



# Stability, elastic properties and electronic structures of the stable Zr–Al intermetallic compounds: A first-principles investigation



Y.H. Duan<sup>a,b,\*</sup>, B. Huang<sup>a</sup>, Y. Sun<sup>a</sup>, M.J. Peng<sup>a</sup>, S.G. Zhou<sup>a</sup>

<sup>a</sup> School of Material Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

<sup>b</sup> Key Lab of Advance Materials in Rare & Precious and Nonferrous Metals, Ministry of Education, China, Kunming 650093, China

## ARTICLE INFO

### Article history:

Received 31 October 2013

Received in revised form 9 December 2013

Accepted 9 December 2013

Available online 16 December 2013

### Keywords:

First-principles

Zr–Al compounds

Phase stability

Elastic properties

Electronic structures

## ABSTRACT

To better clarify and understand the phase stability and elastic properties of stable Zr–Al binary intermetallic compounds, the structural properties, phase stability, elastic properties, and electronic structures of these compounds in Zr–Al system have been systematically investigated by using first-principles calculations. The calculated equilibrium structures and enthalpies of formation in present work are in good agreement with the available experimental and other theoretical data, and the results of enthalpies of formation show that ZrAl<sub>2</sub> is the most stable. The elastic properties, including elastic constants, Poisson's ratio and anisotropy index, and Debye temperatures were also investigated. It is found that ZrAl<sub>2</sub> is the most anisotropic in Zr–Al binary compounds. Furthermore, the electronic structures were discussed to reveal the bonding characteristics of the compounds.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Due to good mechanical properties at high temperature combined with low absorption cross-section for thermal neutrons, zirconium–aluminum alloys have drawn comprehensive attention in potential structure materials in thermal nuclear reactors [1–3]. Amount of work has been investigated on the Zr–Al alloys in respects of amorphisation [4], nano-phase formation [5], formation of several metastable phases [6] and also making zirconium based pressure tubes with aluminum lining [7]. As reviewed by Murray et al. [8], the Al–Zr system is characterized by the presence of ten stable phases which are ZrAl<sub>3</sub>, ZrAl<sub>2</sub>, Zr<sub>2</sub>Al<sub>3</sub>, ZrAl, Zr<sub>5</sub>Al<sub>4</sub>, Zr<sub>4</sub>Al<sub>3</sub>, Zr<sub>3</sub>Al<sub>2</sub>, Zr<sub>5</sub>Al<sub>3</sub>, Zr<sub>2</sub>Al and Zr<sub>3</sub>Al. The getter potentialities, elastic modulus and combustion synthesis of partial Zr–Al intermetallic compounds (mainly focused on ZrAl<sub>2</sub> and ZrAl<sub>3</sub>) have been investigated [9–11]. The existence of the large number of observed Zr–Al phases is attributed to the fact that the heats of formation for Zr<sub>x</sub>Al<sub>1–x</sub> ( $x = 0.25–0.75$ ) fall on a nearly straight line by using the full-potential linearized augmented Slater-type orbital (LASTO) method [12]. The main contribution to the electric field gradient of Laves phase ZrAl<sub>2</sub> with MgZn<sub>2</sub>-type structure comes from the Zr and Al's *p* electrons [13]. Moreover, the results of mechanical properties of Laves phases ZrAl<sub>2</sub> and HfAl<sub>2</sub> with C14-type structure

show that the anisotropy degree of HfAl<sub>2</sub> is slightly larger than that of ZrAl<sub>2</sub> and ZrAl<sub>2</sub> is brittle and isotropic in shear [14]. The order of relative stabilities of L1<sub>2</sub>, D0<sub>22</sub>, and D0<sub>23</sub> structure in the ZrAl<sub>3</sub> intermetallic compound are D0<sub>23</sub> > D0<sub>22</sub> > L1<sub>2</sub> [15]. By performed nuclear magnetic resonance measurements, ZrAl<sub>3</sub> is more stable than HfAl<sub>3</sub> with respect to the D0<sub>23</sub> structure [16]. Elastic constants of D0<sub>23</sub>–ZrAl<sub>3</sub> single crystal have been measured from the velocity of ultrasonic waves and the estimated Poisson's and Debye temperature of D0<sub>23</sub>–ZrAl<sub>3</sub> are 0.18 and 577 K, respectively [17]. However, there is a lack of the systematical calculations of phase stability, elastic properties and electronic structure for these ten compounds.

