Original Research

Effects of C impurities on the elastic properties of NiAl intermetallics

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Abstract

The atomic configuration and ductility of NiAl intermetallics affected by C impurity have been studied with a first-principles pseudo-potential method. The calculation results indicate that for the substitutional cases, C prefers to replace Ni other than Al in most of the cases except for the Ni-rich case. As compared with the interstitial cases, the C atom can be more easily occupy the Ni-rich octahedron position in both of the Ni-rich and Al-rich cases. The brittleness will be decreased and the ductility will be increased after the NiAl intermetallics doped with the impurity C atom.
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1. Introduction

With many desirable properties such as low density (5.86 g/cm^3), high strength, and high melting temperature, NiAl intermetallics can be widely used in the aerospace industry [1,2]. However, NiAl's possible technological applications are limited by its poor ductility at low temperatures [1,2].

Different methods have been dedicated to manage the brittle behavior of NiAl, such as, micro-structural control through processing and second-phase reinforcement [3–8]. Up to now, the brittleness is still a major obstacle for the practical applications of NiAl.

The interaction between impurity atom (such as C) with metal or metal–alloys is of great technological and scientific interest [9–11]. It is generally accepted that the mechanical properties such as strength, elastic modulus, brittleness in material will have a tremendous variation even by a handful of impurity (ppm) [12–20]. C is considered to be one of the important impurities in NiAl. Only few of C in NiAl

(30 weight ppm) can lead to a large effect in yield strength (30% increases) [21]. Up to now, there is no research published about the association directly between variations of the mechanical properties and atomic configuration after NiAl doped with C impurity. Also, the different cases of C in the interstitial sites in NiAl have never been considered.

With the purpose to combine the microscopic atomic configuration calculated with the macroscopic mechanical properties for the impure case. We introduce the "local elastic constants" to compute the elasticity modulus of NiAl with C. In order to make the calculations achievable, the concentration of C in NiAl in the model we used is much larger than practical situation, namely, "local elastic constants". The evolution of NiAl's ductility can be estimated by the empirical criterions. Such "local" variations can result in the origination and the propagation of the crack under stress.

In this paper, the evolution of atomic configurations, electronic structures, as well as the variations in the elasticity modulus of NiAl due to the presence of the impurity C are studied by ab-intio calculations. Analysis of shear modulus G, bulk modulus B, and Cauchy pressure (C_{12}–C_{44}) allows us know well of the ductile behavior of NiAl with C. Further, we can determine the connection between the atomic bonding in NiAl–C and its elastic properties.

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2. Calculation details

These first-principles calculations were performed by the Vienna Ab-initio Simulation Package (VASP) codes [22]. The ion-electron interaction was described by the ultra-soft pseudo-potential [23], and the exchange-correlation function was characterized within the generalized gradient approximation (GGA) according to the parameterization of Perdew and Wang [24]. We chose a plane-wave cutoff energy 25 Ry after optimization. To make sure that there is no interaction between two nearest C atoms in NiAl supercell, a supercell with the optimized lattice parameters of 8.67 Å was chosen in the three crystalline directions of [001], [010], and [100]. In the section of calculation details, it was sampled by the $(4 \times 4 \times 4)$ k-point grids according the Monkhorst-Pack [25]. The Methfessel–Paxton smearing method was used to integrate the Brillouin zone and account for partial occupancies of the metals near the Fermi level with a smearing width of 0.2 eV, which keeps the convergence of total energy errors below 1 meV.

We got a lattice parameter 2.89 Å after calculation which is quite similar with the experimental value 2.89 Å [26].

3. Results and discussion

3.1. Energetically-favorable site

First, the energetically-favorable site of C in terms of the different sites in NiAl was analyzed. In order to calculate the solution energy of C doped in NiAl, the C atom was installed in Ni substitutional site (NiAlC$_{Ni}$), Al substitutional site (NiAlC$_{Al}$), and three interstitial sites in Bcc structure, respectively.

