Journal of Alloys and Compounds 640 (2015) 233–239

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

First-principles study of the nickel–silicon binary compounds under pressure

Yuhong Zhao [a,*], Hua Hou [a], Yuhui Zhao [b], Peide Han [c]

[a] College of Materials Science and Engineering, North University of China, Taiyuan 030051, China
[b] Department of Mechanical and Electronic Engineering, Hebei College of Industry and Technology, Shijiazhuang 050091, China
[c] College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China

ARTICLE INFO

Article history:
Received 19 January 2015
Received in revised form 24 March 2015
Accepted 5 April 2015
Available online 9 April 2015

Keywords:
First-principles
Ni–Si binary compounds
Elastic properties
Phase stability
Electronic structures

ABSTRACT

The effects of high pressure on structural, stable, elastic, thermodynamic properties and electronic structures of Ni–Si binary compounds (i.e. β-Ni_3Si, γ-$Ni_{31}Si_{12}$, δ-Ni_2Si, θ-Ni_2Si, ε-Ni_3Si_2, ε-NiSi and α-$NiSi_2$) have been firstly studied by first-principles calculation based on density functional theory method within generalized gradient approximation. The calculated lattice parameters of the seven compounds at zero pressure and zero temperature agree well with the available experimental values and previous theoretical data. The values of V/V_0 decrease with pressure going up to 50 GPa and the rate of change decrease gradually. The lattice parameters of $NiSi_2$ are the most sensitive to external pressure change. Ni_3Si, $Ni_{31}Si_{12}$, Ni_2Si (δ) and Ni_3Si_2 are mechanical stability by estimating stability criteria with pressure ranging from 0 to 50 GPa. But Ni_2Si (θ), NiSi and $NiSi_2$ are not mechanically stable with pressure up to 10, 40 and 30 GPa, respectively. The calculated results of bulk modulus B, shear modulus G and Young's modulus E illustrate pressure can improve the hardness of Ni_3Si, $Ni_{31}Si_{12}$, Ni_2Si (δ) and Ni_3Si_2 compounds. In addition, ratio of shear modulus to bulk modulus G/B shows that all the considered compounds are ductile materials except NiSi. The Debye temperature Θ_D of Ni_3Si, $Ni_{31}Si_{12}$, Ni_2Si (δ) and Ni_3Si_2 can be improved with the increase of pressure, so the thermal conductivity can also be improved. Finally, the pressure-dependent behavior of total density of states is analyzed to explore the effect of physical origin of pressure on the structural, elastic and thermodynamic properties of the seven Ni–Si binary compounds.

1. Introduction

The nickel-silicide binary alloys play a significant role in modern electronic device technology due to their remarkable physical and chemical properties as well as low electric resistivity [1,2]. Nickel silicides are promising high temperature electronic materials, which are widely used as interconnectors, ohmic contact, and gate materials for integrated circuits [3,4]. Therefore, investigation on the nickel-silicide systems has drawn great academic field attention.

The nickel–silicon systems have been studied firstly by Guertler and Tammann [5] in 1906. Then, the nickel–silicon systems have been widely investigated by using the method of theoretical calculation and experiments. Mey [6], Nash and Nash [7], Lindhólm and Sundman [8], and Du and Schuster [9] have studied the Ni–Si phase diagram by carrying out the thermodynamic analysis based on experimental data. Lee et al. [10], Foggiato et al. [11], Tous et al. [12], Guihard et al. [13], Tomita et al. [14] and Beregovsky et al. [15] also have done some related research for better understanding the formation mechanism of the nickel–silicon systems. The nanometre-sized nickel-silicide systems, Ni_2Si, NiSi and $NiSi_2$, have been researched by energy-loss near-edge structure and first-principles calculation [16]. Abhaya et al. [17] have investigated bulk nickel silicides (NiSi and $NiSi_2$) by means of the experimental positron lifetime and depth-resolved positron beam measurements. Moreover, Connétable and Thomas [18] have studied the nickel-silicide ordered phases using first-principles calculation. The phases diagram, lattice parameters, formation energy and electronic structures have been calculated and analyzed. However, all these literatures are conducted at zero pressure or at room temperature. Up to now, the effects of pressure on the structural, elastic, thermodynamic and electronic properties of the nickel-silicide binary systems have not been reported yet.