The fundamental understanding of both the mechanical properties and phase stability of intermetallics provided by the results of quantum–mechanical electronic structure calculations have been significantly improved over the last 20 years. Ab initio or first-principles methods based upon electronic density-functional theory (DFT) [18] have been employed to derive a number of bulk and defect properties including enthalpy of formation, the relative stability of competing structures, elastic constants, lattice parameters, and the energies associated with point and planar defects [19,20].

In this work, the first-principles calculations were performed to better clarify and understand the phase stability and elastic properties of Zr–Al binary intermetallic compounds consisting of enthalpy of formation, elastic constants, Young's modulus *E*, shear modulus *G*, bulk modulus *B*, Poisson's ratio *ν* and anisotropy index *A*. Based on the calculated elastic constants and modulus, the

\* Corresponding author at: School of Material Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China. Tel./fax: +86 871 65136698.

E-mail address: [duanyh@kmust.edu.cn](mailto:duanyh@kmust.edu.cn) (Y.H. Duan).

cDebye temperature were also investigated. Further, the electronic structures were discussed.

## 2. Computational method

All calculations were performed by using the first principles calculations based on density functional theory (DFT) implemented in CASTEP (Cambridge sequential total energy package) code [21]. Ultra-soft pseudo-potentials were employed to indicate the interactions between ionic core and valence electrons. The exchange correlation energy was described by using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) parameterization [22]. Valence electrons included in this study for distinct atoms were Al  $3s^23p^1$  and Zr  $4s^24p^64d^25s^2$ . The Monkhorst–Pack scheme was used for  $k$  point sampling in the first irreducible Brillouin zone (BZ). The  $k$  points separation in the Brillouin zone of the reciprocal space were  $18 \times 18 \times 18$ ,  $12 \times 12 \times 6$ ,  $15 \times 15 \times 12$ ,  $12 \times 8 \times 16$ ,  $14 \times 4 \times 12$ ,  $12 \times 12 \times 16$ ,  $10 \times 10 \times 12$ ,  $12 \times 12 \times 16$ ,  $8 \times 8 \times 20$ ,  $18 \times 18 \times 12$ ,  $18 \times 18 \times 18$ ,  $18 \times 18 \times 12$  for Al (fcc), ZrAl<sub>3</sub>, ZrAl<sub>2</sub>, Zr<sub>2</sub>Al<sub>3</sub>, ZrAl, Zr<sub>5</sub>Al<sub>4</sub>, Zr<sub>4</sub>Al<sub>3</sub>, Zr<sub>3</sub>Al<sub>2</sub>, Zr<sub>5</sub>Al<sub>3</sub>, Zr<sub>2</sub>Al, Zr<sub>3</sub>Al,  $\alpha$ -Zr (hcp) respectively. The cutoff energy for plane wave expansions was determined as 400 eV after convergence tests. The separation of the reciprocal space was around  $0.01 \text{ \AA}^{-1}$  and the SCF (self-consistent field) tolerance was set as  $5 \times 10^{-7}$  eV/atom. The crystal structures of ten stable Zr–Al compounds are shown in Fig. 1. The lattice parameters and atomic coordinates are tabulated in Tables 1 and 2, respectively.

## 3. Results and discussion

### 3.1. Structural properties

In present work, the initial crystal structures have been built based upon the experimental crystallographic data of Al,  $\alpha$ -Zr and ten types of Zr–Al intermetallic compounds in Zr–Al binary alloys [23,34], then the lattice parameters and internal coordinates of these compounds were optimized by using first-principle calculations. The optimized lattice parameters are listed in Table 1 compared to the available experimental data. The average deviation between the experiments and the calculated values is about 1%, which is expected for the first-principles calculations using GGA. The calculated lattice parameters of Al,  $\alpha$ -Zr and Zr–Al intermetallic compounds agree very well with the available experimental data. Table 2 lists detailed comparisons between calculations and measurements for atomic coordinates. For these ten phases, the agreement between experiment and theory can be considered as only reasonable. These agreements of optimized lattice parameters and atomic coordinates with the experimental values provide a confirmation that the computational methodology utilized in this work is suitable and reliable.

### 3.2. Enthalpies of formation and phase stability

In order to estimate the structural stability of these Zr–Al intermetallic compounds, the cohesive energy ( $E_c$ ) and enthalpy of formation ( $\Delta H$ ) were calculated.

