



2021

# Thermodynamic Description of the Hf-Pd (Hafnium-Palladium) Binary System

S. Kardellass<sup>a,b</sup>, Z. Zhang<sup>c</sup>, D.O. Poletaev<sup>d</sup>, and M. Ait Boukideur<sup>b</sup>

<sup>a</sup>Equipe de Recherche en Thermique et Energie, École Nationale Supérieure d'Arts et Métiers, Université Mohammed V de Rabat, Morocco.

<sup>b</sup>Laboratoire de Thermodynamique et Energétique, Université Ibn-Zohr, B.P.8106, Agadir, Morocco.

<sup>c</sup>School of Material Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Minhang, Shanghai 200240, China.

<sup>d</sup>The Center of Nanostructured Materials and Nanotechnologies, Belgorod State University, Belgorod, Russian Federation.

## ABSTRACT

In present work, the thermodynamic modelling of the Hafnium-Palladium binary system have been constructed using the CALPHAD (CALculation of PHase Diagram) approach.

The solid solution phases: body-centered cubic ( $\beta$ Hf), hexagonal close-packed ( $\alpha$ Hf), and face-centered cubic (Pd) are described by the solution model with the Redlich-Kister polynomial.

A good fit between experimental data and calculated result for liquid phase was achieved by solution modeling with Hf, Pd and a  $\text{HfPd}_3$  associate, in particular.

Both compounds  $\text{HfPd}_2$  and  $\text{Hf}_2\text{Pd}$  possessing a tetragonal  $\text{MoSi}_2$ -type structure were treated as one phase with the formula  $\text{HfPd}(\text{Hf,Pd})$  by a three-sublattice model with Pd on the first sublattice, Hf on the second, and Pd and Hf on the third one, respectively. The Gibbs energy contribution of ordering phase BCC\_B2 and  $\text{D0}_{24}$  to disordering BCC\_A2 and HCP\_A3 were calculated using three-sublattice model  $(\text{Hf,Pd})_{0.5}(\text{Hf,Pd})_{0.5}(\text{Va})_{0.5}$  and  $(\text{Hf,Pd})_{0.75}(\text{Hf,Pd})_{0.25}(\text{Va})_{0.5}$ , respectively. The homogeneity range of non-linear compound  $\text{Hf}_2\text{Pd}_3$  was well modelled by a two-sublattice model in terms of  $(\text{Hf,Pd})_{0.75}(\text{Hf,Pd})_{0.25}$ .

A set of self-consistent thermodynamic parameters of the Hafnium-Palladium binary system was obtained and the calculated phase diagram and thermodynamic properties reached a good agreement with available experimental data.

## INTRODUCTION

Phase diagrams are the maps for materials and process development. Traditionally, they have been determined purely by experimental approach that is costly, meticulous, and time-consuming. In principle, they can be determined experimentally, but the time required to do so can be significantly longer. This is where the computer simulation and the Calphad (an acronym for CALculation of PHase Diagrams) method comes in and plays an important role (see Fig. 1). The Calphad method is based on the description of the Gibbs energies of the different phases present in a system. These are evaluated in simple systems by least-square fitting of model parameters in order to describe as well as possible the available experimental data (phase diagram and thermodynamic data) on a given system. One of the merits of the technique is its ability to describe metastable equilibrium since the phases are most often described out of their temperature and composition stability ranges [1]. Our purpose is to optimize the thermodynamic description of the Hf-Pd system using both, thermodynamics and phase diagram data and to calculate the phase diagram.

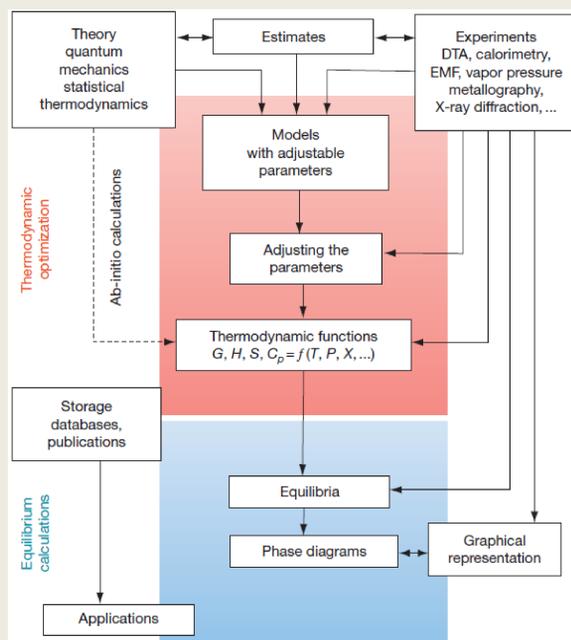
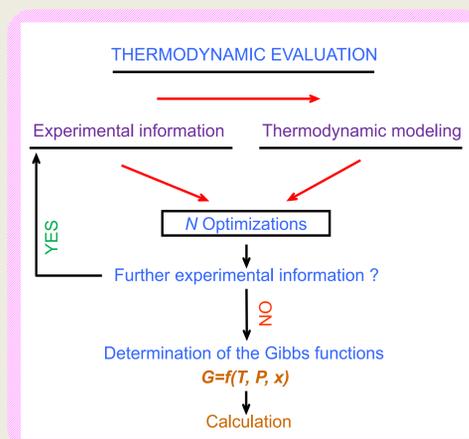


Fig. 1 Diagram illustrating the computer coupling of phase diagrams and thermochemistry approach.

