Effect of P impurity on NiAlΣ5 grain boundary from first-principles study*

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(Received 21 August 2016; revised manuscript received 27 October 2016; published online 20 December 2016)

First-principles calculations based on the density functional theory (DFT) and ultra-soft pseudopotential are employed to study the atomic configuration and charge density of impurity P in NiAl Σ5 grain boundary (GB). The negative segregation energy of a P atom proves that a P atom can easily segregate in the NiAl GB. The atomic configuration and formation energy of the P atom in the NiAl GB demonstrate that the P atom tends to occupy an interstitial site or substitute a Al atom depending on the Ni/Al atoms ratio. The P atom is preferable to staying in the Ni-rich environment in the NiAl GB forming P–Ni bonds. Both of the charge density and the deformation charge imply that a P atom is more likely to bond with Ni atoms rather than with Al atoms. The density of states further exhibits the interactions between P atom and Ni atom, and the orbital electrons of P, Ni and Al atoms all contribute to P–Ni bonds in the NiAl GB. It is worth noting that the P–Ni covalent bonds might embrittle the NiAl GB and weakens the plasticity of the NiAl intermetallics.

Keywords: NiAl Σ5 grain boundary, impurity effect, first principles

PACS: 31.15.ae, 71.20.Lp, 61.72.S–, 74.62.Dh **DOI:** 10.1088/1674-1056/26/2/023101

1. Introduction

Nickel aluminum (NiAl) intermetallics exhibit a lot of attractive properties such as a high melting temperature, low density, good thermal conductivity, excellent corrosion, and oxidation resistance, making it have potential application in the aerospace industry as a new high temperature structure material.[1–3] Its practical application, however, is limited by poor ductility at low temperatures[3] and brittle grain-boundary fracture at elevated temperature.[4] There have been several attempts in the past to improve the mechanical properties of NiAl especially by micro-alloying with Mo, Ti, Ga, and Cr.[5,6]

Many materials exist as polycrystals including NiAl,[3] so the defects of grain boundaries (GBs) are inevitable in the material. The GBs in metals and alloys offer favorable sites for the segregation of impurities. The segregation of impurity in GB can change the structure of GB, even cause a significant variation of the mechanical properties of the material.[7–10] Certain additives have been found to be desirable because they can enhance the cohesive properties of NiAl such as B and some alloying elements like Zr and Mo, while other impurities would cause a deleterious effect, O and C atoms for example, leading to the degradations of various properties of NiAl.[11–15] Thus, it is of great significance to study the NiAl GB to improve its mechanical properties.

In the polycrystalline NiAl intermetallics, a Σ5 GB has been suggested to have good crack resistance, thus causing it to have a strong boundary.[16] Also experimental studies of the Σ5 GB have proven that multiplicity in GBs structures can be observed in real metals. The meaning of the structural multiplicity of GBs structures is relevant to the crystal structure changes and mechanisms of defect interactions.[17]

Impurities such as P in NiAl play important roles in affecting the mechanical properties of this alloy. However, there are few reports about P alloying behavior in NiAl, especially for NiAl GB. For a long time, P was generally regarded as a deleterious element in superalloys and steels.[18,19] A trace amount (ppm) of doping P principally segregates in the NiAl GB. The segregation of P in the NiAl GB hardens the GBs and hampers the process of dynamic recovery or recrystallization during its alloying deformation, leading to the formation of cavities in GBs, which influences the mechanical properties of NiAl.[20] Nevertheless, more and more advantageous effects of P on superalloys and steels have been observed.[21,22] To better understand these effects, studies of the performance of P in NiAl are crucial.

In this article we employ first-principles calculations to study the site occupancy, atomic configuration, density of states and charge density of a P atom in the NiAl Σ5 grain boundary (GB), to try to understand the performance of P in the NiAl GB.

2. Computational method and model

All calculations were based on the density functional theory (DFT) and ultra-soft pseudopotential as implemented in the Vienna *Ab initio* Simulation Package (VASP).[23,24] We

*Project supported by the National Natural Science Foundation of China (Grant No. 51201181) and the Scientific Research Fund of Civil Aviation University of China (Grant No. 08QD14X).

