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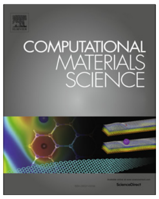

First-principles study of NiAl alloyed with Co

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ABSTRACT

The site preference of Co in NiAl and its effects on structural, elastic, electronic and thermal properties were investigated by performing first principles calculations using density functional theory (DFT). The site preference was investigated by calculating the transfer energy of NiAl alloys with Co. The result shows that Co tends to occupy Ni site. By analyzing changes in electronic density of states, Mulliken population, overlap population and valence charge density, the electronic property and bond characters were discussed. The elastic properties calculation shows that Co increases alloy hardness. Moreover, the pressure and temperature dependences of the thermal expansion coefficient, bulk modulus, Debye temperature and heat capacity in a wide temperature (0–1600 K) and pressure (0–30 GPa) ranges are presented in this study.

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1. Introduction

The intermetallic compound B2-NiAl is one of the most promising engineering materials with attractive chemical and mechanical properties, and it is a contender of next generation of high temperature structure material [1]. The properties include high melting temperature (1638 °C), low density (5.86 g/cm^3), high modulus, high thermal conductivity and excellent environmental resistance. However, room temperature brittleness and high temperature strength shortage seriously limit its practical application, but it can be improved by alloying additions [2–4]. It is known that solid solubility varies with different dopant atoms, and Co has high solubility in NiAl.

The understanding of the alloying effects requires the knowledge of site distributions of ternary elements. The site preference of Co has been investigated extensively by various experimental techniques, such as X-ray diffraction (XRD) [5], Extended X-ray absorption edge fine structure (EXAFS) [6]. Thermal conductivity measurement [7]. The results showed that Co substitute for a Ni site. Theoretical evaluations of the site preference of Co have been conducted by many researchers [8–13]. They get the same conclusion that Co has a consistent preference for the Ni sublattice. There are some investigations about the effect of alloying on properties of NiAl. Kovalev et al. [14] pointed out that alloying with Co has a beneficial effect on the micro-mechanism of fracture and ductile–brittle transition temperature, and this improvement is tied with the change of density of electron states N(EF). The microhardness of NiAl alloys was increased due to solid solution hardening of Co [15].

Through the theoretical and experimental research above, it is worth noting that the theoretical calculations only gave material properties at 0 K and zero pressure, without any thermal effects included. As a potential high-temperature material, the thermal properties cannot be over-emphasized. Practical use of NiAl alloy often occurs at high temperature. Therefore, it is necessary to investigate the influence of Co on the thermal properties. To our knowledge, there is no correlative report about this aspect. To address this interest, we investigate the structural and thermodynamic properties at high pressures and temperatures, by using first-principle calculations combined with the quasi-harmonic Debye model.

In this paper, the site preference of Co in NiAl and its effects on structural, elastic, electronic and thermal properties are investigated by performing first principles calculations using density functional theory (DFT), which would be useful for the understanding and design of the relevant alloys. The influence of Co on the thermal expansion coefficient, bulk modulus, Debye temperature and heat capacity at different pressure and temperature were studied for the first time.

2. Theoretical methods

2.1. Calculation parameters

NiAl has an ordered B2 structure that consists of two interpenetrating simple cubic sublattices, with Ni and Al atoms occupying the corners and the center of the body, respectively. The lattice

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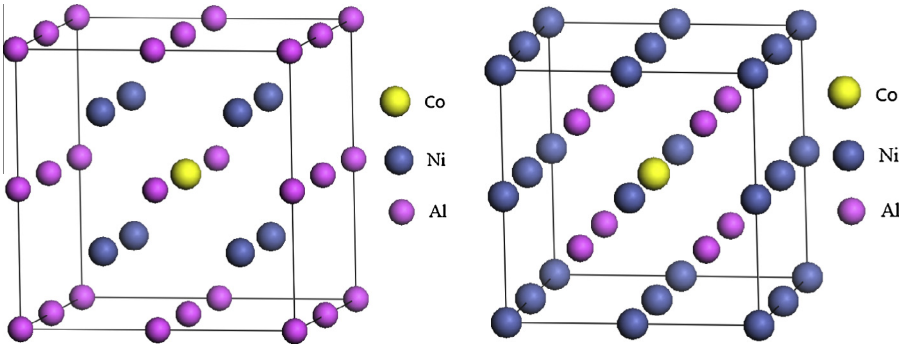

Fig. 1. Original model used in the calculation.

constants are $a_0 = 0.2887$ nm, $\alpha = \beta = \gamma = 90$. A supercell consisting of 16 atoms is devised for the present study, a $2 \times 2 \times 2$ cubic representation of the ordered structure, with one single point defect such as an antisite ($\mathrm{Ni_{Al}}$ or $\mathrm{Al_{Ni}}$) or the ternary element Co on the sublattice. One alloying atom in each supercell corresponds to a fraction of 6.25 at.%. Fig. 1 shows the Al-site and Ni-site defect model respectively.

