GRAIN BOUNDARY PHASE EQUILIBRIUM IN METALLIC SYSTEMS

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ABSTRACT

Progresses in the structural and chemical characterization of grain boundaries in metals are reported. We have developed a solid state method for fabrication of a variety of important grain boundaries. This method is based on a sequence of heavy deformation of single crystals followed by controlled recrystallization. The structure of complex grain boundaries such as the quasiperiodic $45^\circ[100]$ twist in pure aluminum or the periodic $\Sigma 5[310]$ in aluminum-5%Mg alloy has been elucidated. We have found the structural unit (SU) model to be very powerful for the description of quasiperiodic interfaces. The applicability of the SU model to heterophase interfaces is verified for Si-Al interfaces.

Further advances have been achieved in the understanding of the driving forces for grain boundary segregation including elastic and electronic effects. Chemical effects on grain boundary core structure are observed in the case of Al-Mg alloys and Sr doped Si.

ACCOMPLISHMENTS

A summary of the research accomplished under the Department of Energy, Office of Basic Energy Science, Division of Materials Science (Contract # DE-FG02-87ER45285) follows.

We have undertaken an ambitious research program to further advance understanding and control of interfacial properties. This research is a large and diverse body of work around the common theme of grain boundary phase equilibrium. The work performed employs a variety of experimental, theoretical and computational techniques.

1. Grain Boundary Preparation

We have developed a novel method for the production of some specific grain boundaries in aluminum, whose atomic structure can be imaged with current high resolution microscopes. The method consists of a cross rolling of aluminum single crystals followed by a heat treatment. Careful control of the rolling and annealing conditions produces perfect twin, perfect $\langle 100 \rangle$ low angle tilt, and perfect $\langle 100 \rangle 45^\circ$ twist plus tilt grain boundaries.

Publication: M. Shamsuzzoha and P. A. Deymier, "Preparation of Some Specific Grain Boundaries in Aluminum for HREM Studies by Cold Rolling and Annealing," Scripta Metall. Mat. 24, 1303 (1990).

2. Atomic Structure of Interfaces by HREM

With HREM, we have studied the structure of simple low angle and coincident periodic grain boundaries in aluminum. We have found good agreement with the predictions of conventional geometrical theories such as coincident site lattice (CSL),

0-lattice and displacement shift complete (DSC) lattice theories. In addition to generally accepted concepts for relaxation at grain boundaries, we have identified new structural relaxation processes at secondary grain boundary dislocations. The investigation of grain boundary structure has been extended to more general complex boundaries.

We have also investigated a family of aperiodic boundaries. The experimental resolution of their grain boundary core structure led us to extend the structural unit model for periodic grain boundaries to aperiodic ones. We then have turned to the complex case of heterophase interfaces and resolved the structure of boundaries between aluminum and silicon. To characterize the core structure of the interfaces, a structural unit model has again been developed, based on Si bond conservation.

- (a) We have reported for the first time the atomic structure of the core of a $6^\circ[001]$ low angle tilt grain boundary in an F.C.C. metal as resolved by HREM. The observed primary dislocation content of the $6^\circ[001]/(110)$ low angle tilt grain boundary in aluminum is in excellent agreement with the grain boundary predicted by the 0-lattice geometrical model.

Publication: M. Shamsuzzoha, D. J. Smith, and P. A. Deymier,
"Atomic Structure of a $6^\circ[100]$ Tilt Grain Boundary in Aluminum by HREM,"
Scripta Metall. Mat. 24, 1611 (1990).

- (b) We have studied the atomic structure of secondary dislocations (SGBD) at $\Sigma 3[\bar{1}10]/(\bar{1}\bar{1}1)$ twin grain boundaries in pure aluminum with HREM. The Burgers vectors of the SGBDs in the twin boundary are completely in accord with the theoretical predictions based on CSL and DSC lattice dislocation theories. We reported some significant differences between the predicted

core structures of SGBDs and the actual structures. SGBDs with Burgers vectors in the plane of the twin exhibit a delocalization resulting in a local alteration of the translational state of the grain boundary.

