# Origin of intergranular embrittlement of Al alloys induced by Na and Ca segregation: Grain boundary weakening

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Using a first-principles computational tensile test, we show that the ideal tensile strength of an Al grain boundary (GB) is reduced with both Na and Ca GB segregation. We demonstrate that the fracture occurs in the GB interface, dominated by the break of the interfacial bonds. Experimentally, we further show that the presence of Na or Ca impurity, which causes intergranular fracture, reduces the ultimate tensile strength when embrittlement occurs. These results suggest that the Na/Ca-induced intergranular embrittlement of an Al alloy originates mainly from the GB weakening due to the Na/Ca segregation.

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Grain boundary (GB) embrittlement in metals induced by impurity segregation has been known for quite a long time, but its physical origin is still not fully understood. One prevalent approach to understand the GB embrittlement is to calculate the segregation energy difference between a GB and a fracture free surface using the Rice-Wang model,[1] based on which whether a segregating impurity in the GB is an embrittler or a cohesion enhancer can be determined. This method underlies the effect of impurity on intergranular embrittlement from an energy point of view and has been successfully applied to Fe and Ni GB's.[2]

On the other hand, to understand the GB embrittlement, it is indispensable to accurately examine the response of a GB with impurity segregation to a tensile or shear stress, because a fracture process is directly associated with local stress. With the rapid development of computing capability, the ideal strength (tensile or shear) of materials can be determined by a first-principles computational tensile test (FPCTT) or shear test. In addition to single crystals (for Al, see Refs. 3–6), this method has been successfully applied to several clean GB's.[7–10] The first FPCTT to understand the impurity-induced GB embrittlement was made on a Ni GB by Yamaguchi *et al.* recently.[11] But in their calculation, the fracture surface was arbitrarily set between the two atomic layers in the GB and the FPCTT's were performed without any atomic relaxation, which can result in inaccurate stress values.

Recently, it has become possible to investigate the effect of trace amount of impurity (ppm) on the mechanical properties of Al alloys, aided by the development of high-purity materials preparation and trace-impurity detection technique. For an Al–5% Mg alloy, the trace amount of Na or Ca impurity has been shown to induce high-temperature embrittlement, but such embrittlement disappears in a base alloy with Na concentration lower than 0.01 ppm.[12,13] Because the contamination of these impurities is inevitable in the process of Al recycling and their removal is quite hard, it is obviously important to clarify the GB embrittlement mechanism induced by these impurities, so as to develop effective methods to suppress the embrittlement. So far, however, there are only very limited theoretical studies of impurity effect on the properties and embrittlement of Al GB's.[14–16,18,19] The FPCTT, which reveals the stress-strain relation until the break point of GB, has not yet been made.

Here, we perform a more complete FPCTT (i.e., including the fully atomic relaxations) on an Al GB with impurity segregation of Na and Ca. We show that the tensile strength of the Na- and Ca-segregated GB (Na/Ca-GB) is reduced in comparison with the clean GB. We demonstrate that the fracture occurs at the GB interface, characterized by the break of interfacial bonds. Experimentally, we further show that the presence of Na or Ca impurity, which causes intergranular fracture, reduces the ultimate tensile strength (UTS) when embrittlement occurs. These results indicate that both Na and Ca segregation induces Al GB weakening, which is responsible for the GB embrittlement.