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employed the generalized gradient approximation (GGA) with the Perdew and Wang (PW91).[25] 400 eV was used as a cut-off energy for the plane wave basis. The Brillouin zones were sampled with 2×4×8 k points by the Monkhorst–Pack scheme.[26] When a convergence criterion of the force on each atom was less than 10^{-3} eV/Å, all atomic positions were fully relaxed at a constant volume. The selected NiAl Σ5 (310)/[001] tilt grain boundary is considered to be a typical coincidence boundary in NiAl, which is formed by rotating a grain by 36.9° along the [001] axis and using (310) as its boundary plane. The supercell of NiAl Σ5 GB we constructed is shown in Fig. 1, whose three-dimensional (3D) parameters are 19.38 Å×9.10 Å×5.65 Å. After the test calculation, the supercell we constructed was large enough to insert a P atom at the NiAl Σ5 GB. This supercell is set to contain four (001) atomic layers, including two Ni layers and Al layers with 40 Ni atoms and 40 Al atoms, respectively. To meet the periodic boundary condition, the supercell consists of two symmetric boundaries in the direction of [310]. For the direction of [001], the length of supercell is chosen to be twice the CSL to keep the symmetry of the configuration.

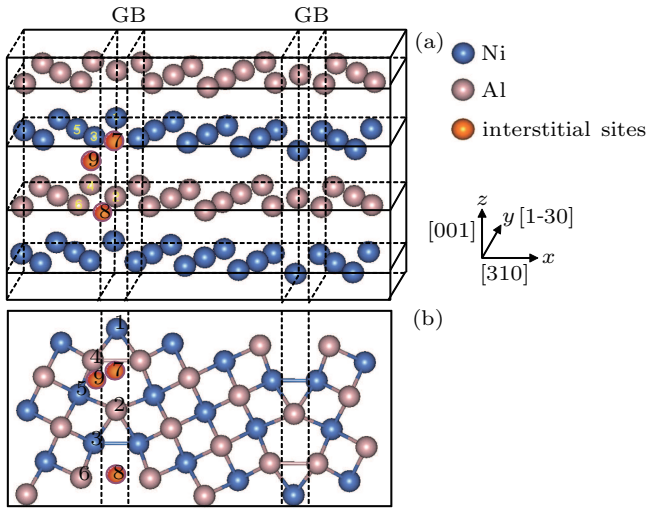


Fig. 1. (color online) (a) Supercell of NiAl Σ5 (310)/[001] GB, (b) upward view of the above supercell. The numbers 1, 3, and 5 represent the Ni atoms substituted by a P atom, and the numbers 2, 4, and 6 denote the Al atoms replaced by a P atom, while numbers 7 to 9 are the interstitial sites occupied by a P atom.

3. Results and discussion

3.1. Formation energy

For identifying the most preferred sites of P in the NiAl Σ5 GB, we first compute the formation energies in different cases after optimization of structure. We set up nine different and representative sites in the GBs for P atom (as shown in Fig. 1), six of which are substitutional and the remaining three are interstitial cases.

The calculation formula of the formation energy is presented below. If the P atom substitutes for an Al or Ni atom, the formation energy reads

$$E_{\mathrm{P}}^{\mathrm{f}} = E_{\mathrm{NiAl-P}}^{\mathrm{T}} - E_{\mathrm{NiAl}}^{\mathrm{T}} - E_P + \mu_{\mathrm{Ni/Al}}, \quad (1)$$

where $E_{\mathrm{NiAl-P}}^{\mathrm{T}}$ and $E_{\mathrm{NiAl}}^{\mathrm{T}}$ represent the total energies of the NiAl GB supercell with and without P, respectively; E_{P} refers to the energy of a single P atom and its value is equal to −0.17 eV; $\mu_{\mathrm{Ni/Al}}$ is the chemical potential of one Ni or Al. If P occupies an interstitial site, the formation energy is calculated by

$$E_{\mathrm{P}}^{\mathrm{f}} = E_{\mathrm{NiAl-P}}^{\mathrm{T}} - E_{\mathrm{NiAl}}^{\mathrm{T}} - E_{\mathrm{P}}. \quad (2)$$