Publication: M. Shamsuzzoha, P. A. Deymier and D. J. Smith, "A HREM Study of Secondary Dislocations in $\Sigma 3[\bar{1}10]/(\bar{1}\bar{1}1)$ Grain Boundaries in Aluminum," *Phil. Mag.*, in press.

- (c) High resolution electron microscopy images of a $\Sigma 3[\bar{1}10]/(\bar{1}\bar{1}1)$ bicrystal produced by heavy cold rolling and annealing show a multiplicity of grain boundary core structures. We reported a remarkable example of two grain boundary states separated by a partial grain boundary dislocation with Burgers vector $\vec{b} = 1/12 [112]$, implying a change in translational state. We have demonstrated that all other structures are related through continuous transport of atoms from one grain to the other, resulting in $[\bar{1}\bar{1}1]$ grain boundary steps without the formation of secondary dislocations. Symmetry arguments and calculations of the energy associated with the observed structure show that all grain boundary translational states, except the perfect twin, are metastable.

Publication: P. A. Deymier, M. Shamsuzzoha and J. D. Weinberg, "A Study of Grain Boundary Translational States in a $\Sigma 3[\bar{1}10]/(\bar{1}\bar{1}1)$ Bicrystal," *Acta Met.*, in press.

- (d) We have observed for the first time, and studied by HREM, a $[100]45^\circ$ twist plus 17.5° tilt mixed character aperiodic grain boundary in aluminum (see Fig. 1). Most of the boundary is asymmetric and exhibits coherency or misfit

dislocation due to lattice mismatch across the interface. The boundary structure was found to be constituted of two basic structural units and could not be characterized on the basis of CSL, DSC or the 0-lattice geometric models. Each of the two basic structural units constitutes the sole structure of similar delimiting twist plus tilt boundaries formed at tilt angles of 13.29° and 19.47° . Steps and microfacets observed at the boundary can also be characterized within the framework of the same structural unit model.

Publication: M. Shamsuzzoha, D. J. Smith and P. A. Deymier, "The Atomic Structure of a $[001]45^\circ$ Twist Plus 17.5° Tilt Grain Boundary in Aluminum by High Resolution Electron Microscopy," *Phil. Mag.*, in press.

- (e) We have proposed the extension of the structural unit model of grain boundaries to quasiperiodic interfaces. A quasiperiodic tiling representation for nonperiodic grain boundaries appears to offer a suitable frame for the geometrical description of such boundaries (see Fig. 2). The HREM images of a $45^\circ[100]$ twist grain boundary and a $45^\circ[100]$ twist plus 17.5° tilt boundary provide experimental evidence for the relaxation of quasiperiodic grain boundaries into short length structural units. The structural unit model of grain boundaries may be stated as: any long quasiperiodic boundary is constituted of a mixture of short length structural units. The short length units are representative structural units of short period or quasiperiodic delimiting grain boundaries.

Publication: P. A. Deymier, M. Shamsuzzoha and J. D. Weinberg,

"Experimental Evidence for a Structural Unit Model of Quasiperiodic Grain Boundaries," J. of Mat. Res., in press.

- (f) Using HREM, we have studied interfaces between aluminum and silicon in samples prepared by solidification of Al-Si eutectic liquid. The Al and Si grains have a common $[110]$ axis with a misorientation between the grains of 70.5° . The silicon $(\bar{1}\bar{1}\bar{1})$ planes match with the aluminum (111) plane every 3 $(\bar{1}\bar{1}\bar{1})_{\text{Si}}$ and 4 $(111)_{\text{Al}}$ interplanar spacings. The structure of the interface lying along a common $\{112\}$ plane can be described with structural units constructed on the basis of Si bond conservation. Other macrofacets in this boundary have been investigated showing that the grain boundary core structure is controlled by Si (111) microfacets, while aluminum atoms merely fill in the gaps to satisfy the tetrahedral coordination of Si (see Fig. 3).

Publication: M. Shamsuzzoha, P. A. Deymier and D. J. Smith,

"HREM Study of Al-Si Interfaces," Proceedings, Symposium K, Defects in Materials, M.R.S. Annual Meeting, 1990.