In this paper, we calculated the structural, elastic, thermodynamic and electronic properties of Ni_3Si, $Ni_{31}Si_{12}$, Ni_2Si, Ni_3Si_2, NiSi and $NiSi_2$ by first-principles calculation within the frame work of density function theory (DFT). The pressure ranges from 0 to

* Corresponding author. Tel.: +86 15035172958.
E-mail address: zyh388@sina.com (Y. Zhao).

http://dx.doi.org/10.1016/j.jallcom.2015.04.027
0925-8388/

50 GPa with a step of 10 GPa. We firstly present a systematic study on pressure dependences of the nickel-silicide binary compounds. The main focus is elucidated the effects of pressure on mechanical properties and phase transformation.

2. Computational methods

All the calculations in this work are performed by first-principles plane-wave ultrasoft pseudopotential method [19,20] within density functional theory (DFT) [21], which is implemented in Cambridge Serial Total Energy Package (CASTEP) code [22]. The generalized gradient approximation (GGA) method with the Perdew–Wang91 (PW91) parameterization [23] is applied for determining the exchange-correction function. The cutoff energy of atomic wave functions, E_{cut}, is set to be 440 eV. Atomic electronic configurations in this study are Ni $3d^8\ 4s^2$ and Si $3s^2\ 3p^2$. Brillouin zone integrations are performed by using a Monkhorst–Pack k point mesh and a grid of $8\times8\times8$, $5\times5\times2$, $6\times8\times4$, $8\times8\times6$, $2\times3\times4$, $5\times8\times5$ and $6\times6\times6$ k point are set to be the sampling of β-Ni_3Si, γ-$Ni_{31}Si_{12}$, δ-Ni_2Si, θ-Ni_2Si, ε-Ni_3Si_2, ε-NiSi and α-$NiSi_2$, respectively. All the structural optimizations and properties are under hydrostatic pressure which ranges from 0 to 50 GPa with a step of 10 GPa. The separation of the reciprocal space is around 0.01 Å and the self-consistent field (SCF) tolerance is set as 5.0×10^{-7} eV/atom.

3. Results and discussion

3.1. Structural properties

The crystallographic date and calculated values of lattice parameters α_0, b_0 and c_0 at 0 GPa of Ni–Si binary compounds are tabulated in Table 1 below together with available experimental and theoretical data for comparison. From Table 1, we can find that the calculated values of lattice parameters are in good agreement with experimental values [7,24–29] and previously calculated values [18], which indicate that the proposed computational methodology in this work is available and the simulative results are dependable.

In order to study the structural change with pressure, variations of unit cell volume at an applied hydrostatic pressure in the range of 0–50 GPa with a step of 10 GPa are calculated. The pressure–volume (P–V) curves can reveal the volume changes under external pressure. And it can be obtained by fitting the third order Birch–Murnagham equation [30], as follows:

$$P=\frac{3}{2}B\left(\left(\frac{V}{V_0}\right)^{-7/3}-\left(\frac{V}{V_0}\right)^{-5/3}\right)\left(1+\frac{3}{4}(B'-4)\left(\left(\frac{V}{V_0}\right)^{-2/3}-1\right)\right) \quad (1)$$

where V is the unit cell volume at external pressure, V_0 is the unit cell volume at zero pressure. B and B' are the bulk modulus and its pressure derivative, respectively. The B and B' are usually expressed as:

$$B=-V\left(\frac{\partial P}{\partial V}\right)_{P=0} \quad \text{and} \quad B'=-\left(\frac{\partial B}{\partial P}\right)_{P=0} \quad (2)$$