We employ a first-principles total energy method based on density functional theory with local density approximation and ultrasoft pseudopotential as implemented in VASP.[17] The plane-wave cutoff energy is 15 Ry. We construct the supercell containing two Al $\Sigma 9(2\bar{2}1)/[110]$ tilt GB's, as shown in Fig. 1. The supercell size is $28.685 \times 8.443 \times 5.629$ Å without the applied strain according to the calculated Al lattice constant of 3.98 Å, sampled by a $(1 \times 4 \times 8)$ special **k**-point grid. The double coincidence-site-lattice periods in the [110] direction are adopted in order to separate the impurity atoms. Four atoms of $E$, $E_1$, $E_2$, and $E_3$ in the GB's that are symmetrically equivalent (Fig. 1) are substituted with Na or Ca for impurity segregation. We chose these atom sites because they are energetically favorable segregation sites (as shown in the following) as well as their most significant structural disorder such as the reduced number of coordination, which is expected to have the largest effect on the GB. For example, atom $E$ has only 7 first nearest-neighbor atoms, while

 

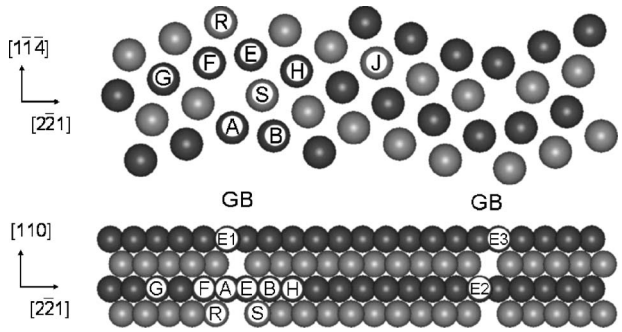


FIG. 1. Top view (upper panel) and side view (lower panel) of the supercell of Al $\Sigma 9(2\bar{2}1)/[110]$ tilt grain boundary. The supercell contains 84 atoms in the four (110) atomic layers. Four atoms of $E$, $E_1$, $E_2$, and $E_3$ in the GB's are substituted with Na or Ca for impurity segregation.

another interfacial atom $F$ has 9, as compared with 12 for the bulk atoms. In the FPCTT, we introduce a uniaxial tensile strain with an increment as small as 1%–2% in the GB normal direction $[2\bar{2}1]$. To simplify the calculation, the lattice dimensions in the GB plane are fixed, neglecting the Poisson's effect.[3,7–11] In each tensile step, the energy relaxation iterates until the forces on all the atoms are less than $10^{-3}$ eV Å$^{-1}$. More details can be found elsewhere.[9]

First, to show energetically if Na or Ca has a tendency to segregate into an Al GB, we calculate total energies with substitution of Na or Ca atom for one of the Al atoms in the GB (e.g, atom $E$ in Fig. 1) and the bulk (e.g, atom $J$). The energies are lowered by ~0.3 and 0.5 eV/atom for Na and Ca segregation, respectively, indicating that both Na and Ca segregation are energetically favorable. This is possibly because the GB can provide more space than the bulk for larger Na or Ca atom[16] and hence relax the compressive stress induced by Na or Ca.

Using the calculated segregation energies of Na and Ca, we can estimate impurity segregation concentration in the GB. According to the McLean equation,[20]

$$C_{GB} = \frac{C_{bulk}\exp(-E_{seg}/RT)}{1 + C_{bulk}\exp(-E_{seg}/RT)}, \quad (1)$$

where $C_{GB}$ and $C_{bulk}$ are the impurity concentrations in the GB and bulk, respectively, $E_{seg}$ is the impurity segregation energy, $T$ is the absolute temperature, and $R$ is the universal gas constant. Considering the segregation energy of Na in the Al GB of −0.3 eV and the typical embrittlement temperature of 300 °C,[12,13] we can obtain that the Na concentration in the GB is ~400 times higher than that in the bulk, which indicates that almost all the impurity will segregate into the GB. This suggests that embrittlement of Al alloy originates from Na GB segregation although it is difficult to see segregated Na in the Al GB in the experiment.[12,13,21] For the Ca case in which the segregation energy is −0.5 eV, the Ca concentration in the GB is shown to be much higher than that in the bulk (more than 20 000 times).

Next, we determine if Na or Ca is an embrittler in an Al GB by estimating the segregation energy difference of Na and Ca in a GB ($\Delta E_{GB}$) and a fracture free surface ($\Delta E_{FS}$).