During the calculation of NiAlC$_{Ni}$ and NiAlC$_{Al}$ cases, the solution energy of E_C^f can be calculated by

$$E_C^f = E_{NiAl-C}^T - E_{NiAl}^T - E_C + \mu_{Ni/Al} \tag{1}$$

where E_{NiAl-C}^T is the energy of the supercell of NiAl with C impurity system. E_{NiAl}^T is the energy of the pure NiAl system. Here, we treated E_C as the energy of an isolated C atom, and directly choose the value 8.01 eV using the first-principles calculations [27]. $\mu_{Ni/Al}$ is the chemical potential of bulk Ni or Al atom.

For the interstitial cases, the solution energy of C is

$$E_C^f = E_{NiAl-C}^T - E_{NiAl}^T - E_C. \tag{2}$$

First, the solution energy of C in NiAlC$_{Ni}$ and NiAlC$_{Al}$ cases were calculated. We considered the chemical potentials of Ni or Al during the whole calculation [28,29]. The formulations can be found in our previous work [18].

The solution energy of C for the NiAlC$_{Ni}$ (Ni site) and NiAlC$_{Al}$ (Al site) cases are shown in Fig. 1. It is a function of the different values of the chemical potential $\Delta\mu$. The solution energy of C in NiAlC$_{Al}$ case is larger than in NiAlC$_{Ni}$ case among most of the value of $\Delta\mu$, except for the C surrounded by Ni atoms (Ni-rich). Energetically speaking, C prefers to replace Ni other than Al in most of the surrounding environment.
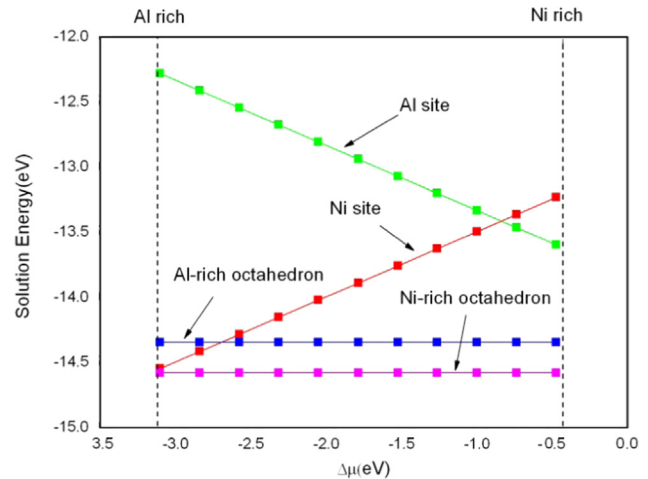

Fig. 1. Solution energy of C in NiAl as a function of the difference between the atomic chemical potentials of Ni and Al ($\Delta\mu = \mu_{Ni} - \mu_{Al}$). The lower limit of $\Delta\mu$ corresponds to $\mu_{Al} = \mu_{Al}^{bulk}$, and the upper limit of $\Delta\mu$ corresponds to $\mu_{Ni} = \mu_{Ni}^{bulk}$.

Then, we put C atom in to three interstitial sites in B2–NiAl: Ni-rich octahedron interstitial (NiAlC$_{Ni-octa}$), Al-rich octahedron interstitial (NiAlC$_{Al-octa}$) and tetrahedron interstitial (NiAlC$_{tetra}$) (in Fig. 2) respectively. We found an interesting thing that C atom placed in to a tetrahedron interstitial site firstly, and it moves to a nearest Ni-rich octahedron interstitial site finally after the supercell and atomic position were relaxed. Another fact is the solution energy of C in NiAlC$_{Al-octa}$ case is much higher than in NiAlC$_{Ni-octa}$ case. These suggest that among all three interstitial sites in B2–NiAl, C prefers to site in the Ni-rich octahedron interstitial site during the whole range of $\Delta\mu$. We calculated the solution energy in NiAlC$_{Ni-octa}$ case is -14.6 eV. It does not dependent on the value of $\Delta\mu$.