3. Molecular Dynamics (MD) Simulations of Grain Boundaries in Aluminum

We have developed a MD computer program for the simulation of aluminum bicrystals. The interatomic forces between aluminum atoms are modelled with density dependent pseudopotentials. We have identified artifacts associated with boundary conditions in MD which inhibit or favor some grain boundary relaxation processes. The computer code is currently used to study the stability of structural units in aperiodic grain boundaries.

- (a) We have quantified for the first time the effect of boundary conditions in MD simulations of grain boundaries. We have demonstrated that localized stresses induced by standard periodic boundary conditions initiate the melting of grain boundaries at temperatures below the bulk melting point. Periodic boundary conditions, however, do not appear to affect relaxation of defected grain boundaries (with vacancies) by grain boundary/sliding migration.

Publication: V. Campos, I. Vazquez and P. A. Deymier, "On Periodic Boundary Condition and Grain Boundary Migration Sliding," in preparation.

- (b) We have just completed one of the first MD simulations of quasiperiodic grain boundaries. The simulation of $45^\circ[100]$ twist plus 13.29° and 19.47° tilt character grain boundaries has demonstrated that structural units in these boundaries are stable. Local relaxation within the core of the units has been identified with local contrast variation in HREM images of a $45^\circ[100]$ twist plus 17.5° tilt character boundary. 13.29° and 19.47° tilt are delimiting misorientations for the 17.5° tilt boundary (see Fig. 4).

Publication: J. D. Weinberg, M. Shamsuzzoha and P. A. Deymier, "Molecular Dynamics Simulations of $45^\circ[100]$ Twist Plus Tilt Grain Boundaries in Aluminum," submitted to Ultramicroscopy, Proceedings of the N.S.F. Workshop on Structure and Properties of Interfaces, Wickenburg, AZ, 1991.

4. Impurity Segregation at Grain Boundaries

We have undertaken a theoretical analysis of the dominant mechanisms for equilibrium solute segregation at grain boundaries in metals. These mechanisms include the accommodation of excess strain from solutes which fit poorly in the host material. Elastic and electronics mismatch are the major contribution to the excess energy.

Original experimental work is also underway to characterize the interdependence between the morphology of interfaces in alloys and their chemical composition. The ultimate objective is the control of morphology and atomic structure by chemical additives.

- (a) *Elastic energy of interaction of point defects with grain boundaries.* Analytical expression for the elastic energy of interaction of a point defect with an A-B-A planar defect, a plane of dilatation, and half a plane of dilatation in a planar defect have been derived.

The excess energy of a spherically symmetric point defect in the neighborhood of a planar defect is short range. It varies as the inverse of the fourth power of the distance of the defect from the planar defect. This energy can be attractive or repulsive depending upon the elastic constants of the core region B and the semi infinite region A.

The interaction energy of one point defect with an infinite plane of dilatation in the planar defect is zero. However, the elastic energy of interaction of the point defect with a half plane of dilatation in the planar defect is long range. It varies as the inverse of the distance from the tip of the plane and the inverse of the square of the distance from the planar defect.

This result offers a dynamical model for segregation in which segregation in some localized region of an interface fuels further segregation to eventually fill in the boundary.

Publication: P. A. Deymier, L. Janot, J. Li and L. Dobrzynski, "Elastic Energy of Interaction of a Point Defect with a Grain Boundary," Phys. Rev. B, 39, 1512 (1989).

- (b) *Electronic energy of interaction of a point defect with a grain boundary.* Analytic expressions for the electronic energy of interaction of a point defect with a planar defect, and with a planar defect containing a point defect have been obtained. The excess electronic energy of a point defect near a planar defect varies as the distance from the planar defect. The energy of the defect within the planar defect varies as the square of the distance from the center of the planar defect. The interaction energy between two point defects, one of which is located in the planar defect, varies as the inverse of the cube of the distance from the planar defect. These energies are sinusoidal functions of the distance and change sign every fraction of an interatomic distance. We have demonstrated that the electronic energy of point defects at large distances from planar defects, does not constitute a strong driving force for segregation. In contrast, at distances within a few atomic radii from the planar defect, the electronic energy may represent a significant contribution to the energy of segregation.

