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The First-Principles Electronic Calculations of Impurity Segregation in Aluminum Grain Boundary

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The structural properties and valence electron-density distributions of the aluminum grain boundaries with pottasium atoms are studied using ab initio pseudopotential method based on the local density-functional theory and local-density approximation. The results show that the valence electron-density was lower in the grain boundaries both with and without pottasium. But the lower region with pottasium was wider than that of without potassium segregation. And the valence electron-density around Al atoms which was close to K atoms was localized in the higher energy valence electrons distribution. Therefore induces the embrittlement of the grain boundaries.

Key words : *ab initio*, pseudopotential, segregation, grain boundary

1. 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 P and B on the tilt grain boundaries in Fe [1] was performed by M. Hashimoto et al. Firstly the structure of grain boundaries was relaxed by using an emprical pair potential and the electronic structure was calculated by linear muffin-tin orital (LMTO) method.

The relaxed Σ9(221)/[110] tilt grain boundary structure of Aluminum using pair potential by the embedded-atom method (EAM) was calculated by M. J. Mills et al. The comparisons between the results of simulations and experimental structure from high resolution transmission electron microscopy (HRTEM) was made in detail, and it was concluded that the EAM method can well described the structure of the grain boundary.

The structure configuration of Σ11 tilt and Σ3 twist grain boundaries in aluminum by EAM and ab-initio approach based on the density functional theory (DFT)[2] and local-density approximation (LDA) [3][4] was calculated by A. F. Wright and S. R. 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 Al-Mg alloy, if the concentration of Na impurity is beyond 0.6ppm, Na tends to segregate on the grain boundary thus induces the embrittlement [5]. Therefore it is necessary to clarify the mechanisms of the grain boundary embrittlement in aluminum.

There are three type 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 brittlemeny [6]. Second is that impurity segregations at the grain boundary make the binding energy of some pairs of atoms over the grain boundary lower [7]. Third is that segregated impurity atom binds matrix atoms around it much strongly, and the binding forces between matrix atoms are weaken [8]. But the embrittlement of aluminum by sodium and pottasium segregation cannot be described by these theories.

In this paper, we calculated the atomic structures and electron density distribution of aluminum Σ9(221)/[110] tilt grain boundaries with and without potassium segregation by *ab initio* pseudopotential method based on LDA-DFT. We also gave the embrittlement

mechanism of aluminum with potassium segregation.

2. THEORETICAL METHOD

The present calculation is performed on ab initio pseudopotentials[9][10] based on the density functional theory (DFT) and local-density approximation (LDA). We use the conjugate-gradient technique based on the Bylander-Kleinman-Lee (BKL) method [11] in order to solve the Kohn-Sham equations. The purpose of BKL method is to obtain a set of occupied wave functions $\{\psi_i\}$ which minimizes energy expectation values of the Hamiltonian with fixed electron density and potenstial. 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 [12]. 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 0.2eV.

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 pseudo-potentials of Troullier and Martins(TM) [13] type generated from the atomic configuration $3s^{1.0}3p^{0.5}3d^{0.5}$. The cutoff radii were 1.80 a.u. for the s orbital and 2.00 a.u.for the p and d orbitals.

For pottasium we used the Bachelet-Hamman-Schü(BHS) [14] pseudopotentials. The valence configurations of K were $3d^{0.05}4s^{0.60}4p^{0.05}$ and the cutoff radii were 1.92 a.u. for the d orbital, 2.52 for the s orbital, 3.24 a.u. for the p orbital, respectively.

The separable form of pseudopotentials by Kleinman and Bylander[15] in which p orbital is the local component was used.

The calculated equilibrium lattice constant of Al was 97.5% of the experimental values (0.405nm), and that of K was 100.4% of the experimental value (0.5225nm). The supercell is constituted as Figure 1, in which there are 84 atoms and two interfaces of AlΣ9(221)/[110] tilt grain boundaries. Four of the atoms in the grain boundaries in the segregation model was replaced by K 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 7,047 and the cutoff energy(Ecut) was 13Ry.

3. RESULTS AND DISCUSSION

The atomic positions of supercell with and without K atoms after relaxazation were shown in Figure 2, which indicates that the Al atoms around K atoms were away from K atoms.

Figure 3 presents valence electron-density distributions near the grain boundaries in the relaxed state of two models. These are interpolated plots perpendicular to the [110] direction. Lighter shades of gray indicate larger electron densities. The valence electron-density was lower in the grain boundaries . For the occasion of potassium segregation, the region of lower valence electron-density is wider than that of without impurity segregation.