All the calculations in this study were performed with the CASTEP code [16], based on the first principles density functional theory, within the generalized gradient approximation (GGA). For the GGA exchange–correlation function, the Perdew–Wang parameterization (PW91) [17,18] was employed. The ultra-soft pseudopotential and plane wave basis sets [19] were implemented. After a series of tests, the cutoff energy was set at 400 eV. The k-points is $8 \times 8 \times 8$ in all calculations and the self-consistent convergence of the total energy is at 5×10^{-7} eV/atom.

2.2. Debye model

In order to investigate the thermodynamic properties of NiAl alloys, the quasi-harmonic Debye model [20] was applied, in which the non-equilibrium Gibbs function $G^*(V;P,T)$ can be written in the form of

$$G^*(V;P,T) = E(V) + PV + A_{\mathrm{Vib}}(\Theta(V);T) \tag{1}$$

where $E(V)$ is the total energy per unit cell, PV corresponds to the constant hydrostatic pressure condition, and the vibration term A_{Vib} is the Helmholtz free energy for lattice vibrations and can be written as

$$A_{\mathrm{Vib}}(\Theta(V);T) = nkT\left[\frac{9}{8}\frac{\Theta}{Y} + 3\ln(1 - e^{-\Theta/T}) - D(\Theta/T)\right] \tag{2}$$

where $D(y)$ is the Debye integral defined as

$$D(y) = \frac{3}{y^3}\int_0^y \frac{x^3}{e^x - 1}dx \tag{3}$$

Θ is the Debye temperature, and n is the number of atoms per formula unit. For an isotropic solid, with Poisson ratio σ, Θ can be expressed as

$$\Theta = \frac{\hbar}{k}\left[6\pi^2 V^{1/2} n\right]^{1/3} f(\sigma)\sqrt{\frac{B_s}{M}} \tag{4}$$

where M is the molecular mass per formula unit, B_s the adiabatic bulk modulus, and $f(\sigma)$ is given by following forms:

$$\sigma = \frac{3B - 2G}{6B + 2G} \tag{5}$$

$$f(\sigma) = \left\{3\left[2\left(\frac{2}{3}\frac{1+\sigma}{1-2\sigma}\right)^{3/2} + \left(\frac{1}{3}\frac{1+\sigma}{1-\sigma}\right)^{3/2}\right]^{-1}\right\}^{1/3} \tag{6}$$

B_s is the adiabatic bulk modulus, which is approximated given by the static compressibility:

$$B_s \cong B(V) = V\frac{\mathrm{d}^2E(V)}{\mathrm{d}V^2} \tag{7}$$

Therefore, the non-equilibrium Gibbs function $G*(V;P,T)$ as a function of $(V;\ P,T)$ can be minimized with respect to V

$$\left(\frac{\partial G^*(V;P,T)}{\partial V}\right)_{\mathrm{P,T}} = 0 \tag{8}$$

By solving Eq. (8), one can get the thermal equation of state (EOS). The isothermal bulk modulus B_{T}, the heat capacity C_{V} and the thermal expansion coefficient α are given by

$$B_{\mathrm{T}}(pP,T) = V\left(\frac{\partial^2 G^*(V;P,T)}{\partial V^2}\right)_{\mathrm{P,T}} \tag{9}$$

$$C_V = 3nk\left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1}\right] \tag{10}$$

$$\alpha = \frac{\gamma C_{\mathrm{V}}}{B_{\mathrm{T}}V} \tag{11}$$

where γ is the Grüneisen parameter, which is defined as:

$$\gamma = -\frac{d\ln\Theta(V)}{d\ln V} \tag{12}$$

The thermodynamic properties of NiAl and doping system were calculated through the quasi-harmonic Debye model.

3. Results and discussion

3.1. Site preferences of ternary elements in NiAl at ground state

Formation enthalpy is the entropy of the compound or solution in relation to the composition-weighted pure elements. The bulk stability of the compound is determined by formation enthalpy. The negative formation enthalpy value implies the structure is thermodynamically stable and the positive value means the structure is instable. In this work, the formation enthalpy of $\mathrm{(Ni_7Co)Al_8}$ was calculated by using the following expression:

$$\Delta H_{\mathrm{(Ni_7Co)Al_8}} = \frac{1}{16}\left(E_{\mathrm{tot}} - 7E^{\mathrm{Ni}}_{\mathrm{solid}} - 8E^{\mathrm{Al}}_{\mathrm{solid}} - E^{\mathrm{Co}}_{\mathrm{solid}}\right) \tag{13}$$

The formation enthalpy of $\mathrm{Ni_8(Al_7Co)}$ is calculated by using the following expression:

$$\Delta H_{\mathrm{Ni_8(Al_7Co)}} = \frac{1}{16}\left(E_{\mathrm{tot}} - 8E^{\mathrm{Ni}}_{\mathrm{solid}} - 7E^{\mathrm{Al}}_{\mathrm{solid}} - E^{\mathrm{Co}}_{\mathrm{solid}}\right) \tag{14}$$

where E_{tot} refers to the total energy of unit cell. $E^{\mathrm{Ni}}_{\mathrm{solid}}$, $E^{\mathrm{Al}}_{\mathrm{solid}}$ and $E^{\mathrm{Co}}_{\mathrm{solid}}$ are the energy per atom of bulk Ni, Al and Co, respectively. The

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