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Determination of thermodynamic and thermo-elastic properties for ductile B2-DyCu intermetallics using molecular dynamics simulations

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ABSTRACT

The thermodynamic and thermo-elastic properties of ductility intermetallic compounds DyCu with B2 structure are investigated with molecular dynamics. The calculated structural properties are in reasonable agreement with the available experimental and previously calculated data. At 300 K, the heat capacity of DyCu is 23.93 J mol^{-1} K^{-1}. At the whole range 0–900 K, the elastic constants decrease with increasing temperature, and satisfy the stability criterions for DyCu compound. The value of B/G ratio for DyCu is greater than 1.75 implying the DyCu intermetallics are ductile, and increases with elevating temperature. Our results mean that the ductility of DyCu can be improved by increasing temperature.

1. Introduction

A new family of intermetallics having unusually high ductility and high fracture toughness at room temperature has been reported by Gschneidner et al. [1]. They are fully ordered, stoichiometric rare-earth B2-type intermetallic compounds with formula RM, where R is a rare-earth element and M is a main group or late transition metal. Those intermetallics are simply formed by arc-melting equal amounts of pure elements in normal-humidity air. Nearly all of the RM compounds are “line-compounds” with exact 1:1 stoichiometry. Over 120 such alloys exist, of the 15 tested to date, most exhibit good ductility. DyCu is one of the 15 compounds of this family so far reported. DyCu shows ductility up to 11–16% elongation in polycrystalline specimens tensile tested at room temperature in ambient air of normal humidity [2]. The fracture toughness (K_{IC}) value of DyCu has been reported to be 25.5 MPa$\sqrt{m}$, which is much larger than that of the well-studied NiAl B2 intermetallic compound (5.1–6.4 MPa$\sqrt{m}$) [3]. However, the thermodynamic, and thermo-elastic properties have not been understood completely. To get a better understanding of the anomalous ductility of DyCu intermetallics, more fundamental investigations of temperature-dependent properties such as structure properties, volume thermal expansion, heat capacity, and thermoelasticity, etc., are obviously required. Therefore, we apply the Molecular Dynamics (MD) approach to investigate the temperature-dependent elastic constants and thermodynamic properties for the novel intermetallics DyCu.

2. Interaction potential and simulation details

The interatomic potential of metal is the foundation of molecular dynamics simulation. Interatomic interactions were modeled by the Embedded Atom Method (EAM) in this present. The EAM is a model developed by Daw and Baskes [4] for calculating the total energy of an arbitrary arrangement of atoms in a metal. It is based on the density functional theory, which asserts that the energy of a solid can be written as unique function of the electron density distribution. The potentials provides a good description of many-body interactions and has already been successfully applied for the study of the bulk, surface and clusters of metals and alloys in our previous investigations [5–8]. The crystal structure for Dy and Cu elements is hexagonal close-packed (HCP) and face-centered cubic (FCC), respectively. In the current EAM, the total energy of a system is approximaed as

$$E_t = \sum \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{i \neq j} \varphi(r_{ij}) + M_i(P_i) + N_i(Q_i) \tag{1}$$

where $F(\rho_i)$ is the energy required to embed an atom with an electron density ρ_i in site i. ρ_i is given by a linear superposition of the spherical averaged electron density of other atom's $f(r_{ij})$. ρ_i is dimensionless. $\varphi(r_{ij})$ is pair potential, $M(P_i)$ and $N(Q_i)$ are the electron density modification terms. When the crystal type is HCP,

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there are two Cauchy relation, its atom arrangement is anisotropy, so this anisotropy is described by another modification terms $N(Q_i)$, while the crystal type is FCC, $N(Q_i)$ term is neglected in Eq. (1). P_i and Q_i are the high order of electron density of other atoms $f(r_{ij})$. The atomic electron density $f(r_{ij})$ is expressed as

$$f(r) = f_e\left(\frac{r_1}{r_{ij}}\right)^{\theta}\left[\frac{r_{ce} - r_{ij}}{r_{ce} - r_1}\right]^2 \tag{2}$$

where f_e and θ are the model parameters, with θ=4.5 for HCP Dy metals, and θ=4.7 for FCC Cu metals. r_1 is the equilibrium nearest neighbor atomic distance for a perfect lattice at 0 K, and r_{ij} is the sepqration distance of atoms i and j. $f(r_{ij})$ is truncated at r_{ce}, where $r_{ce} = r_4 + k_c(r_5 - r_4)$ for FCC Cu metals, and $r_{ce} = r_8 + k_c(r_9 - r_8)$ for HCP Dy metals. r_n shows the equilibrium nth neighbor atomic distance for a perfect lattice at 0 K.

In the present paper, the embedding function $F(\rho_i)$ is expressed as

$$F(\rho_i) = -F_0\left[1 - \ln\left(\frac{\rho_i}{\rho_e}\right)\right]\left(\frac{\rho_i}{\rho_e}\right)^n \tag{3}$$

For HCP metals, the pair potential is taken as

$$\varphi(r_{ij}) = \sum_{l=-1}^{6}\left(\frac{r_{ij}}{r_1}\right)^l \tag{4}$$

The atomic interactions out to the seventh neighbor distance are considered and it is truncated at a specific cut-off distance $r_c = r_7 + k_c(r_8 - r_7)$.

