THEORETICAL STUDIES OF SEGREGATED INTERNAL INTERFACES

Y. Ishida and M. Mori

Institute of Industrial Science, University of Tokyo, 22-1, Roppongi, 7 Chome, Minato-ku, Tokyo 106, Japan

Abstract - Molecular dynamic calculations were performed on the grain boundary structure of iron, especially [100] and [110] symmetrical tilt coincidence-related boundaries segregated with phosphorous atoms with the ultimate purpose to understand the mechanism of grain boundary embrittlement in steels by the grain boundary segregation of IVb to VIb elements. The simulated structures showed the phosphorous segregation alters the grain boundary structure extensively and consequently, the mechanical behavior under an applied stress differs upon impurity atom segregation. The interaction of the segregated interfaces with nearby lattice dislocation and atomic process of crack propagation were simulated also by molecular dynamics technique.

I. INTRODUCTION

Impurity segregation is undoubtedly the most influential parameter of internal interfaces. Interfacial diffusion, migration, sliding, fracture, corrosion and all other chemical and physical properties are strongly affected by the segregation. It is considered that the interface structure itself is altered extensively.(1) Large property changes are expected as the natural consequence of the alteration. In spite of the close relationship between the interfacial structure and impurity segregation, the two studies did not mix well until recently. An Augér metallurgist likes to stay with structureless monolayer of atoms except in a few studies(2), while coincidence-site lattice theoreticians were reluctant to deal with segregated structures. It may be said that lattice imaging electron microscopy is going to bridge the two subjects experimentally and opening the long waited atomic structure study of segregated interfaces.

Calculation of segregated interface has been limited to central force type calculations.(1) (4)-(9) Further modification may be needed because strong segregations especially that of IVb to VIb elements in the grain boundary of iron invariably involves in changes in bonding characteristics. Briant and Messmer(10)-(12), for example, showed a large charge transfer to the impurity and resulted decrease in valence electron charge density between the neighboring Fe atoms using fully quantum mechanical cluster calculations of Slater(13) (SCF-X α SW method), while covalent type bonding is suggested by Losch between impurity and host metal(14).

Further investigation is needed along this line, because the boundary structure assumed by Briant and Messmer is too unrealistic. The local density of electron states(LDOS) calculations(1) have assumed charge neutrality which must be proved.

It is the purpose of the present paper to review our recent atomic studies of the segregated interface through computer simulations, only to prepare theoretically the basic information to be used upon observation of the segregated interface by lattice imaging electron microscopy. Present calculation is limited to coincidence-related tilt type boundaries, because the lattice imaging observation is most likely achieved with tilt type ordered boundaries. The bonding character calculation of the boundaries by SCF-X α SW method as well as molecular dynamical simulations of mechanical properties such as grain boundary fracture are included.

II. MOLECULAR DYNAMIC CALCULATIONS

Interface structures both pure and impurity segregated were simulated by assuming individual atoms obeying the following Newton's law:

$$F_i = - \sum_j^n \frac{\partial V(r_{ij})}{\partial r_{ij}} \quad (1)$$

where r_{ij} is the difference between the vectors of the i th and j th atom position. And $V(r_{ij})$ is interatomic potential. Morse potential(15) was used in the present calculation, whose details are given elsewhere(1). The atom position and velocities were calculated by the following approximate equations. The calculation started for individual atoms with zero velocity.

$$\begin{aligned} a_i(t) &= F_i / m_i \\ v_i(x + \Delta t/2) &= v_i(x - \Delta t/2) + a_i(t) \Delta t \\ r_i(t + \Delta t) &= r_i(t) + v_i(x + \Delta t/2) \Delta t \end{aligned} \quad (2)$$

where m_i is the atomic mass, v_i is the velocity, and r_i is the position of the i th atom. The time unit Δt was taken to be 2×10^{-15} sec. Phosphorous atoms were placed at lattice sites substitutionally near the grain boundary and relaxed by the method described elsewhere(1). Periodic ordering characteristic to the coincidence-related boundaries were no longer used in simulating the structure of the boundary dislocations. A finite region was set for the molecular dynamic calculation as are shown in later figures. The same framework was used to apply stress in fracturing the segregated grain boundary. A grain boundary notch was made by making the atomic forces artificially zero across the notched surface.

