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Aluminum grain boundary decohesion by dense sodium segregation

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Despite numerous investigations, grain boundary (GB) embrittlement of metallic structural materials is a poorly understood fundamental phenomenon in materials science. One of the well-known examples is that minute traces of sodium induce an embrittlement in aluminum alloys that results in drastic failure and limits their applications. From first-principles density function theory calculations, we found that sodium atoms densely segregate and neighbor into the $\sum 5(012)[100]$ GB in aluminum with large segregation energies and that the GB strength drops to only one fifth of the strength of the clean Al GB. Gradual sodium segregation leads to not only a large GB expansion but also to the replacement of stronger Al-Al metallic bonds with the weaker Al-Na mixed ionic-metallic bonds and Na-Na metallic bonds. This result in a drastic GB decohesion that reduces the GB tensile strength dramatically until it approaches the strength of bulk sodium. Dense segregation of sodium forms a Na film along the GB and opens an easy channel for oxidation and corrosion along the GB, which further accelerates the intergranular embrittlement.

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I. INTRODUCTION

Grain boundary (GB) embrittlement (GBE) of metallic structural materials is one of the poorly understood fundamental phenomena in materials science despite numerous investigations. It is now well recognized that mechanical properties, such as the brittleness of an engineered material, can be significantly changed by a small quantity of impurities segregating to grain boundaries.[1] First-principles quantum mechanical calculation has been proved to be a powerful tool to reveal the mechanism at an electronic level. Successful examples include that the Fe GB decohesion by phosphorus is caused by charge transfer between the Fe atoms and the segregant P atoms,[2] the bismuth embrittlement of copper is caused by the large atomic size of Bi, which weakens the interatomic bonding,[3] and the sulfur-induced embrittlement of nickel is caused by a short-range overlap repulsion among densely segregated and neighboring sulfur atoms in the GB resulting in a large GB expansion and decohesion.[4] Another well-known unsolved problem is the sodium-induced embrittlement of aluminum alloys that leads to a drastic failure and decreases its strength significantly. Due to the urgent need for high-performance light metals for use in transportation vehicles in order to decrease fossil fuel consumption, a fundamental understanding of the mechanism of Na-induced decohesion of the Al GB is of highest interest.

Sodium is inevitably introduced into Al alloys from the primary Al production process. Although the solid solubility of Na in Al is extremely low (0.002 at.%),[5] even trace amounts (several parts per million) of Na can drastically reduce the ultimate tensile strength of aluminum.[6] In our previous work,[7] we demonstrated that Na is a strong intergranular embrittler in the Al GB with a potency of +0.62 eV/atom. Our segregation energy calculations[7] showed that the core site on the symmetrical GB plane is the most energetically favorable site for a Na atom in the $\sum 5(012)[100]$ Al GB, but there is also a large driving force for Na to segregate to other GB sites from Al bulk, as judged by the negative segregation energies. Therefore, after Na atoms occupy all preferred sites, more Na atoms might continue segregating to the Al GB and replace Al in other sites. As a result, the dense segregation of Na to the Al GB might be energetically favorable; the effect of multiple Na atoms segregated into the Al GB on its strength is still unknown.

In this work, we demonstrate that dense Na segregation is energetically favored by calculating the segregation energy of the successive segregation of Na into the $\sum 5(012)[100]$Al GB. The influence of multiple Na atoms on the cohesion of a$\sum 5(012)[100]$Al GB is then investigated by means of first-principles calculations with the highly precise full-potential linearized augmented plane-wave (FLAPW) method[8] within the *ab initio* tensile test approach. The calculated atomic and electronic features and theoretical tensile strength data are then used to analyze the physics, which dominates the embrittling behavior of multiple Na atoms in the Al GB.

II. GB MODEL AND COMPUTATIONAL METHOD

The Al $\sum 5(012)[100]$ tilt GB was chosen since it is one of the high-energy and stable GBs in Al, according to experiments.[9] The initial crystal structure of the GB is based on the coincident site lattice (CSL) model; the results of selection, optimization, and validation of the Al GB model were presented in our previous works.[7,10,11] The crystal structure of the Al $\sum 5(012)[100]$ GB is shown in Fig. 1; it consists of 25 layers marked 1 to 13 and −2 to −13. The site 1, which is shared between the two grains, is called "core site." The Na atoms, due to their larger atomic size than that of the Al atom, might occupy the substitutional positions along the GB, which are sites 1, 2/−2, and 3/−3.

The electronic structure was calculated by the FLAPW single-slab method for thin films,[8] which has been proven to be one of the most accurate methods for the computation of the electronic structure of surfaces and solids within density functional theory. No shape approximations are made to the charge densities, potentials, and matrix elements. For both the Al and Na atoms, the core states are treated fully relativistically, and

