Ab-initio Calculations of Sodium Segregation in Aluminum Grain Boundaries

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The structures and valence electron density distributions of the aluminum $\Sigma 9(221)/[110]$ tilt grain boundaries with and without sodium segregation have been studied using an *ab-initio* pseudopotential method based on the density-functional theory and local density approximation. The embrittlement mechanism by sodium segregation has been explained as follows: Sodium segregation made valence electron density in the grain boundary region lower than that in region without segregation. It can be thought that sodium atoms which is segregated in the grain boundary behave as vacancies and made intergranular cohesion weaker. Therefore, we consider that sodium segregation in the grain boundary may be the source of the crack formation.

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I. Introduction

Since the mechanical properties of polycrystalline materials are mainly decided by the behavior of grain boundaries, characterization of grain boundaries is very important. Therefore over the past years a considerable number of studies have been reported on both the grain boundaries' characterization and the embrittlement by the impurity segregation. Recently atomic scale computer simulations have been carried out to study the dynamics of the internal structure of the grain boundary, especially for example as follows.

An investigation of the effect of phosphorus and boron on the tilt grain boundaries in iron⁽¹⁾ was performed by M. Hashimoto *et al.* Firstly the structure of grain boundaries was relaxed by using an empirical pair potential and the electronic structure was calculated by linear muffin-tin orbital method.

The relaxed $\Sigma 9(221)/[110]$ tilt grain boundary structure of Aluminum using pair potential by the embedded-atom method⁽²⁾ was calculated by Mills *et al.* The comparisons between the results of simulations and experimental structure from high resolution transmission electron microscopy was made in detail, and it was concluded that the embedded-atom method was able to describe the structure of the grain boundary very well.

The structure configuration of $\Sigma 11$ tilt and $\Sigma 3$ twist grain boundaries in aluminum by embedded-atom method and *ab-initio* approach based on the density functional theory⁽³⁾ and local-density approximation⁽⁴⁾⁽⁵⁾

was calculated by Wright and Atlas. Considerably large differences between the results by the two methods above on the grain boundary energy were found, which means that *ab-initio* calculation should be used in the complex system including two or more kinds of atoms. However, unfortunately, the *ab-initio* calculations of aluminum grain boundary, to our knowledge, are few.

It is reported that there are a lot of impurities scraps in aluminum recycled from the aluminum can, so the grain boundary embrittlement happens due to impurity segregation, bringing to the negative effects on the mechanical properties of aluminum. For example, as for aluminum magnesium alloy, if the concentration of sodium impurity is beyond 0.6 ppm, sodium tends to segregate on the grain boundary thus induces the embrittlement⁽⁶⁾. Therefore it is necessary to clarify the mechanisms of the grain boundary embrittlement in aluminum.

There are three types of interpretations about embrittlement by the impurity segregation. First is that the impurity atom segregates at grain boundary and makes the distance between matrix atoms in the grain boundary larger and brings to brittleness⁽⁷⁾. Second is that impurity segregation at the grain boundary make the binding energy of some pairs of atoms over the grain boundary lower⁽⁸⁾. Third is that segregated impurity atom binds matrix atoms around it much strongly, and the binding forces between matrix atoms are weakened⁽⁹⁾. But the embrittlement of aluminum by sodium and sodium segregation cannot be described by these theories.

In this paper, we calculated the atomic structures and valence electron density distribution of aluminum $\Sigma 9(221)/[110]$ tilt grain boundaries with and without sodium segregation by *ab-initio* pseudopotential method.

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We also gave the embrittlement mechanism of aluminum grain boundary by sodium segregation.

II. Theoretical Method

The present calculation is performed by *ab-initio* pseudopotential method⁽¹⁰⁾⁽¹¹⁾ based on the density functional theory and local-density approximation. We use the conjugate-gradient technique based on the Bylander-Kleinman-Lee method⁽¹²⁾ in order to solve the Kohn-Sham equations. The purpose of Bylander-Kleinman-Lee method is to obtain a set of occupied wave functions which minimizes energy expectation values of the Hamiltonian with fixed electron density and potential. After running all the state, the Hamiltonian matrix is diagonalized in the subspace spanned by the improved trial wave functions and the mixing scheme of Kerker⁽¹³⁾. In dealing with metallic systems, it is necessary to introduce fractional occupancies. To obtain smooth variation of the occupancy number, it is convenient to use Gaussian broadening of the one-electron levels. In this study, the width of the Gaussian is 0.2 eV. According to the Hellman-Feynman forces from the total energy of the system, relaxation of the grain boundaries can be easily performed.

For aluminum we used the optimized pseudopotential of Troullier and Martins⁽¹⁴⁾ type generated from the atomic configuration $3s^{1.03}3p^{0.53}3d^{0.5}$. The cutoff radii were 0.0952 nm for the *s* orbital and 0.106 nm for the *p* and *d* orbitals. For sodium we used the Bachelet-Hamman-Schlüter⁽¹⁵⁾ pseudopotential. The valence configurations of sodium were $3s^{0.60}3p^{0.05}3d^{0.05}$ and the cutoff radii were 0.0979 nm for the *s* orbital, 0.127 for the *p* orbital, 0.238

a.u. for the *d* orbital, respectively. The separable form of pseudopotentials by Kleinman and Bylander⁽¹⁶⁾ in which *p* orbital is the local component was used. The calculated equilibrium lattice constant of aluminum was 97.5% of the experimental values (0.405 nm), and that of sodium was 97.8% of the experimental value (0.4225 nm).