III. STRUCTURE OF IMPURITY SEGREGATED GRAIN BOUNDARIES

The molecular dynamical calculation showed the interface structure of lowest energy differ completely upon impurity atom segregation even though the periodic unit structure is of the same length corresponding to the coincidence system. There are many metastable configurations but in Fig. 1 lowest energy configurations are shown. Reflecting the tilt type symmetry, the distorted prism type structure is characteristic of both $\Sigma=5$ and $\Sigma=9$ boundaries. In case of phosphorous segregated boundary, however, the columnar Fe_3P type prism structure is typical and the distribution of this prism structure is wide in zigzag pattern along the boundary. Naturally, the layer of the lattice distortion along the boundary appears rather wide.

The fluctuation in the hydrostatic stress surrounding individual atoms near the boundary is a useful parameter to define the thickness of phosphorous segregated boundary. Fig. 2 shows hydrostatic stress of each atom near the boundary. The radius corresponds to either excess or deficit in the hydrostatic stress off the matrix value as shown here in the figure. The distribution of the hydrostatic stress gets much wider in phosphorous segregated boundaries. For the case of the comparison those with hydrostatic compression are shown in black circles and white circles for hydrostatic tension.

Fig. 1. Grain boundary structures(a,b) of a $\Sigma=5$ and (c,d) of a $\Sigma=9$ coincidence boundary(a,c) without P and (b,d) with P segregation. Double circles indicate P atom positions. Black and white circles indicate atom sites one plane above or below that of the rest.

Fig. 2. Hydrostatic stress of atoms in coincidence boundaries of Fig. 1. White and black circles indicate tensile and compression sites respectively.

IV. OBSERVATION OF IMPURITY SEGREGATED GRAIN BOUNDARIES

A conventional transmission electron micrograph does not give details of the impurity segregated atomic structure. It only gives some hint of the effect of segregation from the shape or the remaining image of the dislocation. Lattice imaging microscopy has a potential to observe such an impurity segregated structure especial-

Fig. 3. The structure of grain boundary dislocations (a,c,e) without P and (b,d,f) with P segregation. The Burgers vectors are $a/5[02\bar{1}]$ (a,b), $a/9[22\bar{1}]$ (c,d) and $a/9[114]$ (e,f).

Photo 1. Lattice imaging electron micrograph of $\Sigma=11$ coincidence boundary of gold¹⁷

Photo 2. Lattice imaging electron micrograph of an epitaxial $[100]$ tilt boundary of iron¹⁸⁾

ly in coincidence-related pure tilt boundaries. The micrograph like Photo 1 is with white spots along the $\Sigma=11$ coincidence related grain boundaries of gold.(17) The white image is difficult to simulate by changing the focusing condition. It is thus suspected that the image is related to the impurity atom segregation along the boundary. Phosphorous atom segregation in iron boundary is one of the popular subjects of the lattice imaging observation.(18) Only limited success, however, has been achieved in imaging the segregated boundary. Photo 2 is one example which is not coincidence-related symmetrical tilt boundary. It is an epitaxial boundary parallel to a densely packed lattice plane which does not contain periodic structure unit.