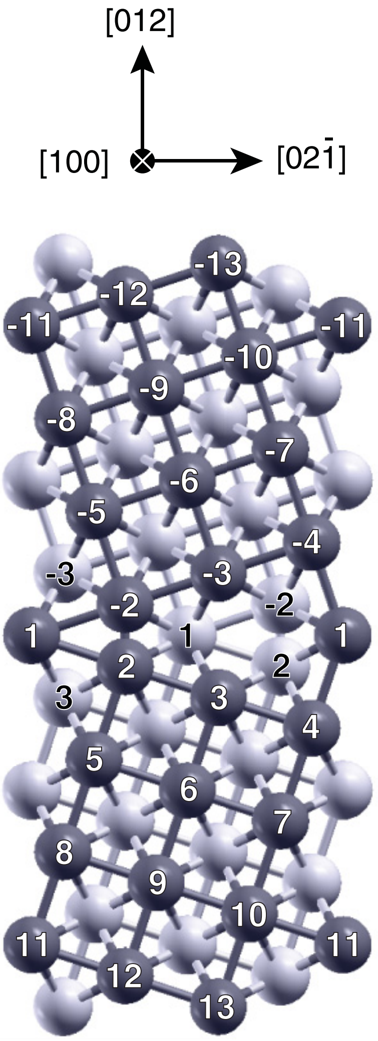


FIG. 1. (Color online) Crystal structure of the computational cell of the GB. The atomic sites are labeled by numbers counted from the GB plane. The structures repeat along the [02$\bar{1}$] direction. The dark gray and light gray atoms represent atoms in layers with $y = 0$ (in the paper plane) and $y = 0.5$ (beneath the paper plane) along the [100] direction, respectively. Site 1 is on the mirror plane which is also the GB plane; Sites i and $-i$ ($i = 2$ to13) have mirror symmetry. The three directions [100], [012], and [02$\bar{1}$] are shown by arrows. The [012] direction is parallel to the z axis.

the valence states are treated semirelativistically (i.e., without spin-orbit coupling). The exchange correlation contribution to the potential was included using the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof functional.[12] An energy cutoff of 218 eV was employed for the augmented plane-wave basis to describe the wave functions in the interstitial region, and a 1100-eV cutoff was used for the star functions, depicting the charge density and potential. Muffin-tin radii were chosen to be 2.3, for both Al and Na and a two-dimensional $\boldsymbol{k}$-point mesh of 7×7 was employed. Within the muffin-tin spheres, lattice harmonics with angular momentum quantum number ℓ up to 8 were adopted.

Convergence was assumed when the average root-mean-square differences between the input and output charge and spin densities are less than $1 \times 10^{-5}\ e/(\text{a.u.})^3$. To simulate the bulklike environment for the GB case, the positions of the three outermost Al layers (sites 11, 12, 13 and −11, −12, −13) were fixed to their face-centered cubic (fcc) coordination and distances as in bulk Al; all other atoms in the unit cells were fully relaxed by atomic force minimization. Equilibrium relaxed structures were assumed when the atomic forces on each atom became less than 0.01 eV/a.u.

III. SEGREGATION ENERGY AND SEGREGATION SEQUENCE

Before investigating the effect of multiple Na atoms on the Al GB fracture energy, the segregation energies of multiple Na atoms were calculated to determine whether multiple Na atoms can segregate energetically from the Al bulk to Al GBs one by one and what are the most favorable sites for sequential segregation of the multiple Na atoms along the Al GB. The segregation energy is defined as the energy needed for a Na atom to diffuse from a bulk site to a GB site and can be calculated as $\Delta E_{\text{Seg}} = E_{\text{GB}} - E_{\text{Bulk}}$, where E_{Bulk} is the total energy of the system with a GB and one Na atom occupying a bulk site and E_{GB} is the total energy of the system with a GB and the same Na atom occupying the Al the site along the GB. The sites 6/−6, which most closely approximate bulklike sites in this structural model, were chosen for Na atoms when calculating E_{Bulk}. In order to find equilibrium geometries of the GB with Na atoms in the substitutional sites, a series of total energy calculations were carried out in which the unit cell sizes were increased in the direction normal to the GB plane in small increments, starting from the CSL model size. For each increment, the total energy of the system was calculated with full relaxation. The expansion at which the total energy of the GB reaches its minimum corresponds to the equilibrium GB state.

In our previous work,[7] we determined that the first Na atom has a strong preference to segregate to the core site 1 with the segregation energy of −0.84 eV/atom, which is more than twice as large as the energy to segregate to any other site; hence, Na will occupy sites 1 until all available sites are exhausted. If more Na is present in the system, it will start segregating to other sites. To determine the preferred sites for further segregation, the second Na atom was put in site −6 in the presence of a Na atom in site 1 to calculate E_{Bulk} and then put in sites 2 (or −2, which are equivalent due to symmetry) and 3/−3 when calculating E_{GB}. All the calculated segregation energies and the corresponding expansion distances are listed in Table I. It was found that the segregation energy of the second Na atom to sites 2/−2 (−0.68 eV/atom) is much lower than the segregation energy of the second Na to sites 3/−3 (−0.003 eV/atom). This is unexpected since sites 3/−3 are the loosest sites along the GB, and the segregation of the second Na to sites 3/−3 is likely to result in a smaller distortion of the GB and a lesser increase of the mechanical energy of the system. Indeed, the segregation of Na to site 3/−3 does not result in an additional expansion of the GB, which remains at the same level (0.95 a.u.) as in the case of Al GB with one Na atom, while the segregation of the second Na atom to sites 2/−2 leads to a significant additional GB expansion

TABLE I. Calculated segregation energies and expansion distances of multiple Na atoms at the different positions in the Al GB. The underlined site number indicates the position of the added ith ($i = 1$–5) Na. The segregation energies for the preferred positions are marked in bold.