The bulk modulus B and its pressure derivative B' under zero pressure of Ni–Si binary compounds are also listed in Table 1. The calculated B of Ni_3Si, NiSi and $NiSi_2$ accord well with previously reported [31–34]. Again, the present computation parameters and conditions selected are reliable. Unfortunately, no other available experimental or theoretical calculation values can offer us for comparison. Fig. 1 shows the pressure–volume (P–V) curves of Ni–Si binary compounds. We can easily find that the ratio of V/V_0 decrease with the increase of pressure for all the seven compounds. Moreover, the ratio of change of $NiSi_2$ is maximum while Ni_3Si is minimum, elucidating that the lattice parameters of $NiSi_2$ are the most sensitive to external pressure change while the effect on Ni_3Si is the lowest. However, it is difficult to compress the crystal when pressure enhanced, because the distance reduces and the repulsive interaction strengthens between atoms. By fitting the pressure–volume curves, the following functions for Ni_3Si, $Ni_{31}Si_{12}$, Ni_2Si (δ), Ni_2Si (θ), Ni_3Si_2, NiSi and $NiSi_2$ can be acquired, respectively:

$$V/V_0=0.99910-0.00417\times P+2.49567\times10^{-5}\times P^2 \quad (3)$$

$$V/V_0=0.99958-0.00432\times P+2.54526\times10^{-5}\times P^2 \quad (4)$$

$$V/V_0=0.99977-0.00443\times P+2.52719\times10^{-5}\times P^2 \quad (5)$$

$$V/V_0=0.99947-0.00439\times P+2.61347\times10^{-5}\times P^2 \quad (6)$$

Table 1
The structure data of Ni–Si binary systems under zero pressure, including lattice parameters α_0, b_0 and c_0 (Å), bulk modulus B (GPa) and its pressure derivative B'.

Phase	Composition (at.% Si)	Space group	Pearson symbol	Species	Lattice parameters (Å)			B (GPa)	B'
					α_0	b_0	c_0		
				This work	3.517	3.517	3.517	214.07	4.72
β Ni_3Si	25.0	*Pm-3m*	cP4	Experiment	3.506 [24]	3.506	3.506	201.7 [31]	–
				Calculation	3.516 [18]	3.516	3.516	213.9 [32]	–
				This work	6.691	6.691	12.328	173.70	4.30
γ $Ni_{31}Si_{12}$	27.9	*P321*	hP43	Experiment	6.671 [7]	6.671	12.228	–	–
				Calculation	6.668 [18]	6.668	12.319	–	–
				This work	5.059	3.730	7.080	189.64	3.84
δ Ni_2Si	33.3	*Pnma*	oP12	Experiment	5.009 [25]	3.732	7.066	–	–
				Calculation	5.079 [18]	3.700	7.069	–	–
				This work	3.915	3.915	5.020	203.06	4.33
θ Ni_2Si	33.3	*$P6_322$*	hP6	Experiment	3.805 [26]	3.805	4.809	–	–
				Calculation	3.916 [18]	3.916	4.992	–	–
				This work	12.278	10.854	6.937	182.96	3.66
ε Ni_3Si_2	40.0	*$Cmc2_1$*	oS80	Experiment	12.229 [27]	10.805	6.924	–	–
				Calculation	12.229 [18]	10.798	6.924	–	–
				This work	5.151	3.372	5.656	155.26	3.25
ε NiSi	50	*Pnma*	oP8	Experiment	5.177 [28]	3.325	5.616	–	–
				Calculation	5.165 [18]	3.378	5.621	168.0 [33]	–
				This work	5.446	5.446	5.446	139.23	4.33
α $NiSi_2$	66.7	*Fm-3m*	cF12	Experiment	5.406 [29]	5.406	5.406	–	–
				Calculation	5.470 [18]	5.470	5.470	160.0 [34]	–