Given different chemical potentials of Ni and Al atoms, the chemical potentials should be taken into consideration in the substitutional cases.[27,28] The maximal values of μ_{Ni} and μ_{Al} are equal to those in the face-centered bulk crystalline phases, denoted as $\mu_{\mathrm{Ni}}^{\mathrm{bulk}}$ and $\mu_{\mathrm{Al}}^{\mathrm{bulk}}$ respectively. In NiAl bulk, we have

$$\mu_{\mathrm{Ni}} + \mu_{\mathrm{Al}} = \mu_{\mathrm{NiAl}}^{\mathrm{bulk}} = \mu_{\mathrm{Ni}}^{\mathrm{bulk}} + \mu_{\mathrm{Al}}^{\mathrm{bulk}} - \Delta H, \quad (3)$$

where ΔH is regarded as the heat formation of NiAl. Hence, the value range of the atomic chemical potentials can be obtained as

$$\mu_{\mathrm{Ni}}^{\mathrm{bulk}} - \Delta H \le \mu_{\mathrm{Ni}} \le \mu_{\mathrm{Ni}}^{\mathrm{bulk}}, \quad (4)$$

and

$$\mu_{\mathrm{Al}}^{\mathrm{bulk}} - \Delta H \le \mu_{\mathrm{Al}} \le \mu_{\mathrm{Al}}^{\mathrm{bulk}}. \quad (5)$$

Define $\Delta\mu = \mu_{\mathrm{Ni}} - \mu_{\mathrm{Al}}$, then we will have the following relation:

$$\mu_{\mathrm{Ni}}^{\mathrm{bulk}} - \mu_{\mathrm{Al}}^{\mathrm{bulk}} - \Delta H \le \Delta\mu \le \mu_{\mathrm{Ni}}^{\mathrm{bulk}} - \mu_{\mathrm{Al}}^{\mathrm{bulk}} + \Delta H. \quad (6)$$

In accordance with the previous results, the values of $\mu_{\mathrm{Ni}}^{\mathrm{bulk}}$, $\mu_{\mathrm{Al}}^{\mathrm{bulk}}$, and $\mu_{\mathrm{NiAl}}^{\mathrm{bulk}}$ are −5.48 eV, −3.69 eV, and −10.49 eV, respectively.[29] Thus we obtain ΔH to be 1.31 eV, which is consistent with the experimental result of ∼ 1.20 eV.[30]

Figure 2 shows the variations of the formation energy of a P atom within different sites of the NiAl GB. For the substitutional cases, the formation energy is a function of chemical potential. For convenience, S1, S3, and S5 are used to indicate the cases of one P atom replaced by a Ni atom in the NiAl GB (corresponding to numbers 1, 3, and 5 in Fig. 1), and S2, S4, and S6 for the cases where a P atom is replaced by an Al atom (corresponding to number of 2, 4, and 6 in Fig. 1), where S1 and S2 are in the grain boundaries, S3 and S4 are the first closest sites of NiAl GB and S5 and S6 are the second closest sites; moreover I7–I9 indicate the three different interstitial sites, respectively (corresponding to numbers 7, 8, and 9 in Fig. 1).

As shown in Fig. 2, when a P atom substitutes for a Ni atom in GBs (S1) or near GBs (S3 and S5), the formation energy of S3 is lower than those of S1 and S5; and when a P atom substitutes for an Al atom in GBs (S2) or near GBs (S4 and S6), the formation energy of S4 is lower than those of S2 and S6. These results suggest that a P atom prefers to replace the atoms that are the first nearest to GBs instead of the

atoms in GBs in the substitutional cases. The higher formation energy in the NiAl GB may be due to the GB effect. For substitutional cases S3 (P substitutes for Ni) and S4 (P substitutes for Al), when in the extremely Al rich environment, P tends to replace a Ni atom, while in the Ni rich environment, P prefers to substitute for an Al atom. But the range of the lowest formation energy of S4 is larger than that of S3, that is, there is little chance that a P atom replaces a Ni atom, which is similar to the result in the NiAl bulk. In Ref. [31], it is reported that a P atom prefers to occupy exclusively the Al sites no matter whether the NiAl alloy is Al-rich or Ni-rich. From the physical explanation,[32] the atomic radii are 100 pm for a P atom, 125 pm for an Al atom, and 135 pm for a Ni atom, respectively.[33] The difference in atomic radius between the P atom and the Al atom is smaller than that between the P atom and the Ni atom. If a P atom substitutes for an Al atom, the lattice distortion of NiAl caused by substitution is smaller. So a P atom tends to replace an Al atom rather than a Ni atom in the NiAl GB. In the following sections, we will not study the case of S3.

