Enthalpies of formation of TM–X compounds (X=Al, Ga, Si, Ge, Sn). Comparison of ab-initio values and experimental data

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ARTICLE INFO

ABSTRACT

Nowadays first-principles calculations have achieved considerable reliability for the prediction of the properties of materials. These calculations are based on the density functional theory. In the present work, we have obtained a large number of enthalpies of formation of binary intermetallic compounds of transition metals with the elements Al, Ga, Si, Ge or Sn. The ab-initio values have been calculated with VASP in the generalized gradient approximation. We have compared the calculated enthalpies of formation of compounds to the values obtained with calorimetric methods. An excellent agreement is observed in the cases of aluminum and silicon based compounds. We also observe that in the case of highly negative values of enthalpies of formation of early transition metal alloys the experimental values are often more negative than the calculated values but it is not the case in Pt based compounds. In the cases of the Pt, Mo, Ru, Rh compounds with Al, Ga, Si, Ge or Sn, a very nice agreement between calculated and experimental values is observed.

1. Introduction

The prediction of the thermodynamic stability of phases as function of temperature, pressure and chemical composition is for several decades a key task of material science. The CALPHAD method "Calculation of phase diagrams" is based on the fact that a phase diagram is a representation of the thermodynamic properties of a system. Thus, if the thermodynamic properties are known, it would be possible to calculate the multi-component phase diagrams. However a difficulty related to the Calphad approach is the fact that it requires experimental input. Providing sufficient experimental data is often challenging and accompanied by expensive sample preparation and the necessity of high precision measurements. Further some necessary input (e.g., energetics of metastable or even unstable phases) can be missing due to the lack of corresponding samples. The ab-initio approach constitutes therefore a very promising possibility to explore experimentally inaccessible phase space regions and to evaluate existing experimental data. Some review papers are devoted to these questions [1–5].

The purpose of the present work is to calculate the enthalpies of formation of a large number of intermetallic compounds of transition metals with the elements Al, Ga, Si, Ge, and Sn and to compare these data with the available experimental values.

Systematic comparisons of calculated and experimental values of enthalpies of formation are scarce. We may quote the works of Zhang et al. [6] concerning binary magnesium compounds, the one of Wang et al. [7] concerning aluminum compounds and the one of Xing et al. [8] concerning intermetallics TM and TM3 with T=Ti, Zr, Hf and M=Ru, Rh, Pd, Os, Ir, Pt. However a great number of ab-initio investigations have been performed in binary systems in order to check the stability of the known compounds or to predict the existence of ordered structures. These researches concern hafnium, ruthenium, rhenium, platinum binary compounds [9–12], and also 80 binary alloys of transition metals and noble metals [13]. Recently Van Der Geest and Kolmogorov [14] studied the stability of 41 metal-boron systems at 0 GPa and 30 GPa from first principles.

2. Computational method

The density functional (DFT) calculations presented in the present work were performed with the Vienna ab-initio simulation package (VASP) [15,16] making use of the projector augmented waves (PAW) technique [17,18]. For the generalized gradient approximation (GGA) exchange correlation functional, the Perdew-Berke-Erzenhof parameterization (PBE) [19] was adopted. For the Brillouin-zone integration, the Methfessel-Paxton [20] technique with a modest smearing of the one-electron levels (0.2 eV) was used. The number of k points for the Brillouin-zone

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integration is chosen such a way that the number of irreducible k points multiplied by the number of atoms in the cell is greater than 500. A gamma centered k-point grid is used for the hexagonal and rhomboedric structures. For all other structures, a Monkhorst-Pack [21] grid is used.

The energy convergence criterion is 10^{-5} eV/atom. The choice of the plane-wave cutoff is very important. The value indicated in the POTCAR file of VASP must be increased of 30% at least. The same cutoff must be used for the calculation of the total energy of the pure elements. For very large cells, the calculation of the total energy can be first performed with lreal=true (integration in the real space), but a final calculation with lreal=false (integration in the reciprocal space) must be performed in order to calculate the energies of formation of all compounds of the system in the same conditions. All calculations have been performed using the "accurate" setting within VASP to avoid wrap-around errors. With the chosen plane-wave cutoff and k-point sampling, the precision of the reported enthalpies of formation is estimated to be better than ± 0.5 kJ/mol of atoms. Care must be taken with the relaxation effects. The relaxations must be performed with respect to the volume and the shape of the cell, and also with respect to the positions of the atoms in the cell. Care must be paid that at the end of the relaxation scheme the cell presents the expected symmetry. If it is not the case, the new symmetry is more stable than the expected one. It is possible in calculations to keep a given symmetry.

Another important point is the electronic configuration of the atoms when two pseudopotentials are given for an element in the VASP pseudopotential database. This can be an electronic configuration corresponding to the valence electrons or an electronic configuration which includes the semi core electrons. In some cases, this choice can be important and must be precised. In the majority of the cases, we used electronic configurations including the semi core electrons (for example: Ti sv, Zr sv, Hf pv, V sv, Pd pv). For the p elements, the semi core d electrons were considered for Ga and Sn. For Ge, the calculations have shown that it is not necessary to include the d electrons of Ge. Note that including the semi core electrons increases drastically the computer time for two reasons: the increase of the number of electrons and the necessity to increase the cuttoff.

