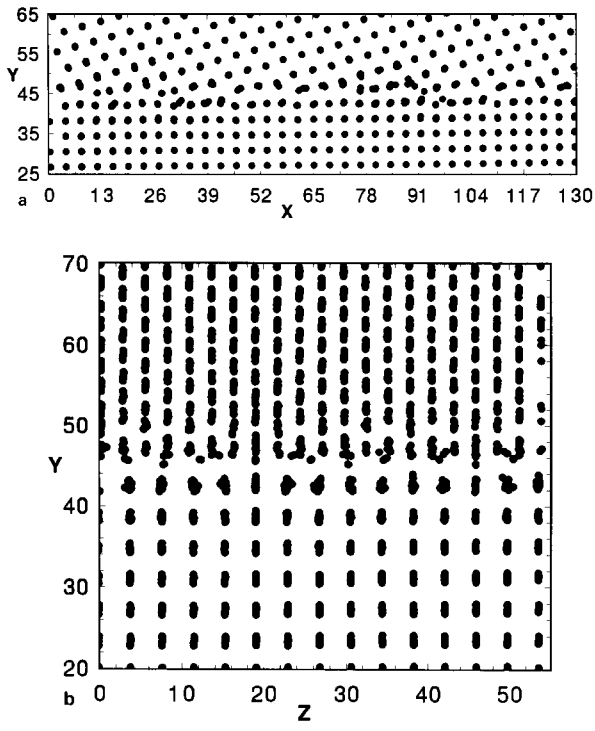

Fig 5 (a) *XY* projection of relaxed equilibrium grain boundary structure in $\theta = 19\,47°$ bicrystal (b) *ZY* projection of relaxed equilibrium grain boundary structure in $\theta = 19\,47°$ bicrystal

free energy is lowered even further, increasing the likelihood of a more stable boundary This may be particularly true in the case of the higher stress $\theta = 13\,29°$ bicrystal Thus, a structural unit model for a 45° twist plus a $\theta = [13\,29°$ to $19\,47°]$ tilt is validated

Comparing figs 4a and 5a to the micrograph of fig 1a, relaxations along the boundary appear to be similar In all three cases, the $(1\bar{1}1)$ planes of the upper crystal and the (010) planes of the lower crystal appear to bend and align with each other near the boundary This relaxation results in a minimization of empty space (or excess volume) in the grain boundary core The relaxation is more pronounced in the case of the longer structural unit, Y

Figs 4b and 5b reveal the third dimension of the structures Plane matching between the two crystals in ratios of 1 1 and 3 2 can be seen These ratios are the first two rational approximations to the actual irrational plane spacing ratio of $\sqrt{2}$ This is in agreement with experimental findings where it was shown that in a 45° [100] twist boundary, the $(010)_2$ and $(01\bar{1})_1$ planes match each other after 2 and 3 plane spacings, respectively [7]

5. Conclusion

Interfaces in materials extend over only a few atomic layers Thus, their study requires techniques capable of atomic-level resolution Atomic-level simulation methods have been extensively used to investigate the structure, energy and other properties of internal interfaces The limitations of simulation techniques are well known, but not always fully understood, and include finite time durations, the approximate nature of atomic interaction, and the finite size of the simulated cell (the boundary condition to embed it in a bulk-type surrounding) Atomic-level experimental techniques such as HREM have already provided a wealth of information concerning the structure of interfaces Severe constraints, however, limit the applicability of HREM to the resolution of low-index planes Moreover, imaging of the interface structure places stringent requirements on the alignment precision of these planes, and also places restrictions on the grain boundary plane inclination Finally, the method only provides two-dimensional projections of the interfacial structures

In view of the advantages and limitations of computer simulation and atomic-level experimental techniques, a joint approach combining both methods offers great value for progress in interfacial research This note has given additional evidence to support the structural unit model for 45° twist plus tilt grain boundaries in aluminum The authors hope that this paper demonstrates the benefits of using molecular dynamics computer simulations as a companion to HREM in the study of grain boundary structures When performing simulations, however, caution must be used as to the choice of boundary conditions and other computational considerations, such as in-

teratomic potentials A proper choice of boundary conditions is particularly important when aperiodic bicrystals are being simulated

Acknowledgements

This research utilized the Center for High Resolution Electron Microscopy in the Center for Solid State Science at Arizona State University, established with support from the National Science Foundation (Grant no DMR-89-13384) We are grateful to Dr D J Smith for help with the high-resolution electron microscopy We also thank V Campos for his help with the molecular dynamics simulations The authors acknowledge the receipt of financial support from the US Department of Energy under contract number DE-FG02-87ER45285

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