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# First-principles computational tensile test on a Na-segregated Al grain boundary with an Si additive and an intergranular embrittlement suppression mechanism

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## Abstract

We have performed a first-principles computational tensile test (FPCTT) on a Na-segregated Al grain boundary (GB) with an Si additive. We show that the Si additive in the GB greatly increases both the tensile strength and the toughness of the Na-segregated Al GB. We demonstrate that the final GB fracture is dominated by the breaking of interfacial stronger Al–Si bonds according to the bond evolution with increasing strain. Based on the Na-induced Al intergranular embrittlement mechanism explored before and the present calculation results, we propose a GB-strengthening mechanism by adding a strengthening element such as Si for Al alloy to suppress the intergranular embrittlement by an Na impurity. Such an intergranular embrittlement suppression mechanism can explain the experimental observations.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

It is extremely important that mechanical properties are considered in design and fabrication, including the recycling of Al alloys. Impurities can have large effects on the mechanical properties of Al alloys, through, for example, segregating to grain boundaries (GBs). One example of an impurity is Na, which comes mainly from the primary Al. It has been

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experimentally found that trace amounts (ppm) of Na impurity induce high-temperature embrittlement of Al alloys, and such embrittlement results from impurity segregation at the GBs [1–3]. However, to fully remove the Na impurity from the Al alloy is extremely hard. Thus, it is very important to understand the mechanism of the GB embrittlement induced by the Na impurity, so that we can develop effective methods to suppress the embrittlement.

Many theoretical studies have been made to clarify the GB embrittlement. Using the Rice–Wang model [4], whether a segregating impurity in the GB is an embrittler or a cohesion enhancer can be determined by calculating the segregation energy difference of the impurity in a GB and a fractured free surface [5]. Atomic and electronic structures obtained from a first-principles method can show the effects of a segregated impurity on a GB and give some useful insights [6–13]. With the rapid development of computational ability, the first-principles computational tensile test (FPCTT) can be applied to larger systems such as those containing GBs [14–21]. Through the FPCTT, the ideal tensile strength can be determined, and the fracture process and the fracture mechanism can be investigated on an atomic and electronic scale.

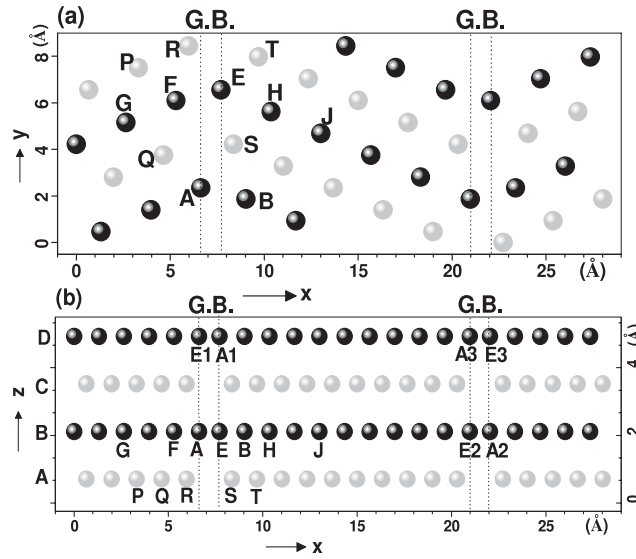
In the previous work we have performed the FPCTT [20] as well as electronic-structure calculations [8–10] on an Al GB with the segregated impurity of Na. We showed that the ideal tensile strength of the Na-segregated GB (Na-GB) is reduced in comparison with the clean GB. The fracture occurs at the GB interface, dominated by the break of the interfacial bonds. Aided by experiments, we revealed that the Na segregation induces the Al GB weakening, leading to the intergranular embrittlement of Al alloy [20].

According to the embrittlement mechanism of Na in an Al GB, we are able to propose two methods to suppress the Al intergranular embrittlement. One is to fully remove Na from the Al alloy, and the other is to increase the GB strength. Because the removal of Na is almost impossible, it is practicable to suppress the Na-induced Al GB embrittlement by increasing the GB strength.

Si is generally considered to be a strengthening element for metals such as Al. Experimentally it has been reported that, for an Al–5% Mg alloy, Si successfully suppresses the embrittlement caused by trace amounts (ppm) of Na [3]. Computationally, we have shown a possible strengthening effect of Si on the Al GB based on the first-principles calculations of the atomic and electronic structures [22]. To further understand how the Si additive affects the mechanical properties of the Al GB with segregated Na, in this paper, we perform the FPCTT to straightforwardly calculate the ideal tensile strength and the ideal toughness of the Na-segregated Al GB with an Si additive. The bond length evolution of both interfacial and bulk bonds in the tensile process has been investigated. A comparison has been made between the clean and Na-segregated GB. Based on these results, we are able to explore the fracture mechanism of the Al GB with Na and Si from an atomic scale, and give an explanation that the Si additive can suppress the intergranular embrittlement of Al alloys due to Na GB segregation.