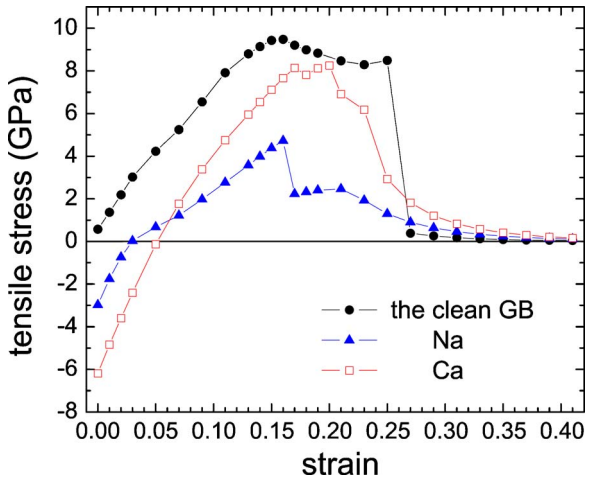


FIG. 2. (Color online) Stress in the tensile direction (the GB normal direction) as a function of strain. Circles, triangles, and squares represent the clean, Na-segregated, and Ca-segregated GB's, respectively. Positive means tensile, while negative means compressive.

$\Delta E_{GB} - \Delta E_{FS}$ is calculated to be +1.5 eV/atom for Na and +0.2 eV/atom for Ca. Consequently, both Na and Ca are a GB embrittler according to the Rice-Wang thermodynamic theory,[1] but the embrittlement effect of Ca is much smaller.

Now, we demonstrate that the segregation of Na and Ca reduces the Al GB strength by performing the FPCTT.[22] The results are shown in Fig. 2. For the clean GB, the stress reaches a maximum of 9.50 GPa at a strain of 16% after a continuous increase with increasing strain.[23] Following a minimum, there appears a second stress maximum of 8.49 GPa at a strain of 25%, beyond which a sharp stress drop to 0.38 GPa occurs. Afterwards the stress decays slowly to zero. The tensile strength of the clean Al GB is thus 9.50 GPa corresponding to the strain of 16%, but the fracture occurs later at 25%.

Both Na and Ca segregation induce Al GB expansion due to the larger atomic radii of Na and Ca than that of Al,[16] leaving a residual compressive stress in the supercell. The applied external tensile strain therefore compensates this compressive stress first and makes the stress become tensile beyond strains of 3% and 5% for the Na and Ca GB, respectively (Fig. 2). With a further increase of strain, the stress goes through two maxima followed by a continuous decrease to zero, similar to the clean GB. The stress at the first maximum for the Na GB is 4.73 GPa at a strain of 16%, and that at the second is 2.73 GPa at 21%, while those for the Ca GB are 8.14 GPa at 17% and 8.26 GPa at 20%, respectively. Thus, the tensile strength is 4.73 GPa for the Na GB and 8.26 GPa for the Ca GB, which is, respectively, 50% and 13% lower than that of the clean GB. This confirms our previous qualitative speculation.[16] Furthermore, the ideal toughness (defined as the strain energy density out to fracture) is calculated to be 0.39 GPa for the Na GB and 0.93 GPa for Ca, which is, respectively, 72% and 32% lower than 1.36 GPa of the clean GB. Thus, the intergranular fracture of the Na GB is easier than that of the Ca GB, and both are easier than that of the clean GB.

As we mentioned above, Poisson's effect has been ne-

glected to save the computational time.[3,7–11] We point out here that although considering Poisson's ratio can change the absolute strengths of the clean, Na and Ca GB's, it will have less effect on the relative strength—i.e., the reduction of the Al GB strength by the segregation of Na or Ca impurity. We can estimate how much the lattice dimensions parallel to the GB plane change according to the experimental Poisson's ratio ~0.35 of Al. Suppose the fracture strain to be 20% in the GB normal direction, which is the case for Na and Ca GB, we can estimate that the strain in the GB parallel directions is ~7%, corresponding to, respectively, ~0.6 and 0.4 Å in these two directions. Compared with the zero-strain lattice dimensions in these two directions (~8.4 and 5.6 Å), such a small change can be expected to not significantly alter the GB structure.