We can also compare the solution energy of C in the interstitial cases and substitutional cases. It is quite clear that, for each value of $\Delta\mu$, C atom has lower solution energy in NiAlC$_{Ni-octa}$ than in the substitution cases. In conclusion, the energetically-favorable site of C atom for the entire surrounding environment is the Ni-rich octahedron site in B2–NiAl.

In both the substitution and interstitial cases, the solution energy of C in NiAl is negative suggests that the impure C would be doped in the NiAl intermetallics energetic automatically.

3.2. Atomic structure and charge distribution

Figs. 3–5 give us the atomic structure and charge distribution for the NiAlC$_{Ni}$, NiAlC$_{Al-octa}$ and NiAlC$_{Ni-octa}$ respectively. Fig. 3(a) shows that there is no obvious change for the structure of NiAl and the same for the charge density plot in Fig. 3(b) and (c). From Fig. 4, we can get the information that C atom could bond with Ni when C in the Al-rich octahedron interstitial sites, and bonds with Al during C in the Ni-rich octahedron interstitial sites (shown in Fig. 5C).

Combined the charge density distribution with the conclusion that C has lower solution energy in NiAlC$_{Ni-octa}$ case than
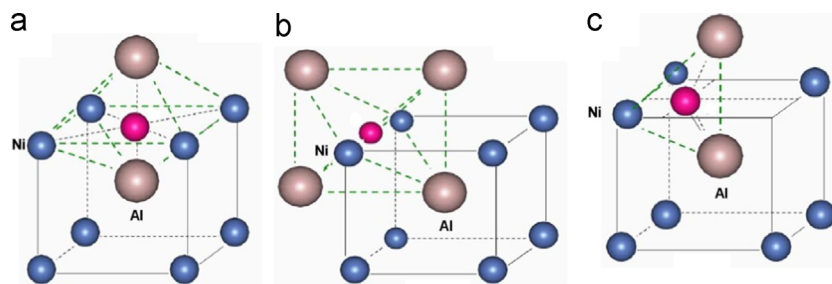
Fig. 2. Different interstitial sites for C in NiAl. (a) Ni-rich octahedron. (b) Al-rich octahedron. (c) Tetrahedron.
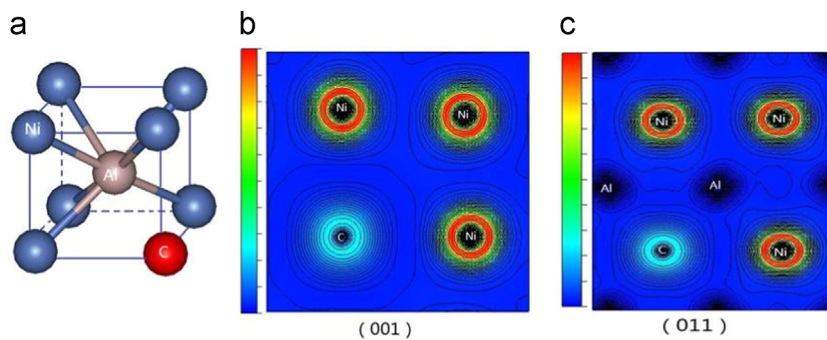