We plotted the figure of valence electron-density distributions divided into three energy states: low (~ -0.55Ry), middle (-0.55 ~ -0.25Ry), and high (-0.25 ~ 0Ry) state as in Figure 4(a)-(c). We found that the electron-density of low state was distributed in the bulk region, while that of middle state was distributed around grain boundary region, and that of high state was

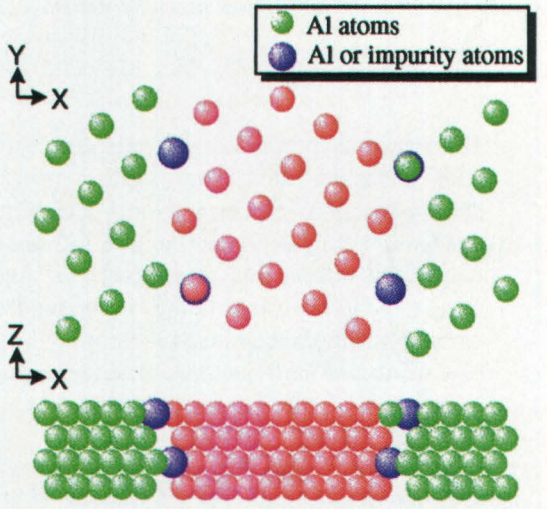

Figure 1 The supercell of AlΣ9(221)/[110] tilt grain boundaries. The size of supercell is 2.897nm x 0.852nm x 0.569nm. The larger circles are the positions of Al atoms which are replaced by K atoms in the model with segregation.

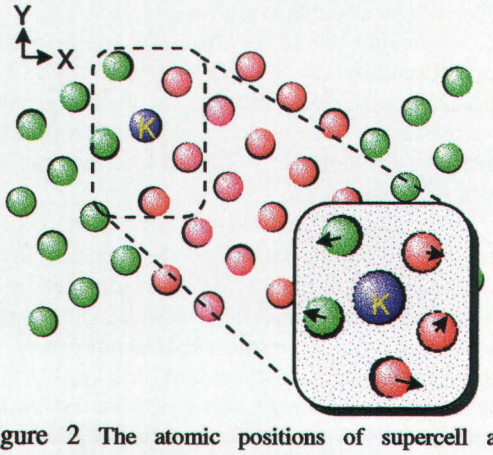

Figure 2 The atomic positions of supercell after relaxazation with and without K atoms in the grain boundaries. ●: Al atoms without segregation. ●: Al atoms with K segregation. The atoms near the grain boundaries (in dashed line rectangle region) are enlarged twice in the bottom-right of the figure. The arrow indicates the direction of atomic movement.

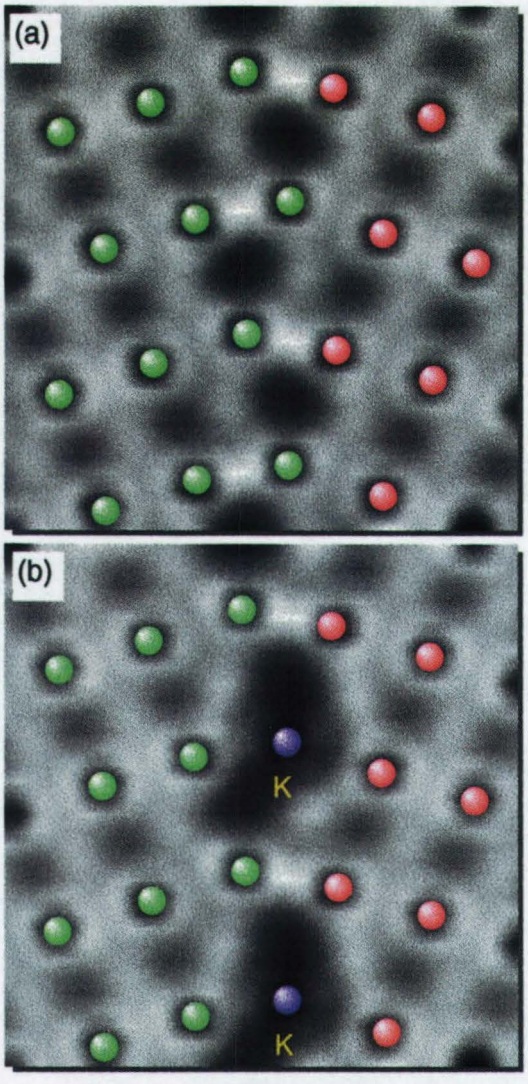

Figure 3 Valence electron-densitiy distributions near the grain boundaries in the relaxed state (a) without K atoms, (b) with K atoms. Lighter shades of gray indicate larger electron densities.

distributed in grain boundary region. The valence electron with high energy relates with the binding force of Al-Al atoms in the grain boundary.We also found that the valence electron-density around Al atoms which was close to K atoms was localized in the higher energy valence electrons distribution.