V. BINDING CHARACTERISTICS OF THE SEGREGATED GRAIN BOUNDARY

The characteristics of atomic bonding at the impurity segregated boundary can differ appreciably in nature. Briant and Messmer(10)-(12) showed that electron charge transfer to impurity atoms from the surrounding iron atoms and the resulted loss of electrons which have been associated with bonding in between the neighboring iron atoms. In the present research the same SCF-X α method is adopted to calculate the bonding state along the boundaries. The local density of states type calculation assuming the charge neutrality may no more be appropriate in accessing the charge transfer between the segregated impurity atom and host metal.(1)(19)(20) As the first calculation $\Sigma=5$ coincidence-related grain boundary of iron simulated by the present molecular dynamical technique was chosen. The calculation is performed because similar calculations having been reported using SCF-X α method(10)-(12) has been on unrealistic atom configuration. It may be easy to calculate but too schematic to be the boundary configuration. Fig. 4(a) is for the total electron density and (b) for total d band electron density. The densities edge of the structure unit is naturally influenced by the finite cluster size. Only the range marked by broken lines may be taken as the repeating unit. The electron density configuration differ only slightly whether total or d band density is calculated mainly because the configuration is for pure iron. Computation of phosphorous segregated boundary in progress would answer the extent of charge transfer between P and neighboring Fe atoms and the resulted decrease in electron charge participating in the Fe-Fe bonds. Fig. 5 shows the density structure constructed from the unit. Electron density at the boundary plane is shown in Fig. 5(a) and the electron density a quarter of one atomic plane off the boundary is shown in (b).

Fig. 4. Contours of (a) total and (b) 3 d band electron charge density across the $\Sigma=5$ coincidence boundary of Fig. 1(a).

Fig. 5. Contours of 3 d electron density (a) in the $\Sigma=5$ coincidence boundary and (b) a quarter of $\{310\}$ plane off the boundary plane

VI. INTERACTION OF LATTICE DISLOCATION WITH IMPURITY SEGREGATED GRAIN BOUNDARIES

Lattice dislocation is likely to interact with impurity segregated grain boundary very differently, because the boundary structure itself differ extensively by the segregation. The interaction is investigated presently as an example, with $\Sigma=9$ coincidence boundaries of iron. It would constitute a basic process connected to mechanical properties of impurity segregated grain boundaries.

(1) Dislocation interaction with pure grain boundaries

In Fig. 6(a) the black points correspond to atoms in the atomic plane one above or below those of white circles. A lattice dislocation marked by b_L is seen to the right in the upper grain. The Burgers vector of the lattice dislocation b_L is $a/2[111]$ type lattice dislocation. Molecular dynamical calculation of the structure after one hundred times of calculation with the repeating unit time corresponding to the 2×10^{-15} sec is shown in Fig. 6(b). The lattice dislocation was absorbed to the pure grain boundary as shown in the figures. The distortion of the structure unit at the boundary clearly show that the dislocation is nearly at the center of the figure. Jaswon and Forman(21) calculated this type of interaction between the grain boundary and the lattice dislocation, which is always repulsive. But if a pair of dislocation core is placed near, the core relaxation allows absorption of a lattice dislocation to even this type of an ordered boundary. The absorbed lattice dislocation, however, is no more stable. It can dissociate into a number of boundary dislocations with smaller Burgers vector. Dissociation of the lattice dislocation was also simulated in the figure; Fig. 6(c) shows the structure after another hundred times of molecular dynamical calculation. The lattice dislocation disintegrated into b_1 and b_2 boundary dislocations. The dislocations are shown in Fig. 3 and also in Fig. 6(d) where the coincidence plot right below shows the Burgers vector as well as the inherent step height corresponding to the resultant boundary dislocation. Conservation of the Burgers vector as well as the step height characterizes the dissociation process;

$$b_L = \sum_i^n b_i^{gb} \quad (3)$$

$$h_L = \sum_i^n h_i^{gb} \quad (4)$$

After 400 times of repeated calculation as shown in Fig. 6(d) the boundary dislocation b_1 with the Burgers vector parallel to the boundary migrated out from the boundary to the left and the boundary dislocation b_2 remained in the center as the result of the repeated calculation. This type of dissociation and migration of the boundary dislocations must be the cause of the image dissipation commonly observed

in thin foil transmission electron microscopy of absorbed lattice dislocation.

Fig. 6. Dislocation interaction with a $\Sigma=a$ coincidence boundary without P segregation. The lattice dislocation $b=a/2[111]$ introduced at (a) was absorbed (b), dissociated (c) into two boundary dislocations $b_1=a/9[221]$ and $b_2=a/18[557]$ and (d) the b_1 moved out by glide.

