Effects of Segregated Ga on an Al Grain Boundary: A First-Principles Computational Tensile Test

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We perform a first-principles computational tensile test (FPCTT) to investigate the effect of segregated Ga (substitutional) on an Al grain boundary (GB). We show that isolated Ga segregation has little effect on the tensile strength of the Al GB, but greatly reduces the toughness and the Griffith fracture energy. The interfacial Al-Ga bond with some ionic character is suggested to be responsible for the nearly unchanged tensile strength and the toughness reduction. Based on the bond length evolution result, we further demonstrate that GB fracture is directly associated with interfacial Al-Ga bonds. [doi:10.2320/matertrans.47.2678]

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1. Introduction

It is well known that Ga is an extreme example of an Al grain boundary (GB) embrittler. Experimentally it has been shown that intergranular brittle fracture occurs due to Ga's segregation (penetration) in the Al GB, and Ga layers can be detected along the fresh fracture surface.^{1,2)} Even without applied load, the Ga penetration can induce a direct failure of the Al GB,¹⁾ which indicates an extremely large effect of Ga on the Al GB. Consecutively, many experimental efforts have been made until recently to explore the segregation behavior of Ga in the Al GB.^{3–7)} These experiments provide the evidence that the Al intergranular embrittlement is caused by Ga GB-segregation, and should be related with the GB weakening. On the other hand, only limited computational studies have been performed about this important issue, in which the GB structure and energetics with Ga segregation have been investigated.⁸⁾ Despite both experimental and computational efforts, the understanding of Ga-induced Al GB-embrittlement mechanism has not been fully reached.

Very recently, we have investigated the effects of different amount of segregated Ga on an Al GB based on atomic and electronic structures from first-principles calculations.⁹⁾ We found a charge drawing effect of Ga from the surrounding Al due to the electronegativity difference between Ga and Al. Because of such charge-drawing effect, the charge density decreases between Ga and Al and even along the Al GB. Increasing Ga segregation amount can enhance such charge-drawing effect. With enough amount of Ga segregation, there forms a heterogeneous α -Ga-like structure, resulting in a great change of GB structure. The charge density reduction thus occurs in both the Ga-Ga bonds and the Al-Ga interface. These effects are suggested to induce Al GB weakening, which should be responsible for the Ga-induced Al intergranular embrittlement.

The charge density reduction from the electronic and

atomic structure investigation, however, can only provide qualitative implication of the segregated-Ga-induced GB weakening. A quantitative investigation is therefore indispensable in order to further understand Ga-induced Al intergranular embrittlement. Here, we perform a quantitative investigation, *i.e.*, a first-principles computational tensile test (FPCTT), on a Ga-segregated Al GB, to examine the response of the GB to a tensile stress. This is a newly-developed technique due to the rapid development of computing capability, and has been successfully applied to even several large systems.^{10–14)} To further extend our previous work, the effects of different amount of segregated Ga on the tensile strength and other properties of the Al GB will be investigated through FPCTT. As a first step, in this paper, we perform FPCTT of an Al GB segregated by isolated Ga impurity. The ideal tensile strength, the ideal toughness and the Griffith fracture energy have been calculated, and the microscopic bond behavior in the tensile process has been thoroughly investigated.

2. Computational Method

We employ a first-principles total energy method based on density functional theory with local density approximation (LDA) using VASP.^{15,16)} In LDA, we use the Ceperley-Alder exchange and correlation functional parameterized by Perdew and Zunger.¹⁷⁾ The interaction between ions and electrons is described by ultrasoft pseudopotentials, and the plane-wave cutoff energy is 15 Ry. We construct the supercell containing two Al Σ 9 (2 $\bar{2}1$)/[110] tilt GBs, as shown in Fig. 1, the same as in our previous reports.^{12–14,18–22)} The supercell size is $28.685 \times 8.443 \times 5.629 \text{ \AA}^3$ without the applied strain according to the calculated Al lattice constant of 3.98 $\text{\AA}$, sampled by $(1 \times 4 \times 8)$ Monkhorst-Pack special k-point grid. The four Al atoms of E, E₁, E₂ and E₃ in the GBs are substituted by Ga atoms. Two periods are taken in the [110] direction in order to isolate the impurity atoms.