Case	Positions of Na atoms	Expansion distance (a.u.)	Total segregation energy (eV/atom)
Na	$\underline{-6}$	0.75	–
	$\underline{1}$	0.95	**−0.84**
	$\underline{2}$	2.00	−0.37
	$\underline{3}$	0.50	−0.38
2Na	$\underline{-6} + 1$	2.00	–
	$1 + \underline{2}$	1.95	**−0.68**
	$1 + \underline{3}$	0.95	−0.003
3Na	$\underline{-6} + 1 + 2$	2.50	–
	$1 + 2 + (\underline{-3})$	2.05	−0.07
	$1 + 2 + (\underline{-2})$	4.30	−0.62
	$1 + 2 + \underline{3}$	4.05	**−0.69**
4Na	$\underline{-6} + 1 + 2 + 3$	4.10	–
	$1 + 2 + 3 + (\underline{-2})$	4.90	**−0.64**
	$1 + 2 + 3 + (\underline{-3})$	3.75	0.65
5Na	$\underline{-6} + 1 + 2 + 3 + (-2)$	6.65	–
	$1 + 2 + 3 + (-2) + (\underline{-3})$	7.20	**−0.88**

(to 1.95 a.u.). These findings suggest that the size effect is not the main factor in determining the preferred segregation site for the second Na atom and that the electronic effects play a major role, which will be analyzed later.

After two Na atoms segregate into sites 1 and 2, the mirror symmetry of the system is broken, and the third Na atom might segregate into sites −2, 3, or −3. From the calculated results listed in Table I, one can see that the third Na atom has a preference to segregate into site 3 with the lowest segregation energy, −0.69 eV/atom. The cell expands to 4.05 a.u. in the direction normal to the GB plane when the system contains three Na atoms. For the case of four Na atoms in the system, we determined that the fourth one should segregate into site −2 with the segregation energy of −0.64 eV/atom, and the cell elongates to 4.90 a.u., normally to the GB plane. The fifth Na atom segregates into site −3 the segregation energy −0.88 eV/atom, and the cell elongates to 7.20 a.u. After that, all possible substitutional sites near the GB plane are occupied by Na, and the GB becomes saturated.

To summarize, from segregation energy calculations it is found that the dense segregation of Na atoms into the Al GB is energetically favored. The segregation sequence is site 1 → site 2 → site 3 → site −2 → site−3. With more Na segregated into the GB, it expands continuously along the z axis (0.95 → 1.95 → 4.05 → 4.95 → 7.20 a.u.) from the 0.45 a.u. expansion of clean Al GB, as shown in Fig. 2.

IV. FRACTURE PATH AND ENERGY

The GB strength can be characterized by its fracture energy ΔE_{frac}, which is defined as the difference between the total energy of an unbroken GB, E_{GB}, and the total energies of the resulting two free surfaces (FS) E_{FS1} and E_{FS2}, per unit cell area S of the cleavage plane: $\Delta E_{\text{frac}} = (E_{\text{GB}} - E_{\text{FS1}} - E_{\text{FS2}}/S)$. With the different number of Na atoms segregating to the GB, the symmetry of the GB system will vary, which allows several possible ways ("fracture paths") that the GB can break, and the corresponding fracture energies should be compared to determine the preferred fracture path. Detailed discussions are included and shown schematically in the previous works.[7,10,11] Usually, the mirror symmetry only allows one unique fracture path for the clean Al GB and the GB with the impurity atom segregating into the core site 1. An asymmetrical GB system, with the impurity atoms segregating to the sites 2/−2 and/or 3/−3, allows at least two possible fracture paths.

The possible fracture paths and their energy were only considered for the system with the lowest segregation energy for Na atoms. As determined in our previous work,[7] only one fracture path is possible for the cases of the clean Al GB and the GB with one segregated Na atom, whose fracture energies are 1.531 and 0.987 J/m^2, respectively. The detailed fracture

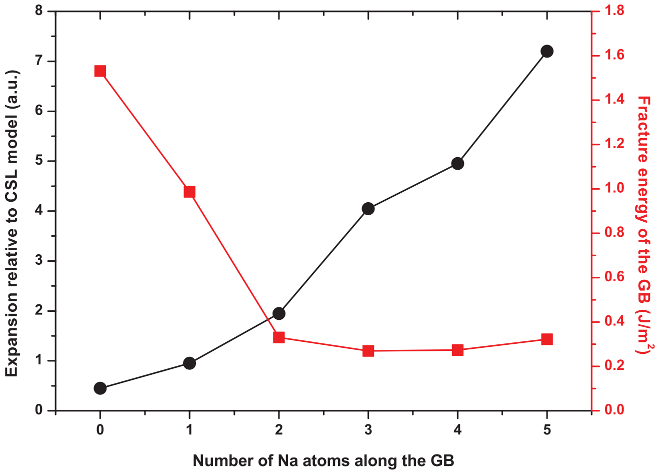
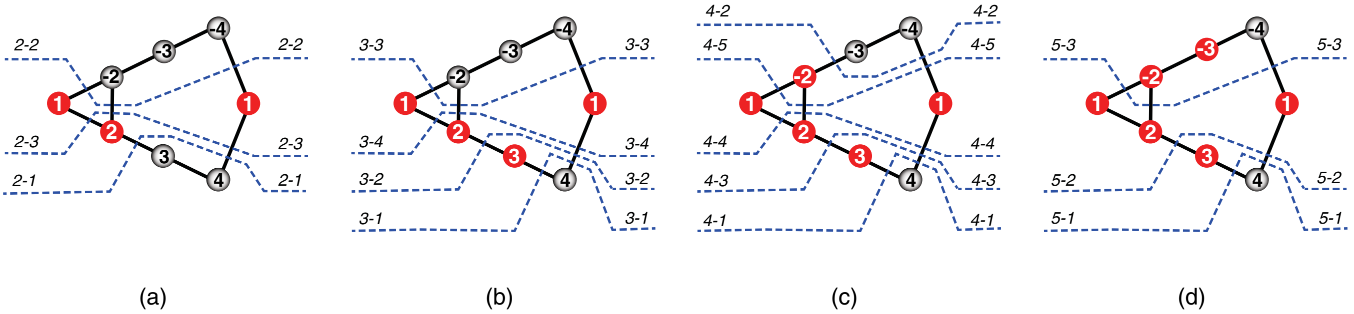