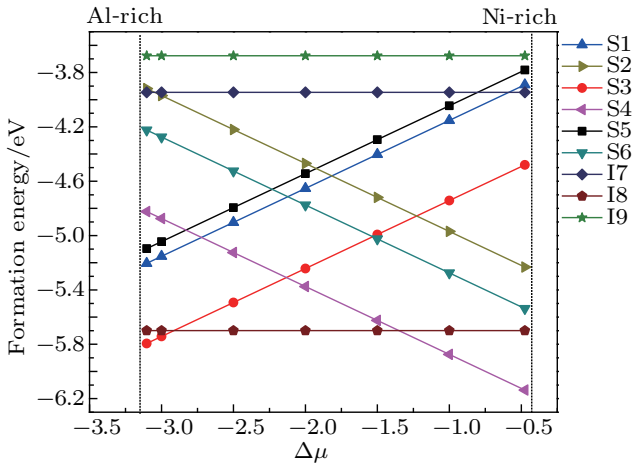


Fig. 2. (color online) Variations of formation energy with $\Delta\mu$ for the NiAl GB occupied by P atoms at different sites. The minimum value of $\Delta\mu$ is $\mu_{\mathrm{Al}}^{\mathrm{bulk}}$, and the maximum is $\mu_{\mathrm{Ni}}^{\mathrm{bulk}}$.

Moreover, when the P atom occupies the interstitial site, the formation energies of I7 and I9 are much higher in the entire range of permissible chemical potential, while the formation energy of I8 is the lowest. After analyzing these three interstitial sites, we find that the P atom stays in the Al-rich environment at the sites of I7 and I9, while the site of I8 is in the Ni-rich environment, indicating that a P atom tends to occupy the site (I8) in the Ni-rich environment rather than the Al-rich environment in the interstitial cases.

In the most range of the permissible chemical potential except the extremely Ni-rich environment, the formation energy of the interstitial case of I8 is lower than those of the substitutional cases of S3 and S4. Thus, a P atom tends to occupy an interstitial site which is in the Ni-rich environment in NiAl GB for most of the range of the permissible chemical potential; in the extremely Ni-rich environment in the NiAl GB, a P atom prefers to substitute for an Al atom, which is the first nearest to the GB. So in the following sections, we choose S4 and I8 for further study.

3.2. Segregation energy

We calculate the segregation energy of impurity P in the NiAl Σ5 GB. The impurity atom preferring to segregate into the GB has a negative segregation energy value, and the positive segregation energy value indicates that the impurity tends to stay in the bulk. The segregation energy E_{S} of P in the NiAl GB can be computed by

$$E_{\mathrm{S}} = (E_{\mathrm{GB}}^{\mathrm{P}} - E_{\mathrm{GB}}) - (E_{\mathrm{B}}^{\mathrm{P}} - E_{\mathrm{B}}), \tag{7}$$

where and represent the total energies of the NiAl GB with and without the impurity of a P atom, respectively, while and are the total energies of the NiAl bulk system with and without a P atom, this NiAl bulk system is formed in the body-centered-cubic structure and has the same atoms and nearly the same size as the NiAl GB. If the segregation energy is negative, the impurity atom is considered to be a segregative atom, indicating that this impurity atom tends to stay in the GB rather than bulk.

We choose the lower formation energy case of I8 in our calculation, and its segregation energy is −4.46 eV. So we can deduce that a P atom is preferable to segregate in the NiAl GB. The negative segregation energy of P impurity in the NiAl GB may be due to the fact that the GB gives more interspace for impurities than in the bulk, so a P atom prefers to stay in the NiAl GB rather than in the bulk. What is more, a P atom and Ni atoms might form new bonds which cause the negative segregation energy.