Fig. 3. (a) C in the Ni sites of NiAl. The configuration is energy-optimized. (b) Charge density plot of (001) plane of C in Ni sites of NiAl corresponding to (a). (c) Charge density plot of (011) plane of C in Ni sites of NiAl corresponding to (a).
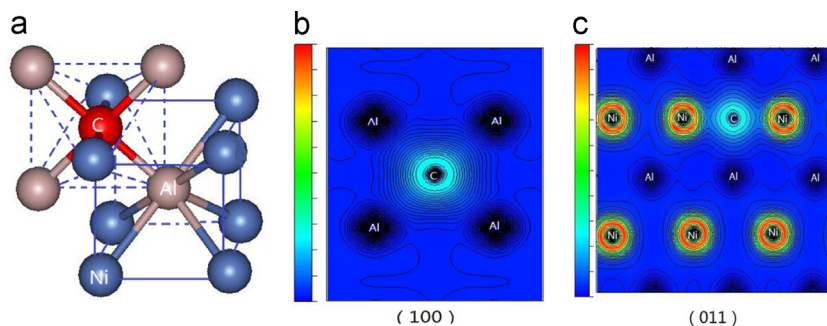

Fig. 4. (a) C in the Al-rich octahedron interstitial sites. The configuration is energy-optimized. (b) Charge density plot of (01)plane corresponding to (a). (c) Charge density plot of (011) plane corresponding to (a).
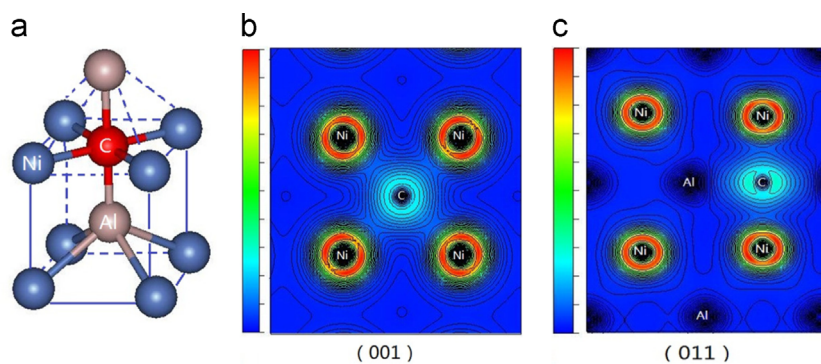

Fig. 5. (a) C in the Ni-rich octahedron interstitial sites. The configuration is energy-optimized. (b) Charge density plot of (001) plane corresponding to (a). (c) Charge density plot of (011) plane corresponding to (a).

in NiAlC$_{Al-octa}$ case, we can get that it is easier for C bond with Al than Ni energetically.

This is also in agreement with the fact that C has higher solution energy in NiAlC$_{Al}$ case than in NiAlC$_{Ni}$ case among most of the value of $\Delta\mu$. It is also easily to understand the physical essence of the bonding preference. C and Al have larger electro-negativity difference(C (2.55, Pauling) and Al (1.95) Ni (2.05)). We can also give the same explanation that why C moves to the Ni-rich octahedron interstitial site when we put C atom into the tetrahedron interstitial site first.

Compare with Fig. 3 and 5, it is obvious that C prefers to bond with Al with bond angle 180°. This phenomenon can also be reflected in the fact that C has the lowest solution energy during C in the Ni-rich octahedron interstitial site not the substitute cases even the substitute cases has larger space in NiAl intermetallics. This C–Al bond may weaken Ni–Al bond in NiAl intermetallics, and further have some effects on the mechanical properties of NiAl intermetallics.

3.3. Elasticity modulus and ductility

Effects of the C–Ni bond on the ductility behavior of NiAl were investigated by calculating the elasticity modulus of pure NiAl and the NiAl–C system. As we all known, there are three elastic constants independent: c_{11}, c_{12} and c_{44} for bcc-NiAl. Here, the NiAl–C supercell still treated as a cubic system since there are no obvious differences for lattice parameters of the supercell between pure NiAl and NiAl–C. Taking NiAlC$_{Ni-octa}$ as an example, the supercell becomes 8.56 Å × 8.56 Å × 9.09 Å for the C atom in the Ni-rich octahedron interstitial, indicating that the supercell is nearly cubic. So the calculated c_{11}, c_{12} and c_{44} of different cases are tabulated in Table 1. Our calculated c_{11}, c_{12} and c_{44} is 208.2 GPa, 132.6 GPa and 112.7 GPa respectively, which are consistent well with the experimental values [30].