FIG. 2. (Color online) The expansion of the GB cell relative to the CSL model size and fracture energy of the GB with respect to the number of Na atoms segregating into the GB.



(a) (b) (c) (d)

FIG. 3. (Color online) Schematic diagrams of possible fracture paths for (a) Al GB with two Na atoms in sites 1 and 2, (b) Al GB with three Na atoms in sites 1, 2, and 3, (c) Al GB with four Na atoms in sites 1, 2, 3, and −2 (d) Al GB with five Na atoms in sites 1, 2, 3, −2, and −3. The red (dark gray) and gray spheres represent Na atoms and Al atoms, respectively. Fracture surfaces are marked with dashed lines.

paths are shown schematically in Fig. 3, and the calculated corresponding fracture energies are listed in Table II. For the two Na atoms case, the lowest fracture energy is 0.333 J/m^2 for the fracture path (2-3), which is almost three times lower than for the two other possible paths. Therefore, the fracture path (2-3) is the way that the GB cell with two segregated Na atoms will break; after fracture, one part is a 12-layer FS with a Na atom in site 2, the other part is a 13-layer FS with a Na atom in site 1. For the three Na atoms case, the lowest fracture energy is 0.270 J/m^2; the lowest fracture energy is 0.274 J/m^2 for the four Na atoms case, and 0.322 J/m^2 for the five Na atoms case. The variation of the fracture energy of the GB with respective to the number of Na atoms segregating into the GB is shown in Fig. 2.

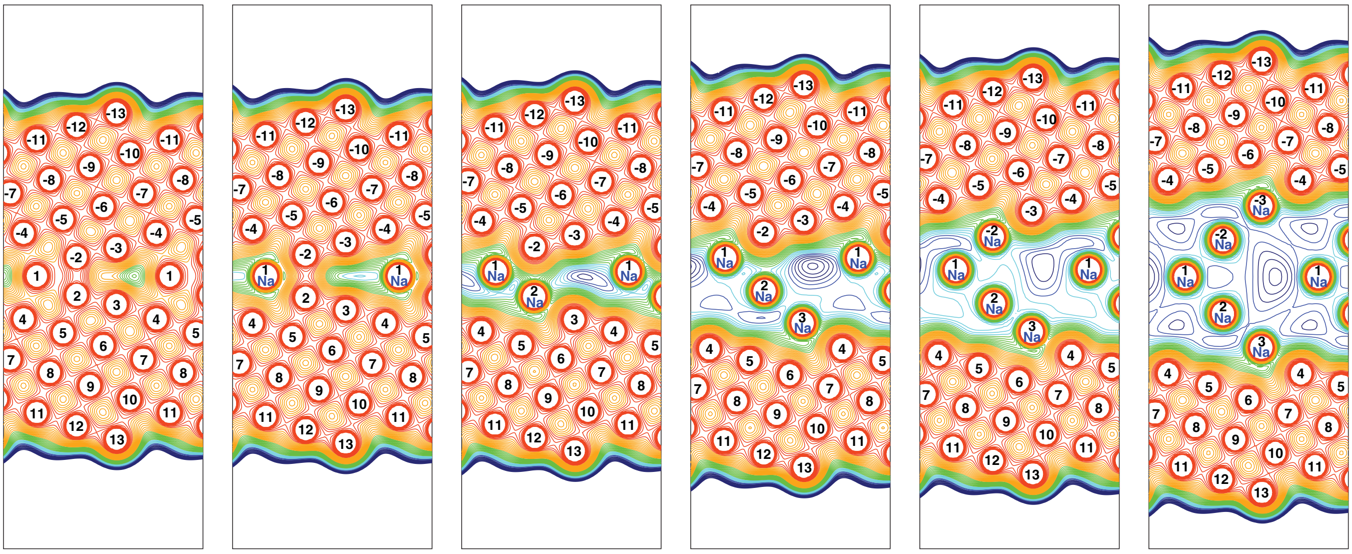
From the Table II and Fig. 2, it is seen that the fracture energy of the GB drops by more than one third (from 1.531 J/m^2 of the clean Al GB to 0.987 J/m^2 for the one Na case) if one Na atom segregates into the GB. The second Na atom segregation will decrease the GB strength even more significantly—by almost two thirds from 0.987 J/m^2 for the one Na atom case to 0.333 J/m^2 for the two Na atoms case. However, further Na segregation does not change the fracture energy very much, which remains about 0.3 J/m^2, or one fifth of the fracture energy of the clean Al GB. This indicates that the critical features of interatomic bonding responsible for the GB strength reduction do not vary significantly if there are three and more Na atoms segregated into the GB. We will discuss this interesting result in details later.

