Computational Materials Science 123 (2016) 70–78

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

First-principles investigation of structural, mechanical and electronic properties for Cu–Ti intermetallics

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ARTICLE INFO

Article history:
Received 27 February 2016
Received in revised form 13 June 2016
Accepted 20 June 2016
Available online 29 June 2016

Keywords:
Cu–Ti intermetallics
Phase stability
Mechanical properties
Electronic structure
First-principles study

ABSTRACT

To design a high-performance Cu–Ti intermetallic coating, first-principles calculation is conducted to systematically investigate the phase stability, mechanical and electronic properties of the Cu–Ti binary intermetallics. The phase stability and mechanical properties are studied by calculating the formation enthalpy and independent elastic constants, respectively. The calculated formation enthalpy indicates that β-Cu_4Ti, CuTi and $CuTi_2$ are stable phases at 0 K, while α-Cu_4Ti, Cu_3Ti, Cu_3Ti_2, and Cu_4Ti_3 are metastable phases. In addition, the mechanical properties of Cu–Ti intermetallics present a positive correlation with their formation enthalpy. The electronic structures of the Cu–Ti intermetallics are evaluated by analyzing the bonds character to reveal the bonding characteristics, which is crucial to the phase stability and mechanical properties. Among the Cu–Ti intermetallics studied, CuTi phase exhibits the highest stability, hardness and a higher brittleness among all Cu–Ti intermetallics, while other Cu–Ti intermetallics show good toughness. Based on the calculated results, a high strength Cu–Ti intermetallic coating consisting of hard CuTi particles on a ductile Cu_4Ti_3 matrix is proposed.

1. Introduction

Copper (Cu) and Cu-based alloys are widely used for various functional components such as conductive springs and interconnections due to their excellent electrical and thermal conductivity [1]. Meanwhile, the strength and wear resistance of Cu-based alloys are critical factors in some specific applications, such as spot welding electrodes and electric railway wires [2], where Cu–Be alloy is now widely used [3]. However, the expensive cost and toxicity prevents its further utilization [4]. Fortunately, the Cu–Ti binary alloys containing 1–6 mol% Ti could work as a good candidate as their electronic and physical properties are close to Cu–Be alloys after ageing [5,6]. Moreover, both of the strength and hardness of Cu–Ti alloys could be improved due to the formation of Cu–Ti intermetallic compounds, while maintaining the high electrical conductivity of bulk alloy [7–9]. Therefore, surface modification by Cu–Ti intermetallic coatings could be a good way to improve the wear resistance of Cu-based alloys. In our previous work, a Cu–Ti intermetallic coating on C17000 Cu–Be alloy by thermo-diffusion method have been successfully prepared [10], but the Cu–Ti intermetallic coating always contains various phases such as Cu_3Ti, Cu_3Ti_2, CuTi and $CuTi_2$, whose mechanical and electrical properties are still unclear. Ghosh [11] investigated the structural stability of Cu–Ti intermetallics by first principles calculations, but the mechanical properties of Cu–Ti intermetallics were not revealed. In addition, there is still a lack of comparison between the crystalline and amorphous Cu–Ti intermetallics [12]. Therefore, to optimize the composition of Cu–Ti coatings and prevent the negative effects caused by the weak Cu–Ti intermetallics, a further systematic study from theoretical perspectives on the Cu–Ti intermetallics is needed.

In the present work, first-principles calculations are conducted to systematically study the phase stability, mechanical properties and electronic structure of Cu–Ti intermetallics. Specifically, the formation enthalpy, elastic constants, elastic modulus, microhardness, Debye temperature, density of state (DOS) and the difference of charge density are calculated. The results could provide suggestions for rational design of Cu–Ti intermetallic coatings on the surface of Cu alloys.

2. Computational method

The Cu–Ti binary phase diagram shows that there are six stable intermetallic compounds in the Cu–Ti binary system, i.e. $CuTi_2$, CuTi, Cu_4Ti_3, Cu_3Ti_2, Cu_2Ti and Cu_4Ti [13]. In addition, some other possible intermetallic compounds, such as $CuTi_3$, Cu_3Ti, were experimentally obtained [14,15]. Table 1 shows the built initial

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http://dx.doi.org/10.1016/j.commatsci.2016.06.015
0927-0256/

crystal structures of the above eight Cu–Ti intermetallics, as well as Cu and α-Ti with the crystallographic data from Refs. [11,13,22]. All calculations were performed with CASTEP code based on the density functional theory (DFT) [16]. The generalized gradient approximation (GGA) in Perdew-Burke-Eruzerh (PBE) formula was applied to describe the exchange-correlation potential [17]. The ion-electron interaction was evaluated by ultrasoft pseudopotentials of Vanderbilt type [18], and the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was chosen to perform Geometry optimizations of these structures [19]. The cutoff energy of 600 eV was used for plane-wave expansions. The k-points meshes within Monkhorst–Pack framework were set as $10 \times 10 \times 10$, $6 \times 6 \times 9$, $6 \times 6 \times 2$, $6 \times 8 \times 8$, $10 \times 5 \times 6$, $11 \times 11 \times 2$, $8 \times 8 \times 2$, $11 \times 11 \times 2$, $1 \times 1 \times 1$, $5 \times 5 \times 3$, $9 \times 9 \times 2$, $8 \times 8 \times 8$, $12 \times 12 \times 12$ for Cu, α-Cu_4Ti, β-Cu_4Ti, Cu_3Ti, Cu_2Ti, Cu_3Ti_2, Cu_4Ti_3, CuTi, $CuTi_2$, $CuTi_3$ and α-Ti, respectively [20]. The geometry optimizations were considered to be converged when the energy change per atom, maximum residual force, maximum atomic displacement, maximum stress were less than 5×10^{-6} eV, 0.01 eV/Å, 5×10^{-4} Å and 0.02 GPa, respectively. The crystal structure of these compounds is shown in Fig. 1. Using the equilibrium structure, the elastic constants and modulus were calculated by the stress-strain method based on Hooke's Law [21].