While for FCC metals, the pair potential is taken as

$$\begin{aligned}\varphi(r_{ij}) = k_0 + k_1 \exp\left(1 - \frac{r_{ij}}{r_1}\right) + k_2 \exp\left[2\left(1 - \frac{r_{ij}}{r_1}\right)\right] \\ + k_3 \exp\left[3\left(1 - \frac{r_{ij}}{r_1}\right)\right] + k_4 \exp\left[4\left(1 - \frac{r_{ij}}{r_1}\right)\right] \\ + k_{-1} \exp\left(\frac{r_1}{r_{ij}} - 1\right)\end{aligned} \tag{5}$$

The atomic interactions out to the third neighbor distance are considered and it is truncated at a specific cut-off distance $r_c = r_3 + k_c(r_4 - r_3)$.

For FCC metals, the energy modified modification term is empirically taken as

$$M(P_i) = -\frac{\alpha P P_e}{(P + P_e)^2},\ P_i = \sum_{j\neq i} f^2(r_{ij}),\ \rho_i = \sum_{j\neq i} f(r_{ij}) \tag{6}$$

While for HCP metals, the energy modification terms are empirically taken as

$$M(P_i) = \frac{\alpha}{4}\frac{(P - P_e)^2}{(P + P_e)^2},\ N(Q_i) = \frac{\beta}{4}\frac{(Q - Q_e)^2}{(Q + Q_e)^2} \tag{7}$$

$$P_i = \sum_{j\neq i} f^{12}(r_{ij}),\ Q_i = \sum_{j\neq i} f^{21}(r_{ij}),\ \rho_i = \sum_{j\neq i} f(r_{ij}) \tag{8}$$

where P_e and Q_e are their equilibrium values.

The Dy–Cu alloy potential is given by

$$\varphi^{ab}(r) = \frac{1}{2}\mu\left[\varphi^{aa}\left(r\frac{r^{aa}}{r^c}\right) + \varphi^{bb}\left(r\frac{r^{bb}}{r^c}\right)\right] \tag{9}$$

where the superscripts a- and b- represent the a- and b-type atoms in the binary alloy, respectively. φ^{aa} and φ^{bb} are the monatomic potentials, which could be given by the monatomic potentials, as shown in Eqs. (4) and (5). r^a and r^b are the a- and b-type atom parameters, respectively. The model parameter r^c is defined as $r^c = (r_1^a + r_1^b)/2$, where r_1^a and r_1^b are the first nearest neighbor distance of the a- and b-type atoms, respectively, and u is the alloy adjustable parameter. All the model parameters, determined from fitting physical attributes such as lattice parameter, cohesive energy, vacancy formation energy, and elastic constants for Dy, Cu, and Dy–Cu intermetallic compound, are listed in Tables 1 and 2. The fitted alloy parameters r^c and u are 3.2079 and 1.145 for the binary Dy–Cu system, respectively.

Table 1
Model parameters of the EAM for Dy and Cu metals. n, f_e and k_c are dimensionless, F_0, α, and β are in ev, $r^p(p=a, b)$in Å.

Metal	n	F_0	$\alpha(\times 10^{-5})$	$\beta(\times 10^{-6})$	k_c	r^p	f_e
Dy	0.47	1.5333	0.37705	−1.9315	0.45	3.5493	1.81585
Cu	1.12	2.2983	−2.8841	–	0.75	2.6570	3.17652

The temperature-dependent thermodynamic properties of DyCu are simulated using MD. The simulations of systems are carried out in two successive ensembles. Some thermodynamical properties such as lattice constant, cohesive energy and enthalpies of formation are determined from the constant temperature-constant pressure (NPT) ensemble simulations. Finally, the constant volume-constant temperature (NVT) ensemble is used to simulated the elastic constants, vibration density of states, heat capacity, vibrational entropy and vibrational free energy. The simulation box is made up of $10a \times 10a \times 10a \times 2 = 2000$ atoms for B2-DyCu alloy.

3. Results and discussion

3.1. Structure properties and volume thermal expansion

Table 3 shows the results of the cohesive energy, enthalpy of formation and lattice parameter for DyCu alloy calculated from the NPT ensemble at various temperature along with the available experimental data as well as the previous calculated data. The EAM calculated lattice parameters for DyCu are compared with the experimental results, which shows good agreement, within about 1%. As shown in Table 3, it is noted that the cohesive energy, enthalpy of formation and lattice constants for DyCu increase as the temperature increases.

Experimentally, the enthalpies of formation for DyCu intermetallics are −0.13 eV reported by Sommer [9]. The present EAM calculated results of DyCu are −0.0918 eV, at 300 K. The comparison with experiment [9] and the present calculated data show a satisfactory agreement for DyCu.

The coefficient of thermal volume expansion is calculated as follows:

$$\alpha_p(T) = \frac{1}{V(T)}\left(\frac{\partial V(T)}{\partial T}\right)_p \tag{10}$$

The value of thermal expansion calculated from Eq. (10) at 300 K for DyCu alloy is $4.74 \times 10^{-5}\ K^{-1}$. In the absence of any available measured data in the literature, they could not be compared. Future experimental work will testify our calculated results.

The melting point is simulated by means of gradual heating. Computer simulations are carried out using 20 K increments around the melting point. Fig. 1 shows the simulated cohesive energy of DyCu as a function of temperature. There is obviously a discontinuity in Fig. 1, which may be due to a solid to liquid phase transformation and the melting point of 1420 K. The calculated result is larger than the experimental value 1228 K [10], because