## 2. Computational method

We employ a first-principles total energy method based on density functional theory using VASP [23, 24]. The local density approximation and ultrasoft pseudopotentials [25, 26] are used. The plane-wave cutoff energy is 15 Ry. We construct the supercell containing two  $\text{Al}\Sigma 9$  ( $2\bar{2}1$ )/[110] tilt GBs, as shown in figure 1, with  $x$ ,  $y$ ,  $z$  axes along  $[2\bar{2}1]$ ,  $[1\bar{1}4]$ , and  $[110]$  directions, the same as in our previous reports [8–13, 16, 17, 20, 22, 27]. 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 a  $(1 \times 4 \times 8)$  special  $k$ -point grid. Four Al atoms of E, E1, E2, and E3 in the GBs are substituted by Na atoms [20]; while another four Al atoms of A, A1, A2, and A3 in the GBs are substituted by Si atoms, indicating an Na-segregated GB



**Figure 1.** Supercell of an  $\text{Al}\Sigma 9(2\bar{2}1)/[110]$  tilt grain boundary. (a) Top view of the supercell. Dark-grey and light-grey spheres indicate the atoms in the B (D) and A (C) layer, respectively. (b) Side view of the supercell. Some atoms are marked for later discussion.

with Si additive. We chose the site A (and its symmetrically equivalent sites A1, A2, A3) as a substitutional Si-additive site, because the site A is one of the interface sites where the bulk fcc symmetry and coordination are greatly reduced similarly to the site E. Si can also occupy the interstitial sites. We consider the substitution case only for the simplification.

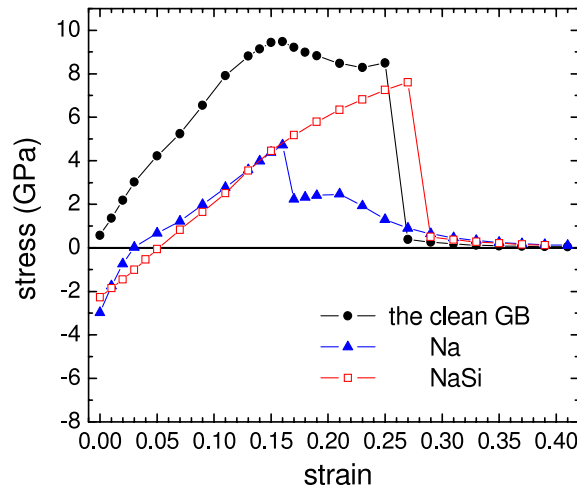
In the tensile test, we introduce a uniaxial tensile strain in the GB normal direction,  $[2\bar{2}1]$ . The lattice dimensions in the GB plane are fixed to simplify the calculation, neglecting the Poisson effect [14–20, 27]. In each strain step, the starting atomic configuration is taken by a uniform 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 [16, 17, 20].

### 3. Results and discussion

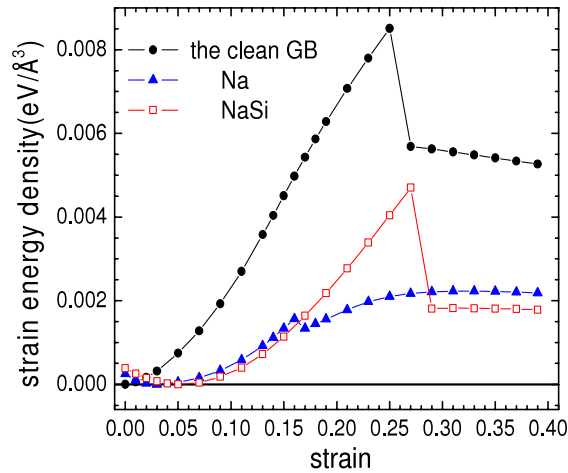
#### 3.1. Ideal tensile strength and ideal toughness

We first see how the stress in the tensile direction (the GB normal direction) changes in the tensile process. The previous studies [20] have shown that the segregation of Na in the GB reduces the Al GB strength. As shown in figure 2, the stress exhibits two maxima with increasing strain for the clean GB and the Na-GB. The stress at the first maximum for the clean GB is 9.50 GPa at a strain of 16%, and that at the second is 8.49 GPa at a strain of 25%, while those for the Na-GB are 4.73 GPa at 16% and 2.73 GPa at 21%, respectively. Thus, the tensile strength is 4.73 GPa for Na-GB,  $\sim 50\%$  lower than that for the clean GB (9.50 GPa).