(2) Dislocation interaction with segregated grain boundary

The same coincidence-related boundary $\Sigma=9$ interacts differently with a nearby lattice dislocation when the boundary is segregated with phosphorous. Fig. 7 shows an example of the lattice dislocation introduced near a segregated coincidence-related boundary of $\Sigma=9$. The lattice dislocation instead of being absorbed towards the center of the boundary repulsed out from the boundary after 500 times of repeated calculation unlike in pure iron boundary. As shown in Fig. 7(b) the lattice dislocation became further away from the boundary. It glided out towards upper right corner by the back stress of the phosphorous unit structure characterizing the segregated boundary. Apparently, the strongly bonded prism structure centered with a phosphorous atom was the cause of the back stress. When the lattice dislocation is placed initially at the boundary instead, the dislocation doesn't move nor dissociate into partial boundary dislocation either.

Fig. 7(c) shows such an example. The dislocation core did not extend along the grain boundary as was the case with the nonsegregated grain boundary. Apparently, the strain field is localized by the resistance of this tightly bound unit prism structures. If the dislocation is forced to move in the segregated boundary, the boundary structure is no more likely to be conserved like in the case of the nonsegregated grain boundary because the structure unit is not just one atomic layer along the boundary but dispersed near the boundary. The nonconservative motion of the boundary dislocation invariably leaves a high energy metastable boundary that might serve as the nucleation site of the grain boundary fracture at low temperatures.

Fig. 7. Dislocation interaction with a $\Sigma=9$ coincidence boundary with P segregation. Lattice dislocation introduced at (a) repulsed away (b) from the boundary. Dislocation introduced at the boundary (c) did not dissociate.

Fig. 8. Simulation of fracture along $\Sigma=5$ coincidence boundary segregated with P (in black circles).

VII. FRACTURE OF IMPURITY SEGREGATED GRAIN BOUNDARIES

A simple example of perfectly brittle fracture of coincidence-related boundary is shown in Fig. 8. A tensile stress was applied horizontally with respect to the grain boundary which is notched at the top. The repeated molecular dynamical calculation for 100 times with each unit equals 2×10^{-15} sec showed the atomic sequence of the fracture. The fracture propagated zigzag skirting through the phosphorous centered prism structure. The weak bondings between the prism unit were broken into the fracture path. This example explains why the reduction in the grain boundary energy by phosphorous segregation doesn't increase the fracture strength of the boundary instead. The reduction in the energy of the structure unit is so large that the high energy due to the weak bonding of the structure unit is partially compensated and lowered the increase in the energy upon fracture. For this experiment a stress of 1-2 GPa was sufficient as far as notch is introduced at one corner of the boundary. The crack propagation speed didn't change much by the impurity segregation. The notch radius, however, was smaller with segregated boundaries rather than with nonsegregated ones. The crack propagation rate must be affected by a slow atomic vibrations along the advancing crack, which simply reflects weak bonding.(2) The crack propagation in more ductile material such as steel is not this much simple because matrix deforms at the same time. The interaction of the lattice dislocation as was discussed in the former chapter has to be incorporated in this rather ductile crack propagation process.

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DISCUSSION

J. Vitek: You showed a simulated fracture for a segregated boundary. Did you do a similar simulation for a pure boundary, and how did the results compare?

Y. Ishida: In the nonsegregated boundary, the artificial notch simply widened and no crack like propagation was noticed.

V. Vitek: Could you explain how one deduces from the change in the local density of states the change in cohesion?

Y. Ishida: The local density of electron orbital states of atom increases at energies around the atomic level ($\epsilon=0$). This means that the bonding states of atom E are decreased, while the non-bonding states are increased.

L. Priester: Concerning the dissociation of dislocations, what do you think about the influence of an element which does not induce embrittlement as C or B in Fe?

Y. Ishida: Molecular dynamic calculations of Hashimoto et al. (1) on B in Fe showed that the small size B atoms take positions in a more flexible manner than P atoms do. A more extensive dislocation core relaxation in the boundary is expected. Dissociation of the dislocation occurs at lower temperatures involving atomic scale shuffling type diffusion of C or B.

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