

Enthalpies of Formation of Equiatomic Binary Hafnium Transition Metal Compounds HfM (M=Co, Ir, Os, Pt, Rh, Ru)

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Abstract. In order to investigate Hafnium transition metal alloys HfM (M= Co, Ir, Os,Pt, Rh, Ru) phase diagrams in the region of 50/50% atomic ratio, we performed ab initio Full-Potential Linearized Augmented Plane Waves calculations of the enthalpies of formation of HfM compounds at B2 (CsCl) structure type. The obtained enthalpies of formation are discussed and compared to some of the existing models and available experimental data.

Introduction

Enthalpy of formation is a basic physical quantity which governs the compound formation and phase stability [1-3]. Experimentally, there are three different methods to determine the enthalpies of formation: vapor pressure, electromotive force, and calorimetric approaches. Experimental measurements are sometimes difficult due to the presence of errors (such as sample impurities, incomplete reaction, and the presence of secondary phases, etc.) [4]. Therefore, in order to complement experimental efforts, there have been many attempts in the past to establish valid theoretical models to predict the enthalpies of formation of compounds [5-9]. The earliest attempt was by Hume-Rothery et. al [5], who proposed empirical rules to predict the formation of alloys by considering the atomic size, electrochemical, and valence electron factors of constituent elements. In the early 1950s, Darken and Gurry [8] constructed a two-dimensional map using the atomic size and electronegativity as the intrinsic parameters to predict the formation of solid solutions. In the early 1970s, Phillips et al. [6,7] proposed a relationship for the enthalpies of formation of the covalent compounds using the ionization energy as a parameter. In the mid-1970s, Miedema et al. [9] proposed a semi-empirical model to calculate the enthalpies of formation for binary transition metal alloys based on the molar volume, electronegativity, and electronic density of constituent elements.

Among these models, the Miedema's model is the most prevalent one and has been applied extensively, although the predicted values are often inaccurate. In 1980 Bennett and Watson [10-12] predict enthalpies of formation of binary transition metal compounds at equiatomic composition based on Friedel approximation of d bands [13,14], the bandwidth W of transition metal is an important factor in this model. In our previous work [15] we have revised values W^* for ZrM compounds (M=Co, Ni, Ru, Rh, Ir, Pt, Pd) to refined d-band's values of enthalpies of formation ΔH^{for} to experimental data. Hafnium is primarily used in the control and safety mechanisms of nuclear reactors, because of its high cross-section for neutron absorption and its high corrosion resistance [16]. Hafnium cladding of nuclear fuel rods is expected to be an important element in the design of future advanced reactors [17]. Hafnium is used extensively as an alloying element in nickel-, niobium- and tantalum-based superalloys, which are designed to withstand high temperatures and pressures. It is an important addition to some titanium, tungsten and molybdenum alloys, where it forms second-phase dispersions (with carbon) that improve material strength under extreme conditions [16,18]. Hafnium alloys are also used in medical implants and devices, due to their biocompatibility and corrosion resistance (see e.g. Ref. [19]). Nickel–titanium–hafnium alloys exhibit shape memory behavior with high martensitic transformation temperatures and good

mechanical properties [20]. Hafnium is added to aluminum–magnesium–scandium alloys, widely used in aerospace applications, to increase their strength following high temperature thermomechanical processing [21]. Some intermetallic compounds of Hafnium and the transition metals Fe, Co, Pd and Pt have been investigated as hydrogen-storage materials because of their capability to form hydrides with high hydrogen to metal ratios at room temperature [22]. Hafnium oxide based compounds have recently found wide application replacing silicon oxide as high-k dielectrics in the production of integrated circuits [23].

Computational method

With the success of density-functional theory DFT[24], first-principles calculation has been proven to be a reliable and precise approach for addressing the ground-state properties of structural materials.

For a binary intermetallic phase (A_xB_{1-x}), the enthalpy of formation (ΔH_{for}) is defined as the difference in total energy of the compound and the energies of its constituent elements in their stable states:

$$\Delta H_{for} = E(A_xB_{1-x})_{tot} - xE(A, solid) - (1 - x)E(B, solid) \quad (1)$$

where E_{Tot} , $E_{(A,solid)}$ and $E_{(B,solid)}$ are the total energies of the compounds and the constituent elements at their ground state, respectively. For equiatomic compounds we have:

$$\Delta H_{for} = E(AB)_{tot} - \frac{1}{2}[E(A, solid) + E(B, solid)] \quad (2)$$

Since the influence of pressure on the condensed phases is ignored and the energies are calculated at 0 K without any entropic contributions, the energy of formation is taken to be the enthalpy of formation.