For the Na-segregated GB with an Si additive (NaSi-GB), the stress becomes tensile beyond a strain of 5% because of the existence of residual compressive stress in the original supercell. The stress reaches its maximum of 7.61 GPa at a strain of 27% after a continuous increase with further increasing strain, then drops suddenly to 0.50 GPa, and slowly approaches zero. Thus, the tensile strength of the NaSi-GB is 7.61 GPa, which is 20% lower than that of



**Figure 2.** Stress in the tensile direction (the GB normal direction) as a function of strain. Circles, triangles, and squares represent the clean, Na-segregated, and Na-segregated with an Si-additive GBs, respectively. Positive means tensile, while negative means compressive.



**Figure 3.** The strain energy density of the clean (circles), Na-segregated (triangles) and Na-segregated with Si-additive (squares) GB as a function of strain. The zero reference energies are set as the minimum energy of the respective case.

the clean GB. However, in comparison with the Na-GB, the tensile strength is increased by 61% due to the addition of Si in the GB.

Furthermore, we can determine the ideal toughness, which is defined as the strain energy density out to fracture, from the FPCTT results. The strain energy density as a function of strain is plotted in figure 3. For the clean GB and Na-GB, the fracture occurs beyond a strain of 25% and 21%, respectively. The ideal toughness is calculated to be 1.36 GPa for the clean GB and 0.39 GPa for the Na-GB [20], respectively. For the NaSi-GB, the energy density reaches a maximum of  $0.0047 \text{ eV } \text{\AA}^{-3}$  at a strain of 27%. Then the energy density shows a sharp drop, and remains almost unchanged afterwards. This implies that the system becomes stable beyond a strain of 27%. Thus, the fracture occurs beyond this strain. The ideal toughness of NaSi-

GB is 0.75 GPa. The value is 45% lower than 1.36 GPa of the clean GB, but 92% higher than 0.39 GPa of the Na–GB. Thus, the addition of Si in the GB greatly increases the tensile strength and the toughness of Al GB with Na segregation.

Because the Si additive increases both the tensile strength and the toughness in comparison with those of the Na–GB, we can conclude that the Na-segregated Al GB with the Si additive is not easier to break under the same applied stress as that without the Si additive. This suggests that Si can suppress the Na-induced intergranular embrittlement of an Al alloy through increasing GB strength and toughness. This is consistent with our previous qualitative conclusion [22].

In figure 2, it is very interesting to see that the stress exhibits only one maximum for the NaSi–GB, different from the clean and the Na–GB in which the stress exhibits two maxima. The underlying reason can be explored by analysing the bond evolution with increasing strain as follows.

