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Electronic structure, phase stability, and vibrational properties of Ir-based intermetallic compound IrX (X=Al, Sc, and Ga)

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ABSTRACT

The phase stability and mechanical properties of *B2* type IrX (X=Al, Sc and Ga) compounds are investigated. Self-consistenttotal-energy calculations in the framework of density functional theory using the Generalized Gradient Approximation (GGA) to determine the equations of state and the elastic constants of IrX (X=Al, Sc, and Ga) in the B2 phase have been performed. The calculations predicted the equilibrium lattice constants, which are about 1% greater than experiments for IrAl, 1.81% for IrGa, and 0.71% for IrSc compound. IrAl is shown to be the least compressible, and it is followed by IrGa and the IrSc compound. The phase stability of the studied compounds is checked. The brittleness and ductility properties of IrX (X=Al, Sc, and Ga) are determined by Poisson's ratio σ criterion and Pugh's criterion. IrGa compound is a ductile material; however, IrAl and IrSc show brittleness. The band structure and density of states (DOS), and phonon dispersion curves have been obtained and analyzed. The position of the Fermi level and the contribution of d electrons to the density of states near E_F is studied and discussed in detail. We also used the phonon density of states and quasiharmonic approximation to calculate and predict some thermodynamic properties such as constant-volume specific heat capacity of the B2 phase of IrX (X=Al, Sc and Ga) compounds.

1. Introduction

The search for new high-temperature materials in oxidizing environments for structural applications and coatings has attracted considerable interest. Iridium-based alloys have been selected as the most promising protective coating materials at ultrahigh temperatures [1–4]. The IrAl compound is proposed as a smart oxidation-resistant coating that can form an aluminum layer as a protective coating on the iridium layer by oxidation [5]. The attractive characteristics of Iridium include high melting point (2739 °K), high elastic moduli, and relatively low oxidation rates compared with other high-melting metals. However, it forms gaseous oxides of IrO_3 and IrO_2 instead of a protective oxide scale in high-temperature oxidizing environments [5–8].

To improve the oxidation resistance and suppress the formation of Ir oxides, alloying with Al has been evaluated. Recently, Ir-based alloys have attracted extensive interest for potential high-temperature structural applications [9,10]. Previous studies have demonstrated that binary alloys in Ir–Al or Ir–Hf systems could form external oxide layers if the concentration of Al or Hf is large enough. The formation of a continuous external layer of $A1_2O_3$ [11] or HfO_2 could prevent the formation of gaseous iridium oxides, and oxidation resistance is improved to a great extent [12]. IrAl was prepared by quenching a melt of the same stoichiometry. It was shown that this compound has a cubic CsCl structure with a cell constant of 2.977 Å [13]. Later on IrAl was prepared by reducing Al_2O_3 in the presence of Iridium at 1600 °C, and a lattice parameter of 2.983 Å was found [14]. Axler and Roof produced the IrAl crystal with a cubic CsCl structure by a molten metal flux containing Th, Ir, and Cu. They measured a lattice constant of 2.9867 Å [15]. The phase diagram of Al–Ir system has been presented [10,16–19] and studied and the existence of Al_9Ir_2, Al_3Ir, $Al_{2.7}Ir$, $Al_{13}Ir_4$ and AlIr has been confirmed. The peritectic temperatures were determined for all the compounds, and a melting temperature of about 2120 °C was found for AlIr [16]. Lee and Worrell prepared Ir–Al alloys of several different compositions. They found that the samples whose aluminum content varied from 40 to 74 at% were either single-orbinary-phase alloys of Ir,

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IrAl, $IrAl_{2.5}$ and $IrAl_3$. A melting temperature of 1600–1650 °C for $IrAl_{2.5}$ and for IrAl of above 1800 °C is suggested [20]. A thermodynamic modeling of the binary Al–Ir system was performed using a combined first-principle and CALPHAD approach. The formation enthalpies of all six stable intermetallic compounds in the Al–Ir system were obtained [21]. The thermodynamic assessment of the Al–Ir binary system was performed using the CALPHAD technique. The thermodynamic quantities, such as the phase equilibria, invariant reactions, and formation enthalpies of the intermetallic phases, were calculated and agree well with experimental data [22]. Binding energy for the nine 4d transition metal aluminides (TmAl) with regard to twelve different AB-structure types has been computed using the full-potential linear muffin-tin orbitals (FP-LMTO) method within local-density-functional approximation (LDA) [23]. The high-temperature compression strength, the creep properties and deformation mechanisms of the Ir-based system with an fcc and a B2 two-phase structure at 1773 °K were discussed [11]. The IrAl phase with a B2 structure was identified by Fleischer as having good high-temperature strength and reasonable toughness at ambient temperature [24]. The significantly higher melting temperature of IrAl is expected to lead to the realization of a useful high- temperature structural material [9,25]. The effect of Co addition to IrAl on oxidation behavior was studied, and Co addition was expected to enhance B2- phase stability. It is concluded that the oxidation resistance of IrAl alloys was dramatically improved by Co addition [4]. Thus, it is found that the addition of Ni improves the ductility of IrAl [5]. The analysis for the electronic structure of intermetallic compounds ScB (B=Cu. Ag, Pd, Rh, Ir, and Ru) is given in terms of local susceptibilities, as well as in terms of a two-band model. Accordingly, ScIr belong to group III; the d spin and orbital contributions originate from A and B sites. The d spin contributions are much smaller than those of groups I or II [26]. This is consistent with high-resolution ultraviolet photoelectron spectra for Sc, ScAg, ScPd, ScIr, and ScRu [27] as well as band-structure calculations [28] which found that there are d contributions to the density of states near E_F originating from the Sc site in ScAg and ScPd, possibly from both sites in Sclr and from the Ru site in ScRu. With a fully automated high-temperature calorimeter the enthalpy of formation of the Ir–Ga liquid system was determined between $1060\ K < T < 1471\ K$, in the molar fraction range $0 < x < 0.54$ [29].