The first-principles calculations were performed using the ABINIT code [25, 26], which is an implementation of the plane-wave pseudopotential total energy method based on the density functional theory (DFT) [27]. The interactions of electrons with ion cores were represented by the Hartwigsen–Geodecker–Hutter (HGH) [28] pseudopotentials. The HGH pseudopotential is easy to use since it has an analytical form with only few necessary parameters. The cutoff energy for the plane wave basis functions was set to be 60 Hartree. The observed ground state structures for each pure element M are listed in Tables 1. In this paper, we report the enthalpies of formation of Hafnium binary compounds HfM (M=Co, Ir, Os, Pt, Rh, Ru) at CsCl type structure (B2) with two atoms at the primitive cell (0 0 0), ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$). The lattice parameters are determined from the fitting of total energy versus molar volume curves using Murnaghan's equation of state [29].

The calculated lattice parameters for the seven HfM compounds, listed in Table 2, are shown in good agreement with available experimental [30-33] values with typical deviations of about 1.32%. The calculated enthalpy of formation of an AB compound, at zero temperature, per atom, is the energy gained by its formation from the most stable modifications of the constituting elemental phases. In Fig. 1, we examine the variations of both ΔH_{DFT} and ΔH_{exp} as black circles, $\Delta H_{Miedema}$ and ΔH_{exp} with up triangle, ΔH_{Watson} and ΔH_{exp} as down triangle.

Results

We begin the discussion of our results with the lattice parameters for the binary compounds listed in Table 2. Comparison of the calculated lattice parameters with those determined experimentally shows good agreement with experiments, with the difference being less than 8.5% for all results. The calculated enthalpies of formation of the binary compounds are compared with the available experimental data in Table 3 [34-36] and plotted in Fig. 1, in which the experimental and calculated values are plotted in the x- and y-axis, respectively.

Table 1: Stable crystal structures of pure elements at room temperature [29].

Element	Structure	Space group	Pearson symbol	Strukturbericht designation	lattice constants(\AA) [29]
Hf	hcp	P63/mmc	hP2	A3	a=b=3.196 c=5.051
Co	hcp	P63/mmc	hP2	A3	a=b=2.507 c=4.069
Os	hcp	P63/mmc	hP2	A3	a=b=2.734 c=4.317
Pt	ccp	Fm-3m	cF4	A1	a=3.924
Rh	ccp	Fm-3m	cF4	A1	a=3.803
Ru	hcp	P63/mmc	hP2	A3	a=b=2.705 c=4.281
Ir	ccp	Fm-3m	cF4	A1	a= 3.839

Table 2: Lattice constants a (in angstrom \AA) of HfM compounds considered in this paper in comparison with experimental and other calculated results.

Compound	Lattice constants a (\AA)			
	Calc	exp	other calc	%deviation
HfCo	3.125	3.231	3.14 [31]	1.26
HfIr	3.204	3.275[32]	-	2.16
HfOs	3.501	3.277[37]	-	2.19
HfPt	3.411	3.3623[33]	3.3623[34]	1.44
HfRh	3.216	3.227[30]	3.23[31]	0.34
HfRu	3.231	3.225 [31]	3.24[31]	0.18

Table 3: Calculated enthalpies of formation (Kj/mole) of the binary compounds compared with the experimental data [34-36], Miedema's model [9] and Watson's model [10].

Comp	ΔH_{DFT}	$\Delta H_{Miedema}$ [9]	ΔH_{Watson} [10]	ΔH_{exp}
HfCo	-49.07	-51,1	-50.03	-47.5 ± 3.1 [34]
HfIr	-108.93	-99.6	-123,59	-96.7 ± 4.8 [35]
HfOs	- 81.09	-77.24	-68.51	-113.7 ± 6.6 [35]
HfPt	-127.23	-131.7	-154,94	-113.0 ± 6.0 [36]
HfRh	-96.81	-92.4	-88.23	-95.8 ± 2.2 [35]
HfRu	-104.25	-75.3	-86.63	-91.8 ± 5.2 [35]

In figure 1, the solid line represents perfect agreement between the calculated and experimental values, and two dashed lines are shown to define an error bar of $\pm 10 \text{Kj/mole}$ is set by the uncertainty in the latest experimental studies of enthalpies of formation of compounds [34-36]. The calculated enthalpies of formation compare favorably with experiment for HfCo and HfRh compounds, with differences often within about 2.5%. The largest discrepancies between first-principles and experimental data are found in the HfIr.