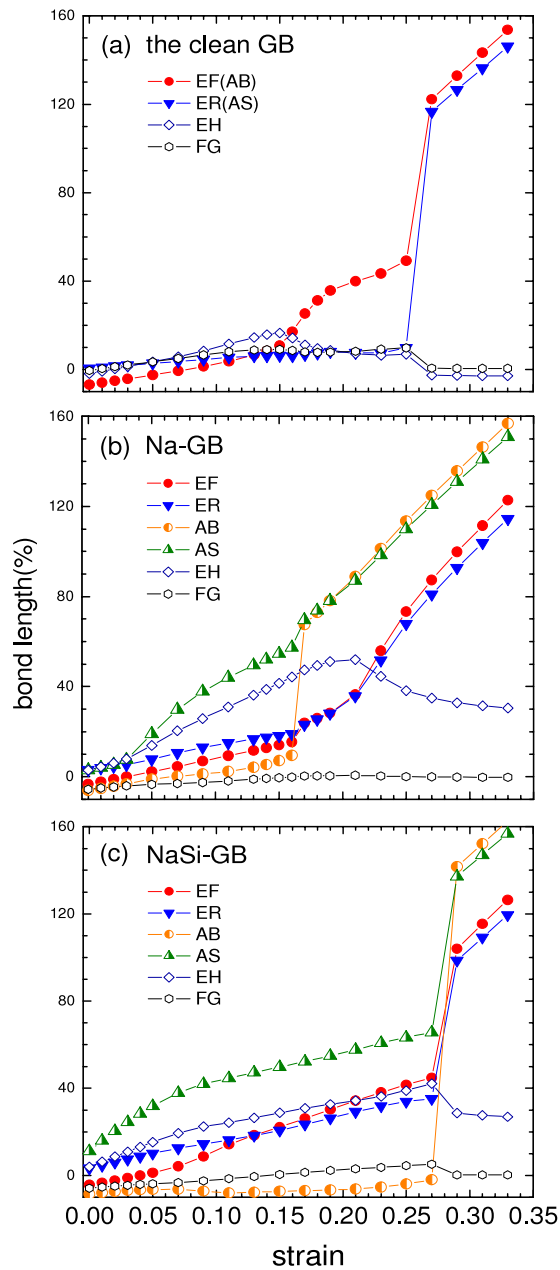
### 3.2. Bond length

Fracture occurs due to atomic bond breaking, which is directly associated with the applied stress. In order to understand the fracture process of the Na–GB with an Si additive from an atomic scale, we analyse bond length evolution with increasing strain, as shown in figure 4. Four representative interfacial bonds (EF, ER, AB, and AS) and two representative back bonds (EH and FG) are shown (see figure 1).

According to our previous analysis [20], the fracture occurs in the GB interface dominated by the interfacial bonds breaking for the clean GB and the Na–GB. For the clean GB (figure 4(a)), the breaking of the EF (AB) bond occurs at a strain of 16%, corresponding to the first stress maximum, another interfacial bond ER (AS) breaks beyond the strain of 25%, corresponding to the second stress maximum (figure 2). The EF (AB) bond breaks first because of the larger projected length of EF (AB) than that of ER (AS) in the tensile direction. The existence of the interfacial bonds with different projected length in the tensile direction is responsible for the presence of the two stress maxima for the clean GB. For the Na–GB (figure 4(b)), the first stress maximum is mainly contributed by the Al–Al bond of AB, which breaks beyond the strain of 16%. The second stress maximum is contributed by the Al–Na bonds of EF and ER, which break beyond the strain of 21% (figure 2). The interfacial Al–Al bonds initially extend and become weaker because of GB expansion caused by Na segregation, leading to their breaking first. The presence of two stress maxima for the Na–GB results from the existence of the bonds containing different species, i.e. Al–Al and Al–Na bonds in the GB.

For the NaSi–GB, the interfacial bonds consist of both Al–Na bonds (EF and ER) and the Al–Si bonds (AB and AS). As shown in figure 4(c), initially, the interfacial Al–Na bonds of EF and ER and the Al–Si bond of AS extend rapidly with increasing strain, while another interfacial Al–Si bond of AB remains almost unchanged. This implies that the Al–Si bond of AB mainly sustains the interfacial stress because of shorter length and thus greater strength [22]. Beyond the strain of 27%, all the interfacial bonds of EF, ER, AB, and AS extend abruptly, with length decreases of the back bonds of EH and FG. This implies that fracture occurs, corresponding to the stress maximum (figure 2).

Although there exist different species of bonds in the GB (i.e. Al–Na and Al–Si bonds), the stress concentrates mainly on one stronger Al–Si bond of AB. The back bond of EH (Al–Na bond) extends by as much as ~42% before the fracture occurs, but it contracts finally. This implies that there exists a competition for the final fracture among the different atomic planes in the GB. The same competition occurs for the Na–GB. Because the Al–Si bond of AB is much stronger than the Al–Na bond of EF, the interfacial AB bond dominates the interfacial fracture, leading to the presence of one stress maximum only.



**Figure 4.** Lengths of the interfacial bonds (EF, ER, AB, and AS) and their back bonds (EH and FG) as a function of strain. (a), (b) and (c) represent the clean GB, the Na-segregated GB, and the Na-segregated GB with Si additive, respectively. 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).

### 3.3. Suppression mechanism for the Al intergranular embrittlement

According to the above analysis, when part of the Al atoms is replaced by Si atoms, the interfacial Al–Al bonds are substituted by the stronger interfacial Al–Si bonds [22]. The GB strength increase due to Si addition is mainly contributed by these stronger Al–Si bonds. Thus,

it becomes clear that the Na-segregated Al GB is strengthened by the Si additive, and the interfacial Al–Si bond is responsible for the GB strengthening. Such a strengthened GB is not easier to break under an applied stress as compared with the Na-segregated one. Consequently, the Al intergranular embrittlement induced by Na segregation can be suppressed by the GB strengthening due to the Si addition.