The McLean equation is used to estimate an equilibrium impurity segregation concentration.[34]

$$C_{\mathrm{GB}} = \frac{C_{\mathrm{bulk}} \exp(-E_{\mathrm{S}}/RT)}{1 + C_{\mathrm{bulk}} \exp(-E_{\mathrm{S}}/RT)}, \tag{8}$$

where C_{GB} and C_{bulk} are the concentrations of impurities in the GB and in the bulk respectively, ES represents segregation energy, T is the aging temperature, and R refers to the molar gas constant. According to the McLean equation, if E_{S} equals zero, the chances for the impurity to stay in the GB and bulk are the same, causing $C_{\mathrm{GB}} = C_{\mathrm{bulk}}$ (C_{bulk} is much smaller than one), that is, the impurity atoms have the same concentrations in the GB and the bulk. If $E_{\mathrm{S}} > 0$, $C_{\mathrm{GB}} < C_{\mathrm{bulk}}$, indicating that the impurity atom tends to stay in the bulk. If $E_{\mathrm{S}} < 0$, $C_{\mathrm{GB}} > C_{\mathrm{bulk}}$, representing that the impurity atom prefers to stay in the GB instead of the bulk.

The typical temperature of 300 K–1500 K and a bulk P concentration of 500 appm–1000 appm are chosen.[35] Figure 3 shows the McLean curves for these selected concentrations and temperatures. In the temperature range of 300 K–1500 K and concentration range of 500 appm–1000 appm, there is an obvious difference in segregation energy between

the GB and the bulk. If the segregation energy is smaller than −1.00 eV in these ranges, the concentration of P in the GB equals 1, that is, P atoms will all stay in the GB no matter what temperature and bulk concentration they are. The segregation energy of P that stays in the most stable interstitial sites in the GB is −4.46 eV, which is much lower than −1.00 eV. As a consequence, almost all the P atoms will prefer to stay in the NiAl GB in the temperature of 300 K–1500 K and a bulk P concentration of 500 appm–1000 appm.

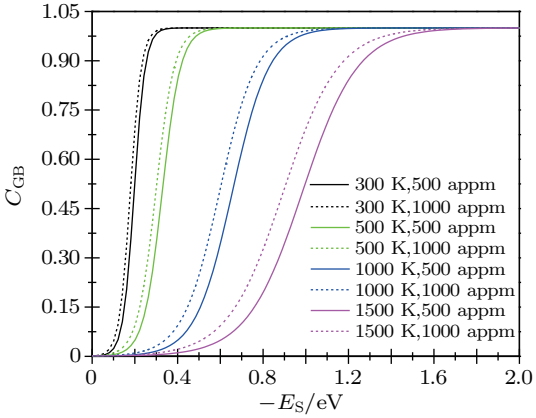


Fig. 3. (color online) Variations of P concentration with segregation energy in the NiAl GB at different bulk P concentrations and different temperatures, obtained according to the McLean equation.

3.3. Atomic configuration

Figure 4 exhibits the atomic configurations of the P atom and its first nearest Ni or Al atoms in the NiAl GB. As depicted in Fig. 4, when a P atom substitutes for an Al atom, the number of the first nearest Ni atoms of the P atom at the sites of S2 and S6 goes to 4, while the number is 6 for the site of S4, that is to say, the P atom of S4 stays in the environment with higher Ni atoms than those of S2 and S6. Furthermore, figure 2 shows that the formation energy of S4 is lower than those of S2 and S6, therefore, the P atom prefers to stay in the Ni-rich environment in the NiAl GB.

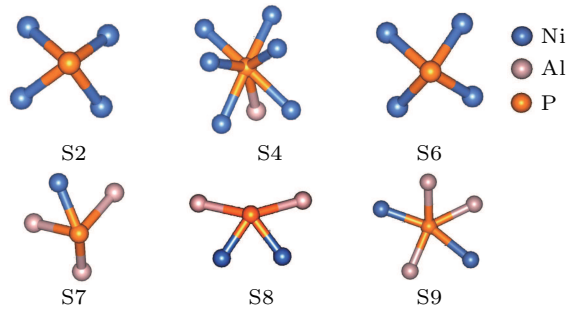


Fig. 4. (color online) Atomic configurations of P atom and its first nearest Ni or Al atoms in the NiAl GB.