V. ELECTRONIC STRUCTURE AND BONDING CHARACTER

The effect of multiple Na atoms on the interatomic bonding characteristics of the Al GB can be investigated in detail on

TABLE II. Calculated fracture energies of multiple Na atoms at the different positions in the Al GB. The underlined site number indicates the position of the added ith ($i = 1{-}5$) Na in the GB. Numbers in parentheses denote the sites that Na atoms occupy on the free surfaces after fracture. The fracture energies for the preferred fracture paths are marked in bold.

		Fracture path			
			Number of atoms in separated surfaces		
Case	Positions of Na atoms	Path	Part I	Part II	Fracture energy (J/m^2)
Clean Al GB	—	0-1	12	13	**1.531**
Na	$\underline{1}$	1-1	12	13(1)	**0.987**
2Na	$1+\underline{2}$	2-1	11	14(1 + 2)	0.939
		2-2	12	13(1 + 2)	0.980
		2-3	13(1)	12(2)	**0.333**
3Na	$1+2+\underline{3}$	3-1	10	15(1 + 2 + 3)	0.822
		3-2	11(3)	14(1 + 2)	0.280
		3-3	12	13(1 + 2 + 3)	0.918
		3-4	13(1)	12(2 + 3)	**0.270**
4Na	$1+2+3+(\underline{-2})$	4-1	10	15(1+ 2 + 3 + (−2))	0.836
		4-2	11	14(1+ 2 + 3 + (−2))	0.828
		4-3	11(3)	14(1+ 2 + (−2))	0.282
		4-4	12(2 + 3)	13(1+ (−2))	0.312
		4-5	13(1 + 2 + 3)	12(−2)	**0.274**
5Na	$1+2+3+(-2)+(\underline{-3})$	5-1	10	15(1+ 2 + 3 + (−2) + (−3))	0.890
		5-2	11(3)	14(1+ 2 + (−2) + (−3))	0.322
		5-3	12((−2) + (−3))	13(1 + 2 + 3)	0.369



(a) Al GB **(b) Al GB+Na** **(c) Al GB+2Na** **(d) Al GB+3Na** **(e) Al GB+4Na** **(f) Al GB+5Na**

FIG. 4. (Color online) The calculated charge densities for (a) the clean Al GB, (b) the Al GB with a Na atom in site 1, (c) the Al GB with two Na atoms in sites 1 and 2, (d) the Al GB with three Na atoms in sites 1, 2, and 3; (e) the Al GB with four Na atoms in sites 1, 2, 3, and −2; (f) the Al GB with five Na atoms in sites 1, 2, 3, −2, and −3; Contours start from 0.002 $e/(\mathrm{a.u.})^3$ and increase successively by a factor of $2^{1/8}$.

the basis of calculated charge densities, electronic densities of states (DOS), and bond lengths. The charge accumulation and depletion directly indicate strengthening or weakening of the chemical bonds, and the DOS and the variation of the bond length can also help to investigate the bond character further. Figure 4 shows the contour plots of the charge density distribution for valence electrons in the (100) plane for the Al GB with different numbers of segregating Na, compared with the clean Al GB case. The calculated local density of states (LDOS) for the Al GB with two Na atoms in sites 1 and 2 are presented in Fig. 5.

In Fig. 4, a continuing significant decrease of charge density can be noted along the GB with the segregation of more and more Na atoms. It is also seen that the cell expands along the z axis with subsequent Na segregation. With one Na segregating into site 1 [Fig. 4(b)], the important metallic Al(2)-Al(−2) bond, which holds the two grains together and contributes most to the GB strength, still exists, although it becomes weaker due to the elongated bond length with the cell expansion. However, the stronger metallic Al(1)-Al(2/−2) bonds in the clean Al GB are replaced with the weaker, predominantly ionic Na(1)-Al(2/−2) bonds, which contribute to a reduction of the GB strength by more than one third.

When the second Na atom segregates into site 2 [Fig. 4(c)], there is no Al-Al bond between the two grains anymore. The grains are held together by the weaker Na(1)-Al(2) and Na(2)-Al(3) bonds and the Na(1)-Na(2) bonds. There is a remarkable charge depletion region around the two Na atoms. From the charge density, it can be seen that the Na(1)-Na(2) bond is much weaker than the Na(1)-Al(2) and Na(2)-Al(3) bonds, thus allowing the fracture path 2-3 (in Table II), which follows the path of lowest charge density, to have the lowest fracture energy. Figures 5(a) and 5(b) show the LDOS for the Na atom replacing Al in sites 1 and 2 in the GB, respectively; Figs. 5(c) and 5(d) show the LDOS for the Al atoms in sites −2 and 3 in the GB, respectively. The Na atom has one valence electron (vs the three of Al), but the electronic density on the Na atom in the GB is significantly lower than one third of Al, indicating that some of the Na electronic charge was transferred to Al atoms in the GB. Therefore, similar to the case of a single Na, the Na(1)-Al(2) and Na(2)-Al(3) bonds have a predominantly ionic character. The remaining Na electrons participate in the weak metallic bonding with neighboring Al and Na. The Na(1)-Na(2) bond has a metallic character since the overall shape of the s- and p-electron LDOS of Na(1) and Na(2) are very similar to each other and the bonding charge is distributed symmetrically between these two atoms.