Si will not segregate in the Al GB because Si and Al can form an AlSi alloy. When Si is added to the Al alloy with the segregated Na, Si will mainly exist in the bulk instead of the GB. In this case, the suppression of intergranular embrittlement induced by Na will not be effective according to the suppression mechanism of GB strengthening as proposed above. However, if the added Si is beyond some critical amount, some Si atoms can also go to the GB, effectively suppressing the GB embrittlement. Experimentally, it has been reported that the intergranular embrittlement of an Al alloy induced by 2 ppm of Na is successfully suppressed by the additional Si of 1480 ppm, but there is no suppression effect if the Si concentration is less than 700 ppm [3]. The 700 ppm is the solution limit of Si in the Al alloy. Hence, Si will be effective for suppressing the intergranular embrittlement of Al alloys induced by Na only beyond the solubility, because Si can go to the GBs. The proposed intergranular embrittlement suppression mechanism is thus consistent with experimental observations.

The proposed intergranular embrittlement suppression mechanism can also be reasonably generalized to other elements that can increase the Al GB strength. Further investigation is in progress.

#### 4. Conclusions

In conclusion, we have performed a first-principles computational tensile test (FPCTT) on an Na-segregated Al GB with an Si additive. We show that both the ideal tensile strength and the ideal toughness of the Na-segregated GB are increased due to the addition of Si in the GB. Based on the bond length evolution with increasing strain, we further demonstrate that the stronger interfacial Al–Si bonds are responsible for GB strengthening, and the breaking of these Al–Si bonds dominates the GB fracture. We propose a GB-strengthening mechanism for suppressing the Na-induced intergranular embrittlement of an Al alloy by adding a strengthening element such as Si, which can explain the experimental observations.

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#### References

- [1] Okada H and Kanno M 1997 *Scr. Mater.* **37** 781
- [2] Horikawa K, Kuramoto S and Kanno M 1998 *Scr. Mater.* **39** 861
- [3] Horikawa K, Kuramoto S and Kanno M 2001 *Acta Mater.* **49** 3981
- [4] Rice J R and Wang J S 1989 *Mater. Sci. Eng. A* **107** 23
- [5] Wu R, Freeman A J and Olson G B 1994 *Science* **265** 376
- [6] Thomson D I, Heine V, Finnis M W and Marazi N 1997 *Phil. Mag. Lett.* **76** 281
- [7] Thomson D I, Heine V, Payne M C, Marzari N and Finnis M W 2000 *Acta Mater.* **48** 3623
- [8] Lu G-H, Suzuki A, Ito A, Kohyama M and Yamamoto R 2000 *Modelling Simul. Mater. Sci. Eng.* **8** 727
- [9] Lu G-H, Suzuki A, Ito A, Kohyama M and Yamamoto R 2001 *Phil. Mag. Lett.* **81** 757
- [10] Lu G-H, Suzuki A, Ito A, Kohyama M and Yamamoto R 2003 *Mater. Trans.* **44** 337
- [11] Lu G-H, Kohyama M and Yamamoto R 2001 *Mater. Trans.* **42** 2238



- [12] Lu G-H, Kohyama M and Yamamoto R 2003 *Phil. Mag. Lett.* **83** 159
- [13] Zhang Y, Lu G-H, Wang T, Deng S, Shu X, Kohyama M and Yamamoto R 2006 *J. Phys.: Condens. Matter* **18** 5121
- [14] Kohyama M 1999 *Phil. Mag. Lett.* **79** 659
- [15] Kohyama M 2002 *Phys. Rev. B* **65** 184107
- [16] Lu G-H, Deng S, Wang T, Kohyama M and Yamamoto R 2004 *Phys. Rev. B* **69** 134106
- [17] Zhang Y, Lu G-H, Deng S and Wang T 2006 *Acta Phys. Sin.* **55** 2901
- [18] Chen J, Xu Y-N, Rulis P, Ouyang L and Ching W-Y 2005 *Acta Mater.* **53** 403
- [19] Yamaguchi M, Shiga M and Kaburaki H 2005 *Science* **307** 393
- [20] Lu G-H, Zhang Y, Deng S, Wang T, Kohyama M, Yamamoto R, Liu F, Horikawa K and Kanno M 2006 *Phys. Rev. B* **73** 224115
- [21] Zhang Y, Lu G-H, Deng S, Wang T, Xu H, Kohyama M and Yamamoto R 2007 *Phys. Rev. B* **75** 174101
- [22] Zhang Y, Lu G-H, Zhang H, Wang T, Deng S and Hu X 2007 *Mater. Sci. Forum* **546–549** 829
- [23] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558
- [24] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
- [25] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
- [26] Kresse G and Hafner J 1994 *J. Phys.: Condens. Matter* **6** 8245
- [27] Zhang Y, Lu G-H, Wang T, Deng S, Kohyama M and Yamamoto R 2006 *Mater. Trans.* **47** 2678