In the tensile test, we introduce an uniaxial tensile strain in

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Fig. 1 Supercell of an Al Σ 9(221)/[110] tilt grain boundary. The supercell includes 4 (110) atomic layers. Layers C and D are equivalent to layers A and B, respectively, due to the double periods in the [110] direction to isolate impurity atoms. (a) Top view of the supercell. Dark-gray and light-gray spheres indicate the atoms in the B (D) and A (C) layer, respectively. (b) Side view of the supercell. 4 blue spheres of E, E₁, E₂ and E₃ in the GBs indicate the substituted Ga atoms. Some atoms are marked for later discussion.

the GB normal direction, $[2\bar{2}1]$. The lattice dimensions in the GB plane are fixed to simplify the calculation, namely, the Poisson's effect is not considered. In each strain step, the starting atomic configuration is taken by uniform scaling from the fully-relaxed configuration of the preceding step to ensure the continuous strain path. The energy relaxation for each strain step is iterated until the forces on all the atoms are less than 10^{-3} eV $\text{\AA}^{-1}$. More calculation details can be found elsewhere.¹²⁾

3. Results and Discussion

3.1 Toughness, fracture energy and tensile strength

Figure 2(a) and (b) shows the supercell total energy (strain energy) and the strain energy density as a function of strain, respectively. For the clean GB and the Ga-segregated GB (Ga-GB), the total energy (strain energy) reaches, respectively, a maximum of 14.50 eV at a strain of 25% and 10.78 eV at a strain of 20% after a continuous increase with increasing strain. Beyond strains of 25% and 20% for the clean GB and the Ga-GB, the total energy of both two cases shows a sharp drop, and remains almost unchanged afterwards. This implies the system becomes stable beyond the strain of 25% for the clean GB and 20% for the Ga-GB. Thus, the fracture occurs beyond these strains. The strain energy density [Fig. 2(b)], which corresponds to the area under the stress-strain curve (Fig. 3), exhibits approximately the same trend as the strain energy evolution in spite of the volume increase with increasing strain.

The ideal toughness (work of fracture) is defined as the strain energy density out to fracture (Fig. 3). The ideal toughness is calculated to be 1.36 and 1.06 GPa for the clean and Ga-GB, respectively. The ideal toughness for the Ga-GB is $\sim 22\%$ lower than that of the clean GB. The Griffith

Fig. 2 (a) The supercell total energy (strain energy) and (b) the strain energy density of the clean (filled circles) and Ga-segregated (opened circles) Al GB as a function of strain. The zero reference energies are set as the minimum energy of the respect case.

Fig. 3 Stress in the tensile direction (the GB normal direction) as a function of strain. Filled circles and opened circles represent the clean and Ga-segregated GB respectively. Positive means tensile.

fracture energy, defined as the requisite energy to create unit crack surface, is directly associated with the total energy after the fracture. In Fig. 2(a), the energy after the fracture is respectively 9.85 and 8.95 eV for the clean and Ga-GB for the present supercell, corresponding to the Griffith fracture energy of 0.83 and 0.75 Jm⁻², respectively. The Griffith fracture energy for the Ga-GB is $\sim 10\%$ lower than that of the clean GB. Both the toughness and the Griffith fracture energy decrease due to the Ga segregation.

Stress in the tensile direction (the GB normal direction) as a function of strain is shown in Fig. 3. For the clean GB,^{12,13} the stress increases rapidly with increasing strain until a strain of 16%, at which the stress reaches its first maximum of 9.50 GPa. Then, the stress decreases slowly and reaches a minimum stress of 8.29 GPa at a strain of 23%. Afterwards, the stress increases again to its second maximum of 8.49 GPa at a strain of 25%, beyond which a sharp drop to 0.38 GPa occurs. Then, the stress decays slowly to zero. Thus, the ideal tensile strength of the clean Al GB is 9.50 GPa corresponding to the strain of 16%. The strain of 25% is the fracture point, consistent with the sharp drop of the total energy beyond this strain.

For the Ga-GB, initially, the stress shows little change until a strain of 15%, as compared with that of the clean GB. Then, the stress reaches its maximum of 9.71 GPa at a strain of 17%. Beyond the strain of 17%, the stress starts to decrease to 8.52 GPa at a strain of 20%, then drops suddenly and approaches to zero. Thus, the ideal tensile strength of the Ga-GB is 9.71 GPa, which is $\sim 2\%$ higher than that of the clean GB. The strain of 20% is the fracture point, consistent with the sharp drop of the total energy beyond this strain.

Thus, through performing the FPCTT, we have clarified that the ideal tensile strength of the Ga-GB is slightly higher than that of the clean GB, but the ideal toughness and the Griffith fracture energy are respectively $\sim 22\%$ and $\sim 10\%$ lower in comparison with the clean GB. The slightly higher tensile strength of GB for the isolated Ga segregation case seems not to agree with our previous speculation of the GB weakening from charge density reduction between the Al and Ga atom.⁹ This is not surprising if we take it into account that the charge-drawing effect due to the isolated Ga segregation is not strong enough to reduce the GB strength.