The enthalpy of formation, $\Delta_f H(A_x B_{1-x})$, of the $A_x B_{1-x}$ compound at zero temperature and zero pressure is obtained from the minimum total energy of the compound (expressed per atom) by subtracting the composition-weighted minimum total energies of pure elements in their standard state.

$$\Delta_f H(A_x B_{1-x}) = E_{A_x B_{1-x}}^{\min} - x E_{\text{stable}-A}^{\min} - (1-x)E_{\text{stable}-B}^{\min}.$$

The $E^{\min}$ values are obtained after volume relaxation, this implies a zero pressure. One must recall that it is preferable that the $E^{\min}$ values (compound and elements) are obtained with the same cuttoff. Let us recall that in publications, it is always necessary to precise the reference state of the formation enthalpies. For example, in the case of tin, A4-Sn is the ground state at $T=0$ K. At room temperature, the stable state of tin is A5-Sn, therefore the experimental enthalpies of formation of Sn based compounds are referred to A5-Sn. In the following, we referred the calculated enthalpies of formation to A5-Sn.

In a given system, we have performed the total energy calculations for all the compounds described in the Pearson's Handbook [22]. Indeed it is necessary to know the space group and the positions of the atoms in the cell to perform a total energy calculation. The calculations have also been performed at a given stoichiometry for other structures than the one observed experimentally in order to check the possibility of precipitation of metastable phases during alloy processing. Such calculations are also helpful to predict the possible stabilization of structures by ternary additions or in ternary systems.

In the present work, we considered perfectly ordered structures. Indeed we have not performed calculations in the case of compounds for which the Wyckoff positions are only partially filled or filled by two species. One exception is the case of the $D8_8$ structure. Let us recall that the $D8_8$ structure (Mn_5Si_3 type, hP16, $P6_3/mcm$, N°193) is often stabilized by impurities at high temperature [23]. These impurities partially occupy the 2b sites at (0, 0, 0) of the $P6_3/mcm$ structure. The complete filling of the 2b sites leads to a perfectly ordered structure. For example, in the Ti–Ga system, the $D8_8$-Ti_5Ga_3 compound is not stable but the Ti_5Ga_4 compound where the 2b sites are completely filled by Ga atoms is stable [22]. Hf_5Sn_3Cu is the prototype of ternary compounds where the 2b sites of the binary compound $D8_8$-Hf_5Sn_3 are filled by Cu atoms [22]. In the present work we have called f-$D8_8$ the $D8_8$ structure where the 2b sites are fully occupied, and sf-$D8_8$ the $D8_8$ structure where only one of the two 2b sites is occupied.

3. Experimental data

After a general look at all the experimental data of enthalpies of formation, the ab-initio calculated enthalpies of formation have been compared with values obtained by calorimetric measurements only. Indeed the values of the enthalpies of formation obtained by indirect methods such as electromotive force measurements or vapor pressure or mass spectrometry have not been considered in the present comparison. The reason is that in these methods the determination of the formation enthalpies is indirect and therefore a large scatter is the more often attached with such determinations. More, the values of the enthalpies of formation are obtained at high temperature and must be extrapolated to ordinary temperature. This point was clearly discussed by Klein et al. [24] in the case of the $ZrAl_2$ compound. Concerning the calorimetric methods, one must pay attention to the temperature of the determination. We have preferred the values given by the authors at ordinary temperature. The reason of this choice is that there is no problem of reference state of the elements and that no correction of heat content of the intermetallic compound has to be done. In the experiments performed by the Kleppa's group [25], the enthalpies of formation are obtained at $T=298$ K allowing direct comparisons with the ab-initio values obtained at $T=0$ K. The values obtained by solution calorimetry (acid solution calorimetry or metal solution calorimetry) have also be retained provided the samples are introduced in the calorimeter from room temperature. Many experimental values may be found in the review paper of Meschel and Kleppa [25] and in all the publications quoted in this paper. Several values of formation enthalpies may also be found in the book of de Boer and co-workers [26]. The bibliography, performed until 1988, concerns transition metal alloys and is very complete.

Experimental values of lattice parameters have been compiled in the Pearson's Handbook [22]. The more often, these values have been measured at ordinary temperature. The compounds are synthesized at high temperature, heat treated during a long time and then quenched to ordinary temperature.

4. Results and comparison with the experimental data

Since the last ten years, we have performed a large number of ab-initio calculations of enthalpies of formation of intermetallic compounds. The first calculations concerning the Ti–Sn, Ta–Si, W–Si, Ti–Si, and Ti–Ga systems [29–33] were performed using the GGA-PW91 [27,28] functional. Since, we used GGA-PBE functional [19]. In order to keep a coherency between the data, we have