Publication: J. Vasseur, P. A. Deymier, A. Akjouj and L.

Dobrzynski, "Electronic Energy of Interaction of Point Defects with a Grain Boundary," in preparation.

- (c) *The role of grain boundary morphology on segregation in Al-Mg alloys.* Al-2% Mg and Al-5% Mg alloys have been prepared and analyzed by electron dispersive spectroscopy and transmission electron microscopy. The low Mg concentration alloy is homogeneous and shows Mg segregation at grain boundaries. The high Mg concentration alloy exhibits numerous precipitates at grain boundaries. However, precipitation initiated by segregation appears to be grain boundary dependent. Moreover, we have observed variable numbers of precipitates along curved boundaries, indicating a dependence of segregation on grain boundary inclination. We are currently working on the implementation of a new method for the study of chemical effects of solutes on grain boundary morphology, using analytical electron microscopy. We plan to measure for the first time, the variation in grain boundary torque with solute chemical potential. These measurements are key to further chemical design of materials microstructure.
- (d) *Atomic structure of interfaces in alloys.* Using HREM, we have imaged a $\Sigma 5[100]/(310)$ grain boundary in an Al-5% Mg alloy. The grain boundary is periodic and constituted of a single structural unit. However, the observed structural units differ from the structure of $\Sigma 5[100]/(310)$ grain boundaries studied by computer simulation. They also differ from HREM micrographs of

pure F.C.C. metals. The difference in structure is related to the presence of Mg atoms within the core of the grain boundary (Fig. 5).

- (e) *Atomic structure of silicon grain boundaries containing Sr.* Crystallographic changes in the $\Sigma 3 \langle 110 \rangle / \{111\}$, $\Sigma 3 \langle 110 \rangle / \{112\}$ and $\Sigma 9 \langle 110 \rangle / \{112\}$ boundaries induced by strontium in the silicon phase of Sr-modified Al-Si alloys have been studied by high resolution electron microscopy. The $\Sigma 3$ boundaries possessing $\{111\}$ and $\{112\}$ planes in pure silicon phase exhibit asymmetric morphologies in the Sr-modified phase. Interaction of various $\Sigma 3 \langle 110 \rangle / \{111\}$ boundaries results in both $\Sigma 3 \langle 110 \rangle / \{112\}$ and $\Sigma 9 \langle 110 \rangle / \{112\}$ boundaries. The resulting $\Sigma 9$ boundaries also show asymmetrical inclination.

Publication: M. Shamsuzzoha, D. J. Smith and P. A. Deymier, "Morphology of Silicon Grain Boundaries in Sr-Modified Al-Si Eutectic Alloys by HREM," submitted to Ultramicroscopy, Proceedings of the N.S.F. Workshop on Structure and Properties of Interfaces, Wickenburg, AZ, 1991.

a

b

Fig. 1 (a) High resolution electron micrograph showing $[100]45^\circ$ twist plus 17.5° tilt grain boundary in aluminum. Incident electron beam is parallel to $[001]_1$ and $[011]_2$.
 (b) Schematic representations of bicrystal showing two basic structural units labelled X and Y.

Fig. 2 Superposition of quasiperiodic tilings onto $45^\circ[100]$ dichromatic pattern. The filled and unfilled circles correspond to lattices 1 and 2, respectively. The octants Q_1 , Q_2 , Q_3 , Q_4 illustrate successive application of the inflation rule of quasiperiodic lattices.

Fig. 3 (a) High resolution electron micrograph of Al-Si $[110]70.5^\circ$ bicrystal. The grain boundary is approximately parallel $(1\bar{1}2)_{\text{Si}}$ plane. A circuit OPQRS is drawn around a misfit dislocation with closure failure $1/3 \langle 111 \rangle_{\text{Al}}$. Two basic structural units are marked A and B.

(b) Schematic representation of the structural units A and B. Each correspond to microsegments parallel to the $(1\bar{1}2)_{\text{Si}}$ and $(1\bar{1}3)_{\text{Si}}$ planes, respectively.