So far we considered only the charge reduction due to the charge-drawing effect that tends to decrease the Al-Ga bond strength, ignoring another important factor. Because of the same charge-drawing effect, the charge localizes around the Ga atom,⁹ which will lead to a somewhat ionic characteristic of the Al-Ga bond. Such characteristic can make the Al-Ga bond stronger than a pure metallic bond. Thus, two competitive factors, the charge reduction and the ionic-bonding characteristic, determine the Al-Ga bond and thus interface strength. When the Ga segregation concentration is low, such as the isolated Ga segregation in the present case, the charge reduction is not so large that the ionic character of the Al-Ga bond plays a major role, which may increase the Al-Ga bond and interface strength. With more Ga segregation, charge between the Al-Ga bond will decrease more.⁹ This makes the charge reduction factor determinative, leading to the weaker Al-Ga bond and interface. Since there only exhibits a slight tensile strength increase of the Ga-GB for the present isolated Ga segregation case, we can expect the tensile strength will decrease with further Ga segregation.

Although the GB with the isolated Ga segregation becomes slightly stronger, it breaks at a smaller strain of 20% as compared with that of the clean GB (25%). This decreases the strain energy of the Ga-GB absorbed in the fracture process until the fracture occurs. The GB toughness with the Ga segregation is thus largely reduced.

Fig. 4 Bond length of the interfacial bonds of EF and ER, and their back bonds as a function of strain. (a) and (b) are for the clean GB, while (c) and (d) for the Ga-segregated GB. The vertical axes are set as $(l - l_{Al})/l_{Al} * 100$, where l_{Al} is the bond length in the perfect fcc-Al (2.814 Å).

3.2 Bond length

The bond length evolution with increasing strain is plotted in Fig. 4. We chose two representative interfacial bonds, *i.e.*,

EF and ER, and all their back bonds for both the clean and Ga-GB in order to understand the fracture process from an atomic view.

For the clean GB [Figs. 4(a) and 4(b)], from the strain of $\sim 15\%$, the interfacial bond of EF has a more rapid increase, accompanied with a length decrease of its back bond EH. This implies that EF bond starts to break, corresponding to the first stress maximum (Fig. 3). Beyond the strain of $\sim 25\%$, another interfacial bond ER extends abruptly together with EF, with length decreases of all the other back bonds. This implies ER breaks, corresponding to the second stress maximum. The length of the interfacial bond of EF and ER extends linearly afterwards, while those of all the other back bonds remain unchanged, implying the fracture occurs. Thus, the fracture occurs at the GB interface, dominated by the interfacial bonds.

In the Ga-GB, the Al atoms E is replaced by Ga, forming the Al-Ga bonds EF and ER in the GB. Overall, both interfacial bonds exhibit the similar behavior to those of the clean GB, as shown in Figs. 4(c) and 4(d). EF extends more rapidly at a strain of $\sim 17\%$, which indicates EF starts to break at this strain, corresponding to the stress maximum (Fig. 3). At a strain of 20%, ER extends abruptly, indicating the GB interface breaks. Similar to that of the clean GB, the fracture occurs at the GB interface, dominated by these interfacial bonds.

However, the EF bond in the Ga-GB exhibits a different behavior in the fracture process from that of the clean GB. In the clean GB [Figs. 4(a) and 4(b)], EF extends continuously after its break starting at the strain of 15% until the strain of 25%, at which ER breaks. This indicates EF can still sustain part of applied stress. Different from the clean GB, Figs. 4(c) and 4(d) show that, in the Ga-GB, EF itself can hardly sustain applied stress after the strain of 17% (the starting point of break). Consequently, stress concentrates mainly on the ER bond, resulting in the ER break at the much smaller strain than that of the clean GB. The Ga-GB thus breaks at the smaller strain than the clean GB, leading to the toughness decrease of the Ga-GB. Hence, from an atomic view, the different behavior of the EF bond between the clean and Ga-GB exhibited in the fracture process is directly associated with the toughness decrease of the Al GB due to Ga segregation.

4. Summary

We have performed a first-principles computational tensile test (FPCTT) on an Al grain boundary (GB) with isolated Ga segregation. We show that the GB tensile strength is increased by only $\sim 2\%$ due to the isolated Ge segregation, but the toughness and the Griffith fracture energy are reduced

by ~ 22 and $\sim 10\%$, respectively. The interfacial Al-Ga bond with some ionic character is suggested to be responsible for the slightly higher tensile strength and the reduced toughness. Based on the bond length evolution result, we further demonstrate that the GB fracture is directly associated with the interfacial Al-Ga bonds. This is the first step to investigate the effect of Ga on an Al GB by FPCTT, which will contribute to the understanding of the Al intergranular embrittlement mechanism. Further investigation of the mechanical properties of the Al GB with different amount of Ga through FPCTT is in process.

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