The cohesive energy is defined as the work which is needed when the crystal is decomposed into isolated atoms. The more negative cohesive energy indicates the released energy is larger in the process of formation of the compound. The cohesive energy ( $E_c$ ) per atom of Zr<sub>*x*</sub>Al<sub>*y*</sub> is calculated by the following expressions:

$$E_c = [E_{\text{total}} - (xE_{\text{Zr}} + yE_{\text{Al}})] / (x + y) \quad (1)$$

where  $E_{\text{Zr}}$  and  $E_{\text{Al}}$  are the total energies of isolated Zr and Al atom, respectively;  $x$ ,  $y$  are the number of atoms in the chemical formula of Zr<sub>*x*</sub>Al<sub>*y*</sub>.  $E_{\text{total}}$  is the total energy of Zr<sub>*x*</sub>Al<sub>*y*</sub>.

Enthalpy of formation of Zr<sub>*x*</sub>Al<sub>*y*</sub> is defined as the difference in total energy of the compound and the energies of its constituent elements in their stable states:

$$\Delta H = [E_{\text{total}} - (xE_{\text{Zr}}^{\text{bulk}} + yE_{\text{Al}}^{\text{bulk}})] / (x + y) \quad (2)$$

where  $E_{\text{Zr}}$  and  $E_{\text{Al}}$  are the total energies of isolated Zr and Al atoms, respectively;  $E_{\text{total}}$  is the total energy of Zr<sub>*x*</sub>Al<sub>*y*</sub>,  $E_{\text{Zr}}^{\text{bulk}}$  and  $E_{\text{Al}}^{\text{bulk}}$  are the total energy of a Zr atom and an Al atom in the bulk state. Negative enthalpy of formation usually means an exothermic process, and a more negative enthalpy of formation corresponds to a better phase stability.

The calculated cohesive energies and enthalpies of formation of the ten binary compounds together with their available experimental and other theoretical calculated data [15,38–41] are tabulated in Table 3 and plotted in Fig. 2 (enthalpies of formation), and in Fig. 2 the present calculated and other theoretical calculated values are plotted in the  $x$ - and  $y$ -axis, respectively. The enthalpies of formation from first-principles calculations compare favorably with ab initio approach (Fig. 2(a)) and CALPHAD approach (Fig. 2(b)) for most compounds. In Fig. 2, the solid line implies a perfect agreement between the present calculated and other theoretical calculated values, and two dashed lines are represented an error bar of  $\pm 2.5$  kJ/mol (Note: in this paper, the unit kJ/mol means kJ/mole of atoms.). With regard to all the stable compounds in the Zr–Al binary system, the first-principles calculated enthalpies of formation agree well with those from the ab initio approach and CALPHAD approach with differences less than 2.5 kJ/mol.

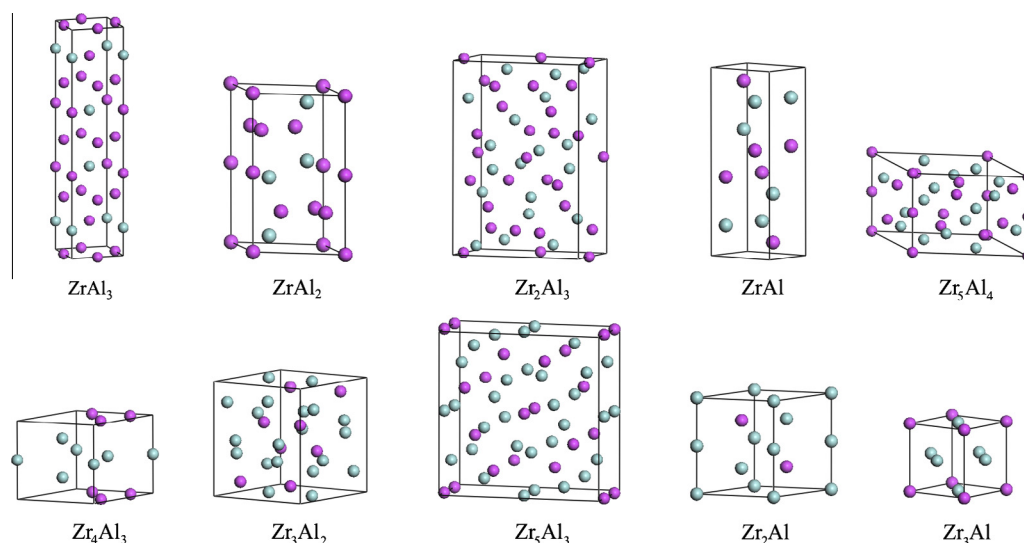


Fig. 1. The crystal structures of ten stable Zr–Al compounds. The purple balls and cyan balls represent Al and Zr, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/1611588>

Download Persian Version:

<https://daneshyari.com/article/1611588>

[Daneshyari.com](https://daneshyari.com)