For a cubic system, the elasticity modulus can be calculated as follows: the bulk modulus $B = 1/3(C_{11}+2C_{12})$, the shear modulus $G = 3C_{44}+C_{11}-C_{12}/5$, the Young's modulus $E = 9BG/3B+G$.

With the purpose of determining the ductility and brittleness of NiAl and NiAl–C system, we used Pugh's criterion [31]: for metals below 1/3 of the melting point, the obstruction of deform plastically is proportional to burgers vector (b) and the elastic shear modulus (G). That is to say, the solidity is proportional to $G \cdot b$. For all pure metals, fracture strength is proportional to B and a (lattice parameter). Then, the pugh ratio (B/G) indicates the plastic range for a pure metal. With Pugh's criterions, the lower the value of B/G, the more brittleness the materials are.

Table 1
Elastic constants (GPa) of the pure NiAl and the NiAl with. C in Ni-rich octahedron interstitial site.

System	c_{11}	c_{12}	c_{44}
NiAl	208.2	132.6	112.7
NiAlC$_{Ni-octa}$	192.90	136.64	106.36
NiAl (experimental)	211.5 [30]	143.2 [30]	112.1 [30]

Table 2
Bulk modulus, shear modulus, Young's modulus, and Poisson's ratio of the pure NiAl and the NiAl with C in Ni-rich octahedron interstitial site, which are determined from the elastic constants. Corresponding B/G and Cauchy pressure of C_{12}–C_{44} are also shown.

	B (GPa)	G (GPa)	E (GPa)	B/G	C_{12}–C_{44} (GPa)
NiAl	157.8	82.74	211.29	1.91	19.9
NiAlC$_{Ni-octa}$	155.39	75.07	193.97	2.07	30.3

Many compounds materials and impurity-containing systems have used Pugh's criterions successfully [3,4,6,32,33]. The B/G values of NiAl and NiAlC$_{Ni-octa}$ are shown in Table 2. It is obvious that C increases the B/G value in the case of Ni-rich octahedron interstitial. The B/G ratio of NiAl is 1.91, which is increased to 2.07 for NiAlC$_{Ni-octa}$. This suggests that the impurity C atom results in the brittleness of NiAl decreases and ductility increases.

In addition, the shear modulus G decreases from 82.74 GPa for the pure NiAl to ~75 GPa for NiAlC$_{Ni-octa}$. We can get the conclusion that C makes the hardness of NiAl reduced and thus bring on the ductibility of NiAl augment.

The angular property of bonding in metals and compounds can be characterized by Cauchy pressure (C_{12}–C_{44}) [32]. Under most situations, with a directional bonding covalent material, the (C_{12}–C_{44}) is negative. From Table 2, we can know that C raises (C_{12}–C_{44}) of NiAl from 19.9 GPa to 30.3 GPa. Means the component of covalent bonding in NiAl reduced after C atom doped in.

In summary, the above two empirical criterions lead to the same conclusion that C results in the brittleness of NiAl decreased and the ductility increased. Hence, the C impurity can act as a possible reason which can increase the ductility of NiAl.

4. Summary

We calculated effects of C impurity content on the atomic configuration, elastic properties and ductility enhancement of NiAl intermetallics. The energetically-favorable site of C atom was calculated by the solution energy. The impurity C atom can go into the Ni-rich octahedron interstitial independent of the surrounding environment. According to the calculated elasticity modulus and the empirical criterions, a certain number of C impurities will reduce the shear modulus (G) and the Cauchy pressure, lead to a decrease of the brittleness and an increase of the plasticity of NiAl. The effects of C on the ductility characteristics of NiAl intermetallics are clarified by our calculations. These results will provide a good reference to the future application of the NiAl intermetallics.

Acknowledgments

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