When the third Na atom segregates into site 3 [Fig. 4(d)], the cell continues expanding normally to the GB plane, causing more charge depletion between the two grains. From the charge density, it is seen that the Na(1)-Na(2) bond is slightly weaker than the Na(2)-Na(3) bond, resulting in fracture path 3-4 (in Table II) which has the lowest fracture energy, with the fracture path 3-2 involving the breaking of the Na(2)-Na(3) bond being a close second. For the case of four segregated Na atoms, the charge density clearly shows the weakest bonds to be the Na(1)-Na(−2) bond [Fig. 4(e)], which results in the the lowest energy fracture path 4-5. Note that this path involves Na(−2) atoms which are also bonded with Al(−3) and Al(−5) atoms; as a result of charge transfer to Al, the Na(−2) atom has fewer electrons available to devote to the Na(1)-Na(−2) bond, which becomes depleted of charge and therefore turns into a weak spot. Similarly, in the case of five segregated Na atoms, the charge density clearly shows the weakest bonds to be Na(2)-Na(3) or, symmetrically, Na(−2)-Na(−3) [Fig. 4(f)]. Again, these bonds are weakened due to charge transfer from Na(3/−3) to Al resulting in the the lowest energy fracture path to be 5-2. In all cases fracture follows the path of lowest charge density.

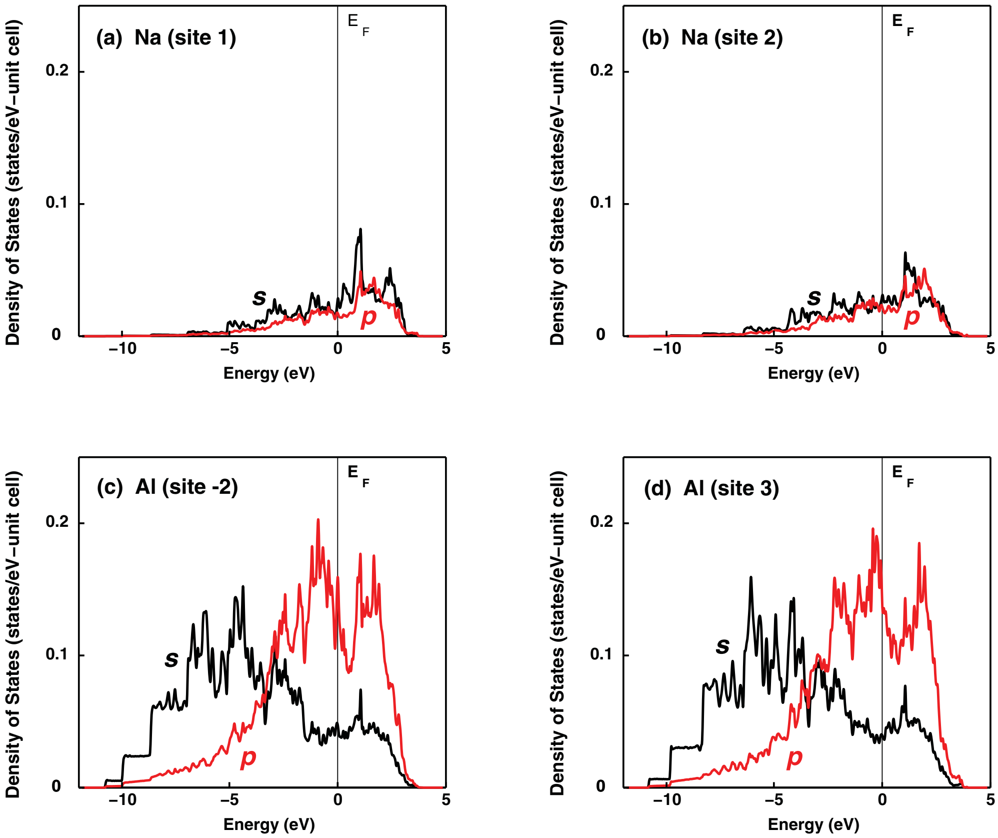


FIG. 5. (Color online) Calculated DOS for two Na atoms and two Al atoms in the GB system in Fig. 4(c): (a) the Na atom in site 1, (b) the Na atom in site 2, (c) the Al atom in site −2, and (d) the Al atom in site 3. The Fermi energy is indicated by E_F.