Despite the promising performances of Ir-based binary compounds in structural and coating application fields, and the intensive investigations on IrAl to improve its mechanical properties such as toughness, ductility, and high-temperature strength, as well as oxidation resistance, only limited information is available for the structural, electronic, and vibrational properties of IrX (X=Al, Sc and Ga) compounds. This article is organized as follows. Section II is devoted to the description of our calculational methods. In Section 3, we discuss the results of our calculations with regard to the structural, electronic, and vibrational properties of IrX (X=Al, Sc, and Ga) compounds, including the checking of their stability. The ductility and brittleness of these intermetallics is examined. A summary is provided in Section 4.

2. Structure and method of calculation

Intermetallics are compounds that are not mixtures and whose crystal structures are different from those of the constituent metals. The crystal structure of an intermetallic compound is determined by the strength and character of bonding in the crystal, which depends on the particular electronic configuration and the relative atomic sizes. Many intermetallics with the composition AB crystallize in the *B2* (CsCl) structure [30].

The ground-state energies and electronic structures were calculated using density functional theory (DFT) [31] within the generalized-gradient approximation (GGA) [32]. The quantum-Espresso code that incorporates the self-consistent ultrasoft pseudopotential method was used [33]. The electronic configurations used were $3s^2 3p^1$ for aluminum, $3d^1 4s^2$ for scandium, $4s^2 4p^1$ for gallium, $5d^7 6s^2$ for Iridium.

A plane-wave basis set with an energy cut-off of 40 Ry was applied. The electronic charge density was evaluated for an approximate kinetic energy cut-off of 400 Ry. The **k**-point meshes for Brillouin zone sampling were constructed using the Monkhorst-Pack scheme [34]; the $(10 \times 10 \times 10)$ **k**-points mesh was used for all calculations. The phonon frequencies were calculated. The lattice-dynamical properties were calculated using the density functional linear response method [35]. The ground state of each compound was found by minimizing the total energy as a function of the lattice parameters. Elastic constants were obtained from the slopes of the acoustic branches in the phonon dispersion curves [36]. The sound velocities correspond to the small-wavelength behavior of the acoustic phonons. These velocities are associated with C_{11}, C_{44} and C_{12} as they are described in [30,36]. Once the single crystal elastic constants are computed, the related polycrystalline properties such as Young's modulus (E), Shear modulus (G) are derived using the following standard relations:

$$G = \frac{C_{11} - C_{12} + 3C_{44}}{5} \tag{1}$$

Young's modulus (E) of a material is a key parameter for mechanical engineering design

$$E = \frac{9BG}{3B + G} \tag{2}$$

Another crucial elastic moduli considered as having a significant implication in engineering science is the elastic anisotropy of crystals A. For a completely isotropic material $A=1$, values smaller or greater than unity measure the degree of elastic anisotropy. The anisotropy factor A is given by

$$A = \frac{2C_{44}}{(C_{11} - C_{12})} \tag{3}$$

Poisson's ratio is also of interest, and it is defined as the ratio of the lateral contraction to the elongation

$$\sigma = \frac{1}{2}\left(1 - \frac{E}{3B}\right) \tag{4}$$

In the quasiharmanic approximation (QHA), the constant-volume specific heat capacity C_v, internal energy E, phonon free energy F and entropy S are given by

$$C_v = 3nNk_B \int_0^{\omega_{max}} \left(\frac{\hbar\omega}{2k_BT}\right)^2 \operatorname{csch}^2\left(\frac{\hbar\omega}{2k_BT}\right) g(\omega)d\omega \tag{5}$$

$$\Delta F = 3nNk_BT \int_0^{\omega_{max}} \ln\left\{2 \sinh \frac{\hbar\omega}{2k_BT}\right\} g(\omega)d\omega \tag{6}$$

$$\Delta E = 3nN\frac{\hbar}{2} \int_0^{\omega_{max}} \omega \coth\left(\frac{\hbar\omega}{2k_BT}\right) g(\omega)d\omega \tag{7}$$

$$S = 3nNk_B \int_0^{\omega_{max}} \left[\frac{\hbar\omega}{2k_BT} \coth \frac{\hbar\omega}{2k_BT} - \ln\left\{2 \sinh \frac{\hbar\omega}{2k_BT}\right\}\right] g(\omega)d\omega \tag{8}$$

where n is the number of atoms per unit cell, N is the number of unit cell, ω is the phonon frequency, $g(\omega)$ is the phonon