3. Results and discussion

3.1. Structural properties

The calculated lattice parameters of Cu–Ti intermetallics are listed in Table 1. Comparing with the literatures [11,13,22], it can be seen that the calculated lattice parameters are close to the reported values with a deviation of less than 1%, indicating the good accuracy of the present work. The deviation between the calculated values and experimental ones are mainly caused by the GGA process and the temperature-dependence of lattice parameters. Especially for $CuTi_3$, the calculated lattice parameter shows an obvious difference from the experimental result for its metastable nature. In addition, Cu_3Ti_2, Cu_4Ti_3 and $CuTi_2$ have similar lattice parameters and structure of body-centered cubic with Cu and Ti atoms stacked along (1 0 0) plane alternately. Moreover, it can be readily seen that the Cu–Ti structure will turn into other low-energy structures of lower symmetry, as Ti content is less than 40 at.%.

3.2. Energies and phase stability

To evaluate the thermodynamic stability of the Cu–Ti intermetallics, the formation enthalpies (E_f) of these phases are calculated by the following equation:

$$E_f^{Cu_xTi_y} = \left[E_t^{Cu_xTi_y} - \left(x \cdot E_{solid}^{Cu} + y \cdot E_{solid}^{Ti}\right)\right] \Big/ (x+y) \quad (1)$$

where E_t and E_{solid} is the total energy of the calculated cell and the energy per atom of the pure constituent in solid state, respectively. x and y is the number of Cu and Ti atoms in the calculated cell, respectively. The calculated formation enthalpies of the Cu–Ti intermetallics are summarized in Table 2, compared with the available experimental results [23] and other theoretical values [11,24]. From Table 2, it can be seen that the calculated formation enthalpies are higher and closer to the experimental values than that in Ref. [11]. Based on the calculated formation enthalpies, the thermodynamic

Table 1
The calculated lattice parameters (a, b and c in nm) of Cu–Ti intermetallics compared with the available experimental and other theoretical results.

Phase	Space group	Lattice parameters			Refs.
Cu	Fm3-m	a = 0.3599			Experiment [11]
		a = 0.3631			This work
		a = 0.3636			Other work [22]
α-Cu_4Ti	I4/m	a = 0.5840		c = 0.3620	Experiment [13]
		a = 0.58853		c = 0.36913	This work
		a = 0.58806		c = 0.37183	Other work [11]
β-Cu_4Ti	Pnma	a = 0.4522	b = 0.4344	c = 1.2897	Experiment [13]
		a = 0.45382	b = 0.4354	c = 1.29627	This work
		a = 0.45401	b = 0.43663	c = 1.29919	Other work [11]
Cu_3Ti	Pmmn	a = 0.5162	b = 0.4347	c = 0.4531	Experiment [13]
		a = 0.5437	b = 0.4322	c = 0.4446	This work
		a = 0.54658	b = 0.43299	c = 0.44342	Other work [11]
Cu_2Ti	Amm2	a = 0.4363	b = 0.7997	c = 0.4478	Experiment [13]
		a = 0.44192	b = 0.79922	c = 0.4579	This work
		a = 0.44285	b = 0.79723	c = 0.45934	Other work [11]
Cu_3Ti_2	P4/nmm	a = 0.3130		c = 1.3950	Experiment [13]
		a = 0.3155		c = 1.3992	This work
		a = 0.31626		c = 1.39514	Other work [11]
Cu_4Ti_3	I4/mmm	a = 0.3120		c = 1.9940	Experiment [13]
		a = 0.3146		c = 1.9920	This work
		a = 0.31525		c = 1.98531	Other work [11]
CuTi	P4/nmm	a = 0.3108		c = 0.5887	Experiment [13]
		a = 0.3124		c = 0.5921	This work
		a = 0.31256		c = 0.59152	Other work [11]
$CuTi_2$	I4/mmm	a = 0.2944		c = 1.0786	Experiment [13]
		a = 0.29375		c = 1.07791	This work
		a = 0.29407		c = 1.06944	Other work [11]
$CuTi_3$	P4/mmm	a = 0.4158		c = 0.3594	Experiment [11]
		a = 0.3979		c = 0.3978	This work
		a = 0.39690		c = 0.39691	Other work [11]
α-Ti	$P6_3/mmc$	a = 0.2944		c = 0.4668	Experiment [11]
		a = 0.2945		c = 0.4627	This work
		a = 0.29229		c = 0.46271	Other work [11]