Fig. 4 (a) Average atomic position of a $[100]45^\circ$ twist plus 13.27° tilt grain boundary in aluminum calculated by molecular dynamics.
 (b) Average atomic position of a $[100]45^\circ$ twist plus 19.47° tilt grain boundary in aluminum calculated by molecular dynamics.
 The 13.27° and 19.47° tilt are delimiting misorientations for $[100]45^\circ$ twist plus 17.5° tilt grain boundary of Fig. 1.

a

b

c

Fig 5 (a) High resolution electron micrograph of a $\Sigma 5[100](310)$ grain boundary in Al-5% Mg alloy. The structural unit of the $\Sigma 5$ grain boundary is illustrated as a "kyte."
 (b) Schematic representation of observed grain boundary. The black and white circles are two successive (100) planes. Note the presence of two atoms in close proximity at the center of the kyte.
 (c) The stable structure of a $\Sigma 5[100](310)$ grain boundary in pure f.c.c. metals as observed in Au (F. Cosandey, S. W. Chan and P. Stadelmann, Scripta Met. 22, 1093 (1988)) and calculated in various computer simulations. The presence of pairs of atoms in the grain boundary structure as observed in the HREM is indicative that at least one of the two atoms is magnesium.

LIST OF PUBLICATIONS (published or in press)

- (1) P. A. Deymier, L. Janot, J. Li and L. Dobrzynski, "Elastic Energy of Interaction of a Point Defect with a Grain Boundary," Phys. Rev. B, **39**, 1512 (1989).
- (2) M. Shamsuzzoha and P. A. Deymier, "Preparation of Some Specific Grain Boundaries in Aluminum for HREM Studies by Cold Rolling and Annealing," Scripta Metall. Mat. **24**, 1303 (1990).
- (3) M. Shamsuzzoha, D. J. Smith and P. A. Deymier, "Atomic Structure of a $6^\circ[100]$ Tilt Grain Boundary in Aluminum by HREM," Scripta Metall. Mat., **24**, 1611 (1990).
- (4) M. Shamsuzzoha, P. A. Deymier and D. J. Smith, "A HREM Study of Secondary Dislocations in $\Sigma 3[\bar{1}10]/(\bar{1}\bar{1}1)$ Grain Boundaries in Aluminum," Phil. Mag., in press.
- (5) M. Shamsuzzoha, D. J. Smith and P. A. Deymier, "The Atomic Structure of a $[001]45^\circ$ Twist Plus 17.5° Tilt Grain Boundary in Aluminum by High Resolution Electron Microscopy," Phil. Mag., in press.
- (6) P. A. Deymier, M. Shamsuzzoha and J. D. Weinberg, "A Study of Grain Boundary Translational States in a $\Sigma 3[\bar{1}10]/(\bar{1}\bar{1}1)$ Bicrystal," Acta Met. & Mat., in press.
- (7) P. A. Deymier, M. Shamsuzzoha and J. Weinberg, "Experimental Evidence for a Structural Unit Model of Quasiperiodic Grain Boundaries," J. of Mat. Res., in press.
- (8) V. Campos and P. A. Deymier, "Molecular Dynamics Simulation of $\Sigma = 5$ Aluminum Bicrystal," Proceedings. Symposium I on Interfacial Structure, Properties and Design, Annual Meeting of M.R.S., Reno, NV, 1988.
- (9) V. Campos and P. A. Deymier, "Mean Square Displacement at the Boundary of an Aluminum Bicrystal," Proceedings. Symposium J on Interfaces Between Polymers, Metals and Ceramics, Spring Meeting of M.R.S., San Diego, CA, 1989.
- (10) M. Shamsuzzoha, P. A. Deymier and D. J. Smith, "High Resolution Imaging of Symmetric Tilt and Mixed Character Boundaries in Al," Proceedings of the XIIth International Congress for Electron Microscopy, 1990.
- (11) M. Shamsuzzoha, P. A. Deymier and D. J. Smith, "HREM Study of Al-Si Interfaces," Proceedings. Symposium K on Defects in Materials, Fall Meeting of Materials Research Society, Boston, MA, 1990.

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