In the interstitial cases, the ratio of Ni atom number in the first nearest-neighbor atoms to P atom number in the I8 case is higher than those of I7 and I9. In addition, figure 2 exhibits that the formation energy of I8 is less than those of I7 and I9. These results could also indicate that a P atom prefers to stay in the Ni-rich environment in the NiAl GB.

The S4 and I8 with lower formation energies are both in the Ni-rich environment, so we can deduce that there are interactions between a P atom and a Ni atom. It is possible that a P atom and a Ni atom form the P–Ni bond. We will make further research through charge distribution and density of states in the next two subsections.

3.4. Charge density

Figures 5(a) and 5(b) show the charge density of a P atom with its first nearest atoms in the case that the P atom substitutes for an Al atom (S4), and figures 4(c) and 4(d) show the charge density of the P atom with its first nearest atoms in the interstitial case (I8).

As depicted in Figs. 5(a) and 5(b), when a P atom substitutes for an Al atom, there is no overlap between the contour of the P atom and that of the Al atom, while the contours of the P atom and the Ni atom overlap with each other. For Figs. 5(c) and 5(d), when the P atom occupies the interstitial site, the contours of the P atom and the Al atom have no overlap between each other, while the overlap is found between the contours of a P atom and a Ni atom.

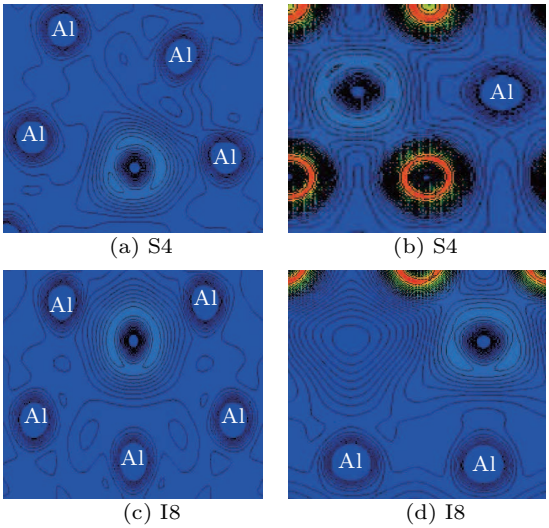


Fig. 5. (color online) Charge distributions of a P atom with its first nearest atoms in the case of S4 and I8. The crystal faces for panels (a) and (c) are (001), (100) for panels (b) and (d).

Hence, no matter whether a P atom is substituted with an Al atom or occupies the interstitial site, the contours of the P atom and the Ni atom overlap with each other, demonstrating that there can exist a possible interaction between a P atom and a Ni atom, and the formation of a Ni atom and a P–Ni bond might occur.

In order to better understand the interactions between a P atom and a Ni atom, we study the charge density difference. The deformation charge density $\Delta\rho$ should be calculated by

$$\Delta\rho = \rho_{\mathrm{NiAl-P}} + \rho_{\mathrm{NiAl,without.Ni1}} - \rho_{\mathrm{NiAl}} - \rho_{\mathrm{NiAl-P,without.Ni1}}, \quad (9)$$

where $\rho_{\mathrm{NiAl-P}}$ represents the charge density of the NiAl GB with P segregating in the GB, $\rho_{\mathrm{NiAl,without.Ni1}}$ is the charge density of the NiAl GB without Ni1 atom, ρ_{NiAl} is the charge density of a pure NiAl GB, and $\rho_{\mathrm{NiAl-P,without.Ni1}}$ is the charge

density of a NiAl GB with P segregating in the GB and without the Ni1 atom.

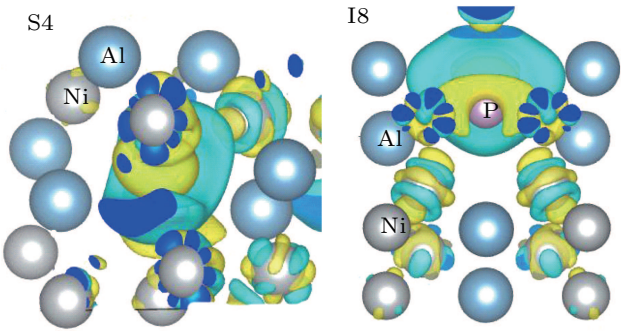


Fig. 6. (color online) Charge density difference between the cases of S4 and I8. Yellow area represents the charge accumulation and the green parts indicate the charge depletion.