It is interesting to see that the stress exhibits two maxima in the extension process in all these cases. The stress at the first maximum is higher than that at the second for the clean and Na GB, while the reverse is true for the Ca GB. In order to understand such fracture process from an atomic view and explain the above phenomena, we analyze bond length evolution with increasing strain, as shown in Fig. 3. We choose four representative interfacial bonds—i.e., *EF*, *ER*, *AB*, and *AS* (Fig. 1). Among these interfacial bonds, *EF* and *AB* have a much larger projected length in the tensile direction than *ER* and *AS*. The length evolutions of two representative back bonds, *EH* and *FG*, are also shown.

In the clean GB, *EF* and *ER* are symmetrically the same as *AB* and *AS*. As shown in Fig. 3(a), the interfacial bond of *EF* (or *AB*) extends more rapidly beyond the strain of ~15%, accompanied with a length decrease of its back bond *EH*. Beyond the strain of 25%, another interfacial bond *ER* (or *AS*) extends abruptly, with decreases of all the back bonds to the lengths nearly equal to or shorter than the bulk one. This implies that the breaking of *EF* (*AB*) and *ER* (*AS*) corresponds to the first and second stress maxima (Fig. 2), respectively. All the interfacial bonds show a linear extension afterwards, while all the back bonds remain unchanged, characterizing the occurrence of fracture. The existence of the second stress maximum is due to the different projected length of *ER* (*AS*) (1.65 Å) and *EF* (*AB*) (2.54 Å) in the tensile direction and the lower stress at the second maximum is due to the stress concentration on *ER* (*AS*) only after the *EF* (*AB*) breaking.

The impurity segregation forms the Al-impurity (*EF* and *ER*) bonds in addition to the Al-Al bonds (*AB* and *AS*) in the GB. Therefore, these bonds respond to the applied strain differently from those in the clean GB. For the Na GB, the Al-Al interfacial bond of *AS* does not contribute to the interfacial strength due to its largely elongated bond length caused by interface reconstruction at the strain of 5%. The first stress maximum is mainly contributed by the Al-Al bond of *AB*, which breaks beyond the strain of 16%. This leads to a rapid extension of the Al-Na interfacial bonds of *EF* and *ER*, but the eventual break-up of these two bonds occurs beyond the strain of 21%, which contributes to the second stress maximum. Because of the rather weak nature of Al-Na bond in comparison with the Al-Al bond,[16] the second maximum exhibits a much lower stress. For the Ca GB, the Al-Al bonds of *AB* also contributes to the first stress maximum at