The supercell is constituted as Fig. 1, in which there are 84 atoms and two AlΣ9(221)/[110] tilt grain boundaries. Four of the atoms in the grain boundaries in the segregation model was replaced by sodium atoms. Four special *k* points in the irreducible part the volume of which is one eighth of the Brillouine zone were used. The numbers of plane-wave was 7047 and the cutoff energy was 176 eV.

Fig. 2 The relaxed structure with and without sodium segregation near the grain boundaries. The black circles indicate the positions of aluminum atoms without segregation, the light gray circles indicate those of aluminum atoms with sodium segregation, and the dark gray circles indicate those of sodium atoms. The arrows represent the direction of atom movement. A series of labels from A to E represent the positions of aluminum atoms without sodium segregation.

Fig. 1 The supercell of AlΣ9(221)/[110] tilt grain boundaries. The size of super cell is 2.847 nm × 0.838 nm × 0.559 nm. The larger circles are the positions of aluminum atoms which are replaced by sodium atoms in the segregation model. The dotted rectangles represent the calculated region of local density of states.

Fig. 3 The valence electron density distributions in the relaxed state, (a) aluminum grain boundary model, (b) sodium segregation model. Lighter gray shades indicate larger electron densities.

III. Results and Discussion

The atomic positions of supercell with and without sodium atoms after relaxation were shown in Fig. 2,

Fig. 4 Local density of states, (a) aluminum grain boundary model, (b) sodium segregation model. We divided into three energy band regions: low (~ -8.16 eV), middle ($-8.16 \sim -4.08$ eV), high ($-4.08 \sim 0$ eV).

Fig. 5 The valence electron density distributions of aluminum grain boundary model. These are divided into three energy band regions which is shown by the Fig. 4: (a) low (b) middle (c) high.

which indicates that the aluminum atoms around sodium atoms were away from sodium atoms. The distance between sodium atom (A') and aluminum atom (B') was 105.4% longer than that between aluminum atom (A) and aluminum atom (B), while A'-D' was 104.0% longer than A-D.

Figure 3 presents valence electron density distributions in the relaxed state of aluminum grain boundary model and segregation model. These are interpolated plots perpendicular to the [110] direction. Lighter gray indicate larger electron densities. The valence electron density was lower in the grain boundaries. For the occasion of sodium segregation, the region of lower valence electron density was wider than that of without impurity segregation.

Local density of states in these two models was shown in Fig. 4. We divided it into three energy parts: low (~ -8.16 eV), middle ($-8.16 \sim -4.08$ eV), and high ($-4.08 \sim 0$ eV), and plotted the figure of valence electron density distributions of the three energy parts, respectively, as in Figs. 5-6. The region of lower valence electron density mentioned above was widest in low electron energy parts.

Fig. 6 The valence electron density distributions of segregation model. These are divided into three energy band regions which is shown by the Fig. 4: (a) low (b) middle (c) high.

Fig. 7 The valence electron density was plotted along A-B-C, where A, B, C represent the atomic sites shown in Fig. 2. The solid lines indicate the valence electron density of the aluminum grain boundary model and broken lines indicate that of the sodium segregation model. The label A' represents the relaxed x-axis position of sodium atom, B' and C' represent those of aluminum atoms with sodium segregation.

Fig. 8 The valence electron density was plotted along A-D-E, where A, D, E represent the atomic sites shown in Fig. 2. The solid lines indicate the valence electron density of the aluminum grain boundary model and broken lines indicate that of the sodium segregation model. The label A' represent the relaxed x-axis position of sodium atom, D' and E' represent those of aluminum atoms with sodium segregation.

The valence electron density was plotted along the atoms A-B-C and A-D-E in Figs. 7-8. The label A represents the aluminum atom which is replaced by sodium atoms on the segregation model. The valence elec-

tron density decreased between A-B and A-D while that between B-C and D-E increased. It was clearly seen in the low energy part. Also the distance between A-B and A-D increased, while that between B-C and D-E decreased.

We explain the embrittlement mechanism by sodium as follows: Sodium segregation made valence electron density around sodium atoms lower than that in region without segregation. It can be thought that sodium atoms segregated in the grain boundary behave as vacancies. The valence electron density was lower in the grain boundaries both with and without sodium segregation comparing with the bulk part. But the lower region with sodium segregation was wider than that of without sodium segregation, which made Intergranular cohesion weaker. Therefore, we consider that sodium segregation in the grain boundary tends to be the source of the crack formation.

It can be considered that this mechanism can also apply to other kinds of tilt grain boundaries because there should be the lower valence electron density regions in these grain boundaries. Sodium segregation tends to occur in these grain boundaries and make valence electron density lower.

IV. Conclusion

Calculations of aluminum $\Sigma 9(221)/[110]$ tilt grain boundaries with and without sodium segregation have been performed by *ab-initio* pseudopotential method based on density functional theory and local-density approximation. The main results obtained are summarized as follows:

- (1) The result of atomic positions of the supercell after relaxation indicates that the aluminum atoms around sodium atoms were away from sodium atoms.
- (2) The valence electron density was lower in the grain boundaries both with and without sodium segregation comparing with the bulk part. But the lower region with sodium segregation was wider than that of without sodium segregation, which made Intergranular cohesion weaker.

Therefore, we consider that sodium segregation in the grain boundary may be the source of the crack formation.

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