Figure 6 shows the deformation charge densities of cases S4 and I8. Deformation charge density is used to investigate the bonding between atoms, which shows the distribution of charge density and the movement of the electrons around the atoms. The weakening and strengthening of chemical bonds are characterized by charge accumulation and depletion, respectively.[36] From Fig. 6, we can see there is an obvious charge accumulation between the P atom and the surrounding Ni atoms, indicating that P–Ni bonds are formed.

3.5. Density of states

The density of states (DOS) can explain the bonding of P–Ni. We study two substitutional and interstitial cases whose formation energies are relatively low, i.e., S4 and I8. Figure 7 exhibits the total DOSs of these two cases. When comparing with the case of a clean NiAl GB, an extra small peak is found at ~ -13.20 eV in total DOS in the cases where a P atom substitutes for an Al atom or occupies the interstitial site in the NiAl GB. Therefore, the introduction of a P atom contributes to the occurrences of such small peaks. The principal peaks near the Fermi energy are related to Ni–Al bonds, so they keep almost unchanged under the addition of a P atom as compared with the clean NiAl GB.

To determine the roots of these small peaks appearing in the total DOS due to the addition of a P atom, we compute the local density of states (LDOS) of the P atom in the NiAl GB, i.e., S4 and I8. Figure 8 shows the local densities of states of a P atom in the NiAl GB for the S4 and I8 cases. In comparison of Fig. 8(a) with Fig. 7(b), when a P atom substitutes for an Al atom (S4), the energy range of the peak of the P 3s orbit is the same as that of the extra peak in the total DOS. A similar result goes to Figs. 8(b) and 7(c), when a P atom occupies the interstitial site (I8), the energy range of the peak of the P 3s orbit is also the same as that of the extra peak in the total DOS, demonstrating that the formation of the P–Ni bond is directly related to the 3s orbit of a P atom added in the NiAl GB.

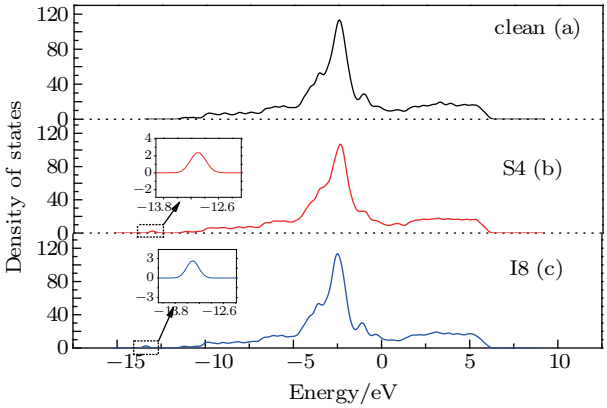


Fig. 7. (color online) Total densities of states for the clean, S4 and I8 cases, respectively, among which the Fermi energies are defined as being zero.

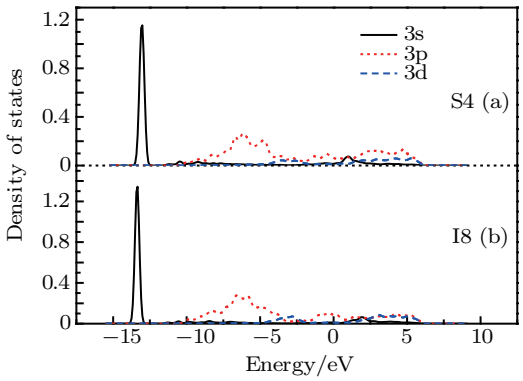


Fig. 8. (color online) Local densities of states of P atom in NiAl GBs for the (a) S4 and (b) I8 cases, in which the Fermi energies are both set to be zero.