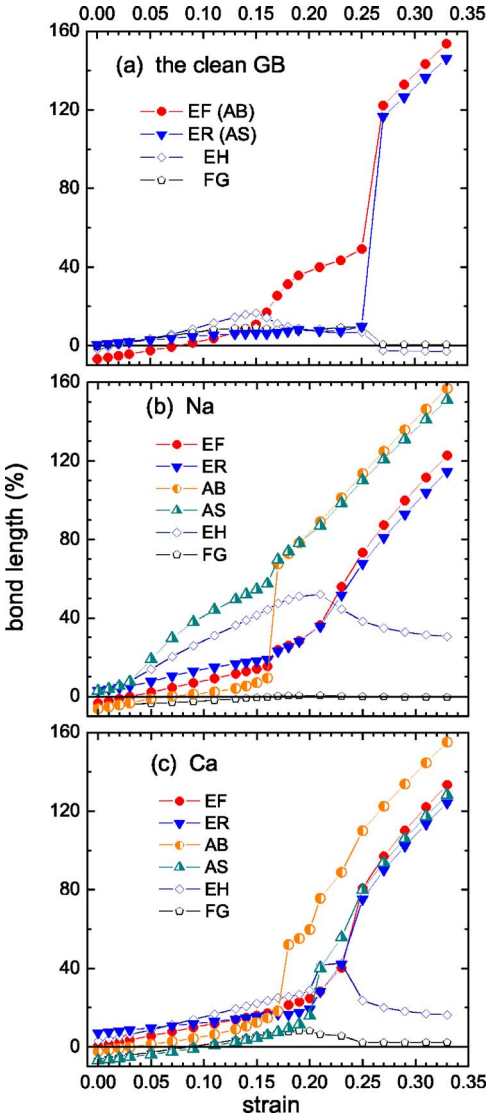


FIG. 3. (Color online) Lengths of the interfacial bonds (*EF*, *ER*, *AB*, and *AS*) and two of their back bonds (*EH* and *FG*) as a function of strain. (a), (b), and (c) represent the clean, Na-segregated, and Ca-segregated GB's, respectively. The vertical axes are set as $(l-l_{\mathrm{Al}})/l_{\mathrm{Al}}\times 100$, where $l_{\mathrm{Al}}$ is the bond length of the perfect fcc Al (2.814 Å).

the strain of 17%, while all the other interfacial bonds including both the Al-Al bonds of *AS* and the weaker Al-Ca bonds of *EF* and *ER* (but stronger than Al-Na bond) contributes to the second stress maximum at 20%. This makes the second stress maximum for the Ca-GB slightly higher.

It should be pointed out that this "double-stress maximum" phenomenon should be a general pattern in the ideal tensile test as long as interfacial bonds are of different kinds, containing either the same type of atoms but having different projected length in the tensile direction or different types of atoms (such as Al-Al and Al-impurity). In addition, this feature may be associated with the character of metallic bonds, because such a phenomenon has not been observed in the FPCTT of SiC GB's.[7,8]

According to the above analysis, when part of the Al atoms in the GB is replaced by an impurity (Na or Ca), inter-

TABLE I. The ultimate tensile strength (MPa) of the Al–5% Mg alloy with and without trace Na and Ca impurities at the different temperatures. The detail of sample preparation can be found in the previous report (Ref. 13). The tensile tests were performed under the Ar atmosphere of $10^2$ Pa with an initial strain rate of $8.3\times10^{-4}$/s.

| Temperature (°C) | 25 | 150 | 200 | 250 | 300 | 350 | 400 |
|---|---|---|---|---|---|---|---|
| Base alloy | 230 | 180 | 150 | 110 | 85 | 62 | 36 |
| Na (2 ppm) | 230 | 175 | 135 | 90 | 75 | 57 | 34 |
| Ca (10 ppm) | 231 | 174 | 136 | 105 | 88 | 66 | 36 |

facial Al-Al bonds break first instead of Al-impurity bonds. These Al-Al bonds initially extend and thus become weaker due to GB expansion caused by Na or Ca segregation.[16] So the substituting weaker interfacial Al-impurity bonds and the remaining weakened Al-Al bonds both contribute to GB weakening. Since the number of interfacial Al-Al bonds becomes fewer with more impurity segregation, the GB strength will decrease with increasing impurity concentration.[11]

Thus, it becomes clear that both Na and Ca segregation weakens the Al GB. It is generally believed that GB weakening due to impurity segregation can directly induce intergranular embrittlement. A well-known example is H-induced Fe or Ni embrittlement resulting from the GB strength reduction.[2,24] Another example is the weakening of a Ni GB with S impurity, causing the Ni intergranular embrittlement.[11] We have known that the embrittlement of Al alloy is associated with Na or Ca GB segregation.[12,13,21] Thus, we further expect that the segregation-induced GB weakening causes the embrittlement, by considering that these GB's with reduced strength can act as a source of cracks or preferential crack paths.