With regard to all the compounds HfM binary system, the first-principles calculated enthalpies of formation agree well with experimental [34-36] with differences less than 10 kJ/ mol of atom. We also provide a comparison for the enthalpies of formation for the ordered compounds from first-principles calculations and the Miedema's approach. Miedema and coworkers [9] developed an extremely simple scheme for predicting the enthalpies of formation of compounds. As reviewed in a recent book [38], based on the Miedema's model, the predicted enthalpies of formation for compounds which consist of at least one transition metal agrees with experimental data in the great majority of cases. Watson & Bennett [10,11] model is based on d band for equiatomic transition metal; they predict enthalpies of formation for only transition metal compounds, comparison show good agreement between our results and watson's ones, except for HfIr.

A comparison between our first-principles calculations and the Miedema's approach and Watson's prediction for HfM compounds is shown in Fig.1 with an error bar set of 10Kj/mole.

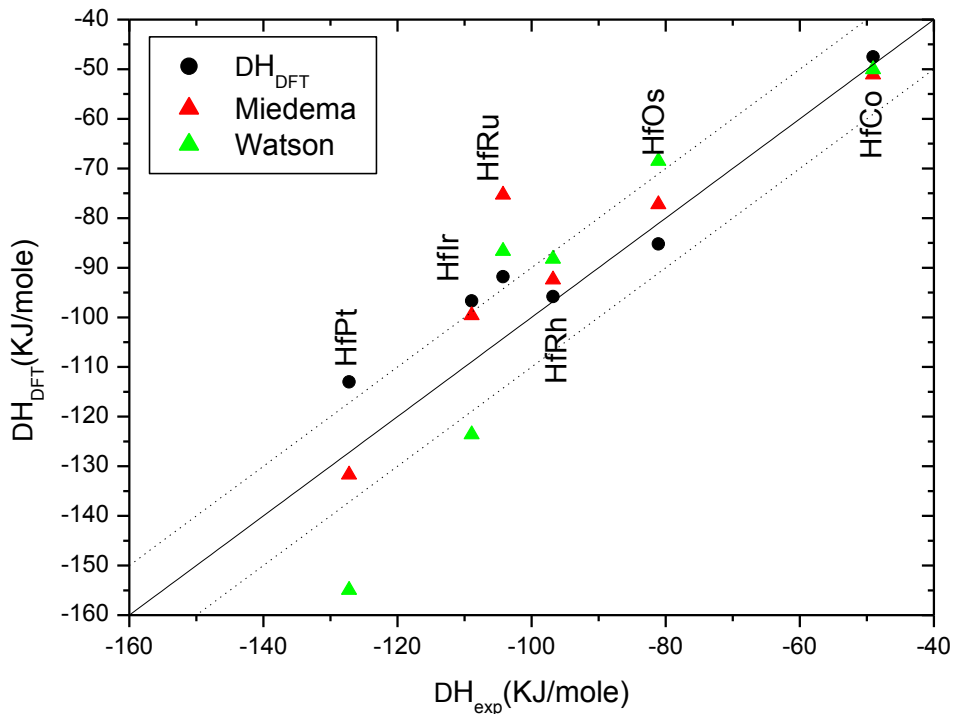


Figure 1: Comparison of calculated enthalpies of formation for the binary equiatomic compounds HfM with experimental measurements [34-36]. The solid line shows unity ($y = x$) while the dashed lines present an error range of 10 kJ/mol.

Conclusion:

We have applied density functional theory to calculate the energetic properties for 6 Hafnium transition metal compounds. For each of these compounds, lattice parameters in its equilibrium structure (B2) and enthalpies of formation of compounds are calculated and compared with available data. We conclude the following:

- (1) The lattice parameters at 0 K obtained by the first-principles calculations can be satisfactorily compared with experimental data.
- (2) The enthalpies of formation for HfM compounds agree with the available experiment and thermodynamic databases for the majority of compounds. Possible sources of error include the uncertainty in the measurement of experimental.
- (3) The comparison of calculated enthalpies of formation with other predictions [9-11], show that Miedema's model is more efficient than Watson's prediction.

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