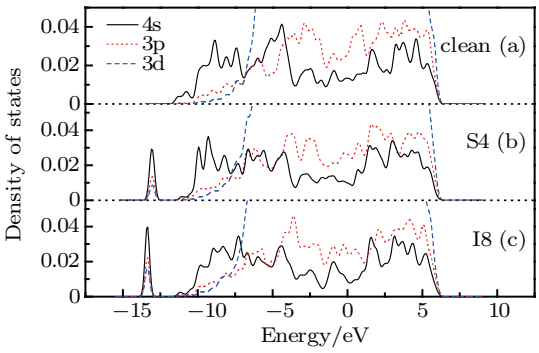


Fig. 9. (color online) Local densities of states of the Ni atom which is the nearest to the P atom in (a) pure NiAl GB and NiAl GBs for (b) S4 and (c) I8 cases. For comparison, the local density of states of the Ni atom in the clean NiAl GB is also shown in this figure, in which the Fermi energies are all set to be zero.

The LDOSs of Ni atom in NiAl GBs with P atom for S4 and I8 cases are shown in Fig. 9. As shown in Figs. 9(b) and 9(c), all the orbits containing 4s, 3p, and 3d of the Ni atom display a notable number of extra peaks in the lower range of energy. These extra peaks have the same energy range as those of the total DOS in Fig. 6 for the S4 and I8 cases respectively, indicating that the orbital electrons of the Ni atom make contributions to P–Ni bonds.

The LDOSs of the Al atom in NiAl GBs with the P atom for S4 and I8 cases are shown in Fig. 10. As shown

in Figs. 10(b) and 10(c), all the orbits containing 4s, 3p, and 3d of the Al atom display an extra peak in the lower range of energy, while the extra peaks for the S4 case are more obvious. These extra peaks have the same energy range as those of the total DOS in Fig. 7 for the S4 and I8 cases respectively, suggesting that the orbital electrons of the Al atom also make contributions to P–Ni bonds, especially in the case that the P atom substitutes for the Al atom.

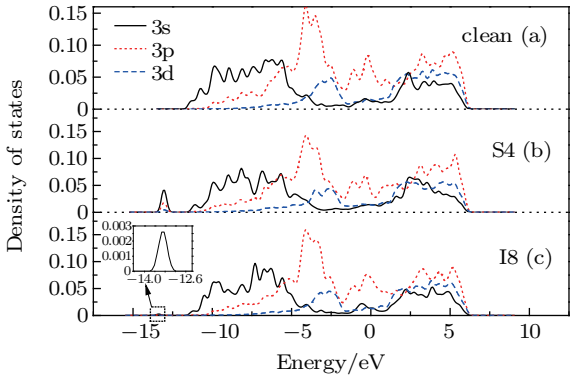


Fig. 10. (color online) Local densities of states of the Al atoms which are the nearest to P atoms in (a) clean NiAl GB and NiAl GBs, for (b) S4 and (c) I8 cases. For comparison, the local density of states of Al atom in the clean NiAl GB, is also shown in this figure, in which the Fermi energies are all set to be zero.

4. Conclusions

First-principles calculations based on the density functional theory (DFT) and ultra-soft pseudopotential method are conducted to investigate the site occupancy, atomic configuration, density of states and charge distribution of the P atom in the NiAlΣ5 grain boundary (GB). The P atom whose segregation energy is −4.46 eV is demonstrated to prefer to segregate in the NiAl GB. The formation energy and atomic configuration of the P atom in the NiAl GB show that the P atom is preferable to stay in the Ni-rich environment in the NiAl GB forming P–Ni bonds. In most of the range of the permissible chemical potential, the P atom tends to occupy an interstitial site which is in the Ni-rich environment in the NiAl GB; when in the extremely Ni-rich environment in the NiAl GB, the P atom prefers to substitute for the Al atom which is the first nearest to GBs. As for charge density, the contours of P atom and Ni atom overlap with each other, indicating that a P atom likes to bond with a Ni atom rather than an Al atom. The deformation charge density also exhibits that a P atom and a Ni atom can form a new bond due to an obvious charge accumulation between the P atom and the surrounding Ni atoms. The observation of the density of states further demonstrates that there are possible interactions between a P atom and Ni atoms and the orbital electrons of P, Ni, and Al atoms all make contributions to P–Ni bonds in the NiAl GB. Significantly, the P–Ni covalent bonds might embrittle the NiAl GB and weaken the plasticity of the NiAl intermetallics. The theoretical results offer a meaningful reference for improving the mechanical properties of NiAl intermetallics.

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