The previous studies[12,13] have shown that, in comparison with the base alloy, the embrittlement, characterized by reduction in area (RA) of the alloy (the amount of ductility reduction), occurs at the temperature range of 150–400 °C with 2 ppm Na and 200–250 °C with 2 or 10 ppm Ca. Away from these temperatures, RA remains unchanged, and hence no embrittlement occurs. Correspondingly, as shown in Table I, the UTS of the Al alloy with Na or Ca decreases as compared with the base alloy within the respective temperature range, while there is no such reduction outside the range. Combined with the fact that the Al–5% Mg alloy with Na or Ca impurity exhibits intergranular fracture when embrittlement occurs, while the base alloy exhibits transgranular fracture,[12,13] the UTS reduction together with the RA suggests that the weakened GB's due to impurity segregation results in the intergranular embrittlement. Based on this, we can further predict from the FPCTT that Na will induce more significant GB embrittlement than Ca, owing to much lower GB strength with Na than that with Ca. This is consistent with the experimental observation of the more apparent UTS reduction (Table I) and the more significant RA reduction of the Na segregation case.[12,13]

We can reveal the essential role of weakened GB's on the embrittlement by analyzing an actual fracture process. Local plastic deformation is initialized first, followed by dislocation accumulation and transmission at the GB's that are weakened by Na or Ca segregation. A large stress concentration then occurs at these weakened GB's, where crack origination or extension can be eased, leading to the brittlelike fracture with both lower RA and UTS. Such a mechanism will not be effective outside those embrittlement temperature ranges, which may be caused by the GB recrystallization.[25]

For high-temperature embrittlement, whether the embrittlement occurs at a specific temperature range or not is believed to depend on the competition between ductility reduction due to stress concentration associated with GB sliding and dislocation accumulation and ductility recovery due to GB recrystallization.[25] Consequently, there will be not only one factor to influence the final UTS and RA results. However, the GB weakening, as suggested by the FPCTT, can be the main factor leading to the UTS and RA reduction. The reason lies in the following two facts. First, the intergranular fracture occurs in the Al–5% Mg alloy with Na or Ca impurity in comparison with the transgranular fracture in the base alloy.[12,13] Second, as discussed above, the calculated lower tensile strength of the Na GB than that of the Ca GB is consistent with the experimental observation of more apparent UTS and RA reduction of Al alloy with Na impurity than with Ca.

Finally, we point out that because the actual fracture process is much more complicated considering such as dislocation-dominated plastic behavior, the calculated tensile strength cannot directly compare with those from the experiment.[9] For example, the UTS of the base alloy are lower than 250 MPa according to the experimental results (Table I), and these values are much lower than the calculated ones. This is mainly because we did not consider the role of dislocation on the fracture. For Al, the experimental strength is macroscopic stress associated with plastic deformation due to its ductile nature, and such plastic deformation is easily initiated under much lower local stress than the GB tensile strength.

In conclusion, we have performed a first-principles computational tensile test to determine the tensile strength of an Al grain boundary with Na and Ca segregation. We show that the Na and Ca segregation reduce the tensile strength of the Al GB, and the breaking of interfacial bonds dominates the GB fracture. Experimentally we further show that the Na or Ca impurity, which induces the intergranular fracture, lowers the ultimate tensile strength of the base Al-Mg alloy when the embrittlement occurs, which implies that the embrittlement of Al alloy is associated with the weakened GB's. These results suggest that the Al intergranular embrittlement originates mainly from the GB weakening due to the Na orCa segregation. By increasing GB strength, we can reduce the Na- or Ca-induced GB embrittlement and improve the mechanical properties of Al alloy. For example, Si, which has been computationally shown to increase the Al GB strength,[26] was observed to suppress the embrittlement.[13]

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