VI. MECHANISM OF NA-INDUCED GBE

Sodium is an undesired impurity element in aluminum alloys with a very low solubility. Our previous work[7] and the works by Lu *et al.*[13,14] both showed that Na is a strong embrittler in the Al GB. The Na effect on two GBs with different geometries, $\sum 9(2\bar{2}1)[110]$ and $\sum 5(012)[100]$, is similar, which confirms that the embrittling effect of Na in Al is its intrinsic property related with features of its electronic structure and chemical bonding and is unaffected by specific GB structures. Our theoretical results are in good agreement with experimental data.[6]

In this work, we found via accurate *ab initio* calculations that dense segregation of Na atoms into the Al GB is energetically favored. Following a certain segregation sequence into specific sites along the GB (site 1 → site 2 → site 3 → site −2 → site −3), five Na atoms can fully occupy all five GB sites in each unit cell of the $\sum 5(012)[100]$Al GB. Through electronic structure and bonding character analyses, we found that the "size effect" mechanism and the charge-transfer mechanism—the two mechanisms, which traditionally are considered to be responsible for the cohesion or embrittling potency of segregated elements—both contribute to an embrittlement effect caused by Na segregation into the Al GB. First, the segregation of larger Na atoms leads to the Al GB cell expansion, introducing mechanical structural distortions to the GB and the surrounding lattice. In addition, GB expansion disrupts the intergranular bonding of the host Al atoms and results in the formation of a low charge density region along the GB. These two components of the size effect mechanism—mechanical distortion and charge density reduction—both lead to a decrease of GB strength. Second, due to the difference of the electronegativity of the impurity Na atom and host Al atom (Na: 0.93 and Al: 1.61 Pauling units), a charge redistribution between the impurity atom and host atom in the GB will occur. The impurity Na atoms transfer some of their electrons to neighboring Al atoms, thus reducing their cohesion across the GB by replacing the metallic Al-Al bonds with Na-Al bonds with more ionic character. In addition, the electrons transferred from Na redistribute between Al atoms, resulting in additional charge depletion along Na-Al bonds. Thus, similarly to the size effect mechanism, the two components of the charge-transfer mechanism—change of bonding character and charge density reduction—both have a detrimental effect on the GB strength.

With more and more Na atoms segregating to the Al GB, the strong metallic Al-Al bonds are replaced first by the weaker Al-Na ionic-metallic bonds and then by Na-Na bonds, which causes the strength of the GB to decrease via the size effect and charge-transfer mechanisms. However, when the third Na atom segregates to the GB, its strength remains the same (approximately one fifth of the strength of the clean Al GB) and even increases slightly upon further Na segregation. This means that a new mechanism is now responsible for the GB weakening, and we therefore introduce a "bond replacement mechanism." Upon inspection of fracture paths in Table II, we can determine that in the situations of the most dense segregation (cases of 4Na and 5Na), the lowest energy fracture paths involve breaking of Na-Na bonds exclusively. A full replacement of Al-Al bonds with Na-Na bonds takes place within the GB core, and the strength of the GB is now fully determined by the strength of the Na structure forming between the two grains. With dense segregation of Na impurities, the Al GB essentially becomes the Na GB.

To confirm this hypothesis, we calculated the strength of bulk body-centered cubic (bcc) Na, using the same FLAPW method, via *ab initio* cleavage calculations for the (001), (011), and (012) planes. The strength of bulk bcc Na is about $0.42\ \mathrm{J/m^2}$, which is close to the strength of the Al GB after Na dense segregation ($0.32\ \mathrm{J/m^2}$). These results further confirm that the strength of the Al GB is determined by the Na-rich structure between the two grains, resulting from Na dense segregation. The lower value for the Na-saturated Al GB than that for bulk Na comes from the presence of the GB and the crystal structure difference between the fcc GB and bcc bulk Na. Further segregation may result in structural reconstruction of Na between Al GB grains, which will bring its strength closer to that of bulk Na.

After establishing the mechanism of the Na-induced GBE in Al, we can extend it to the mechanism of the Na-induced GBE in other metals. The universal decohesion properties of Na in metallic GBs result from features of its electronic structure and therefore are intrinsic and not dependent on the GB geometry and, in most cases, on the bulk material itself. Sodium is found to be almost insoluble in most structural metals (e.g., transition metals from fourth to sixths periods, Mg, Al, Sn) and does not form stable compounds with them. Therefore, it is reasonable to expect that Na segregation into their GBs is energetically favored and GBs can become saturated with Na atoms. Compared with the host atoms, the impurity sodium atom has a larger atomic size. Therefore, sodium segregation into GBs would cause an expansion of the GB structure, which weakens the intergranular metallic bonding of the host atoms and leads to the formation of a low charge density region along the GB. Furthermore, Na has fewer valence electrons than these host atoms and the electronegativity of Na is significantly lower than that of most structural metals, which would lead to a charge transfer from Na to host atoms. Both the size effect mechanism and the charge-transfer mechanism work together causing a detrimental effect on GB strength and leading to Na-induced GBE. With progressively increasing Na segregation, the strong metallic host atom bonds would be replaced by the weaker Na-host and then Na-Na bonds, and the GB strength would keep decreasing until it reaches the strength of bulk Na.