We explain the embrittlement mechanism by pottasium as follows. Pottasium segregation made valence electron-density in the grain boundary region lower than that of without segregation. A number of valence electron of pottasium is only one while that of aluminum is three. So it can be thought that pottasium atoms behave as vacancies and made Al-Al binding force weaker. Furthermore the localization of higher energy valence electrons distribution around Al atoms made the electron density of around K atoms much lower., Therefore induces the embrittlement of the grain boundaries.

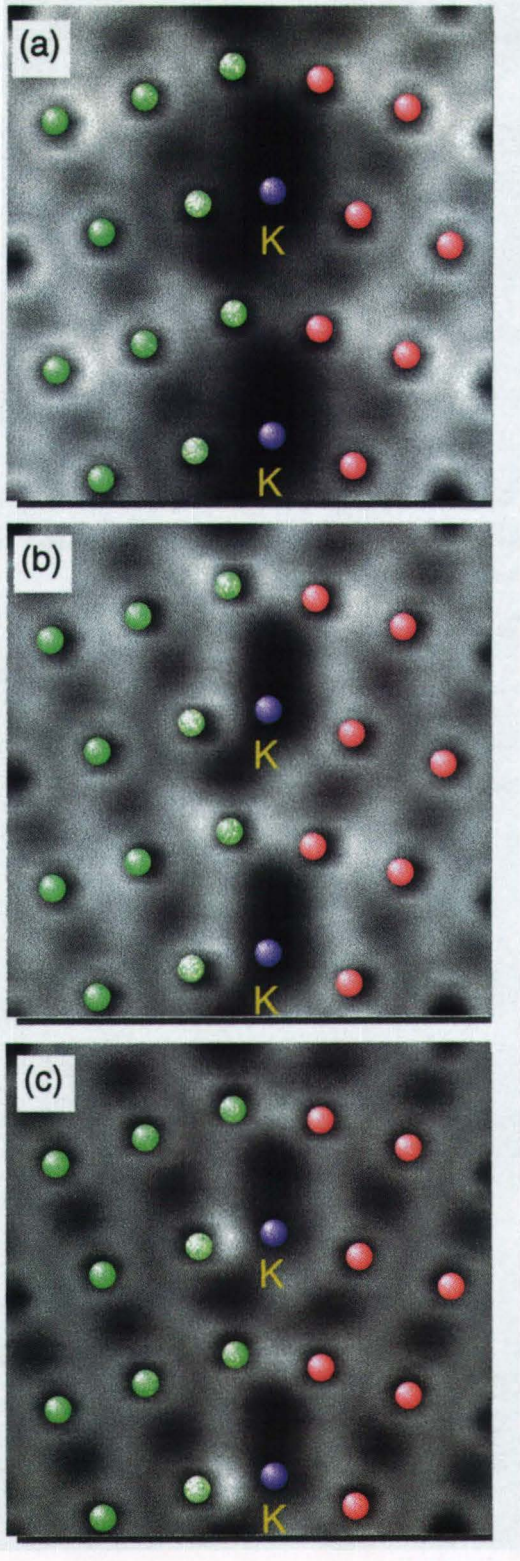

Figure 4 Valence electron-density distributions which is divided into three energy band regions: (a) low (~-0.55Ry) (b) middle (-0.55~-0.25Ry), (c) high (-0.25~0Ry).

4. CONCLUSION

Calculations of aluminum Σ9(221)/[110] tilt grain boundaries with and without potassium segregation have been performed by *ab initio* pseudopotential method based on LDA-DFT. The main results obtained are summarized as follows:

(1) The atomic positions of supercell after relaxazation indicates that the Al atoms around K atoms were away from K atoms.

(2) The valence electron-density was lower in the grain boundaries both with and without pottasium. But the lower region with pottasium was wider than that of without potassium segregation.

(3) The valence electron-density around Al atoms which was close to K atoms localized in the higher energy valence electrons distribution.

Therefore induced the embrittlement of the grain boundaries.

5. ACKNOWLEDGEMENTS

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