After studying the mechanism of Bi-induced embrittlement in Cu, Schweinfest *et al.*[3] postulated that an atomic size effect, rather than charge transfer between the metal atoms and the segregant atoms, dominates the impurity-induced GBE for those impurities whose solid solubility is very low in the bulk metal. While charge transfer may not play a role in the case of Bi segregation to the Cu GB due to a small difference in electronegativity (Bi: 2.02 and Cu: 1.90 Pauling units), our investigation shows that charge transfer is still a very essential mechanism of impurity-induced GBE, even for those elements whose solid solubility is very low in the bulk host material and whose atomic size is larger than that of the matrix element. Na-induced GBE in metals is an example of such an impurity whose embrittling mechanism is a combined effect of charge transfer and atomic size. Another important factor is the strength of the impurity element in bulk form, in cases when it is significantly lower than that of host material. When dense segregation of impurities occurs in GBs, the final strength of the GB is determined by the strength of the impurity structure between two grains due to full replacement of host-host bonds with impurity-impurity bonds. In accordance with the bond replacement mechanism that we introduced here, the final strength of the densely segregated GB can be estimated based on the strength of bulk impurity and host phases. Taking Young's moduli of Al and Na (70 and 10 GPa,[15] respectively) as measures of bulk strength and the adhesive strength of pure Al of $2.03\ \mathrm{J/m^2}$ (Ref. 7), the strength of the Al GB with dense segregation of Na can be predicted to be $0.29\ \mathrm{J/m^2}$, which is close to our calculated value of $0.32\ \mathrm{J/m^2}$. Similarly, considering Young's moduli of Cu and Bi (130 and 32 GPa,[15] respectively) and the adhesive strength of pure Cu of $3.10\ \mathrm{J/m^2}$ (Ref. 3), the theoretical adhesive strength of Cu with dense segregation of Bi can be predicted to be $0.76\ \mathrm{J/m^2}$. As expected, this value is lower than the adhesive strength of Cu with one monolayer Bi segregation ($1.33\ \mathrm{J/m^2}$) calculated by Schweinfest *et al.*,[3] as further Bi segregation will continue to decrease the Cu GB strength. We argue that dense segregation of Bi may be responsible for catastrophic intergranular failure of Cu in the presence of Bi. Analogously, the theoretical tensile strength of Ni GB with dense segregation of sulfur can be predicted, based on the Young's moduli of Ni and S (200 GP and 12 GPa,[16] repectively) and the theoretical tensile strength of bulk Ni (30 GPa[4]), to be 1.8 GPa; this is close to but still lower than the value of 2.5 GPa calculated by Yamaguchi *et al.*[4] for the case of trilayer S segregation.

VII. CONCLUSIONS

From first-principles density functional theory calculations with the FLAPW method, we found that sodium atoms densely segregate into the Al GB with large segregation energies causing the GB strength to drop by almost 80%, from $1.53\ \mathrm{J/m^2}$ to $0.32\ \mathrm{J/m^2}$. It was determined through electronic structure and bonding character analysis that both the size effect mechanism and the charge-transfer mechanism simultaneously contribute to a very strong embrittling effect of Na segregated into the Al GB. Furthermore, densely segregated Na forms a film along the GB creating an easy channel for oxidation and corrosion along the GB, which further accelerates the intergranular embrittlement. We showed that decohesion properties of Na are intrinsic, originating from features of its electronic structure, and that Na would act as a universal GB embrittler for a wide class of structural metals and alloys. We introduced the bond replacement mechanism of GB embrittlement by dense segregation of impurities due to full replacement of host-host bonds with impurity-impurity bonds within the GB core, which states that the strength of the GB with densely segregated impurity atoms will be reduced down to the strength of the impurity element in its bulk form, and have verified its applicability for the cases of Bi segregation in Cu and S segregation in Ni.

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[1] S. F. Pugh, *An Introduction to the Grain Boundary Fracture in Metals* (The Institute of Metals, London, 1991).

[2] R. Q. Wu, A. J. Freeman, and G. B. Olson, Science **265**, 376 (1994).

[3] R. Schweinfest, A. T. Paxton, and M. W. Finnis, Nature **432**, 1008 (2004).

[4] M. Yamaguchi, M. Shiga, and H. Kaburaki, Science **307**, 393 (2005).

[5] S. J. Zhang, Q. Y. Han, and Z. K. Liu, J. Alloys Compd. **419**, 91 (2006).

[6] K. Horikawa, S. Kuramoto, and M. Kanno, Acta Mater. **49**, 3981 (2001).

[7] S. Zhang, O. Y. Kontsevoi, A. J. Freeman, and G. B. Olson, Phys. Rev. B **82**, 224107 (2010).

[8] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981).

[9] G. C. Hasson and C. Goux, Scr. Metall. **5**, 889 (1971).

[10] S. Zhang, O. Y. Kontsevoi, A. J. Freeman, and G. B. Olson, Acta Mater. **59**, 6155 (2011).

[11] S. Zhang, O. Y. Kontsevoi, A. J. Freeman, and G. B. Olson, Phys. Rev. B **84**, 134104 (2011).

[12] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[13] G. H. Lu, A. Suzuki, A. Ito, M. Kohyama, and R. Yamamoto, Philos. Mag. Lett. **81**, 757 (2001).

[14] G. H. Lu, Y. Zhang, S. Deng, T. Wang, M. Kohyama, R. Yamamoto, F. Liu, K. Horikawa, and M. Kanno, Phys. Rev. B **73**, 224115 (2006).

[15] A. M. James and M. P. Lord, *Macmillan's Chemical and Physical Data* (Macmillan, London, 1992).

[16] E. Scafé, A. Nardella, and D. De Filippis, J. Mater. Sci. **40**, 3813 (2005).