## METHODS AND MATERIALS



## CONTACT

<Said Kardellass>  
<Equipe de Recherche en Thermique et Energie, École Nationale Supérieure d'Arts et Métiers, Université Mohammed V de Rabat, Morocco.>

Email: said.kardellass@ensam.um5.ac.ma

## OPTIMIZATION PROCEDURE

Both compounds  $\text{HfPd}_2$  and  $\text{Hf}_2\text{Pd}$  were treated as one phase with  $\text{HfPd}(\text{Hf,Pd})$ . The Gibbs energy contribution of ordering phase BCC\_B2 and  $\text{D0}_{24}$  to disordering BCC\_A2 and HCP\_A3 were calculated using  $(\text{Hf,Pd})_{0.5}(\text{Hf,Pd})_{0.5}(\text{Va})_{0.5}$  and  $(\text{Hf,Pd})_{0.75}(\text{Hf,Pd})_{0.25}(\text{Va})_{0.5}$ , respectively.  $\text{Hf}_2\text{Pd}_3$  was modelled by  $(\text{Hf,Pd})_{0.75}(\text{Hf,Pd})_{0.25}$ , while a solution model has been used for the description of the (Hf) and (Pd) solid solutions. Liquid phase was achieved by solution modeling with Hf, Pd and a  $\text{HfPd}_3$  associate. The excess term of the Gibbs energy of the solution phases was assessed with the Redlich-Kister [2] polynomial equation. The thermodynamic modeling of Hf-Pd binary system was carried out with the help of the CALPHAD method with the help of the PARROT module of the Thermo-Calc software developed by Jansson [3] and Sundman et al. [4]. The program works by minimizing an error sum where each of the selected values is given a certain weight. The weight is chosen by personal judgment and changed by trial and error during the work until most of the selected experimental information is reproduced within the expected uncertainty limits.

## LITERATURE DATA

In 1972, for the first time, [5] investigated the entire Hf-Pd phase diagram in 600 to 2300 °C. They used (DTA) and (XRD). In 1995, [6] revised and reviewed [5]. A thermodynamic study by [7] contradicted some of the previous results. Most recently by using high-T neutron Rietveld refinement and melting point measurements, [8] presented new measurements in order to resolve some contradictions and results need further clarification between [5] and [7]. (DSC) has been applied by [9] and high-T mixing calorimetry by [10], both to determine the enthalpy of formation of  $\text{HfPd}$ . Selhaoui et al. [7] have used (DSC) to measure the  $H_f$  of intermediate phases. The results are referred to the stable pure metals in the equilibrium state.

## THERMODYNAMIC MODELS

### Pure elements

The Gibbs energy function for the element  $i$  ( $i = \text{Pd, Hf}$ ) in the phase  $\Phi$  ( $\Phi =$  body-centered cubic (bcc\_A2), face-centered cubic (fcc\_A1) or hexagonal close-packed (hcp\_A3)) is described by an equation of the following form :

$$G_i^\Phi(T) = a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9}$$

In the present work, the Gibbs energy functions are taken from the SGTE compilation by Dinsdale [11].

### Solution phases (fcc\_A1, bcc\_A2 and hcp\_A3)

The Gibbs energy of one mole of formula unit is expressed as the sum of four terms:

$$G^\Phi - H_{SER}^\Phi = {}^{ref}G^\Phi + {}^{id}G^\Phi + {}^{ex}G^\Phi + {}^{mag}G^\Phi$$

$${}^{id}G^\Phi = RT(x_{Hf} \ln x_{Hf} + x_{Pd} \ln x_{Pd}) \quad {}^{ex}G^\Phi = y_i y_j \sum_{\lambda=0}^n \lambda L_{i,j}^\Phi (y_i - y_j)^\lambda$$

$${}^{mag}G^\Phi = RT \ln(\beta_O + 1)g(\tau) \quad {}^{ref}G^\Phi = x_{Hf} [{}^0G_{Hf}^\Phi - H_{Hf}^{SER}] + x_{Pd} [{}^0G_{Pd}^\Phi - H_{Pd}^{SER}]$$

### Stoichiometric compounds

The Gibbs energy of the  $\text{Hf}_p\text{Pd}_q$  stoichiometric compounds denoted as is expressed as follows:

$${}^0G_{A_p B_q} = \frac{p}{p+q} {}^0G_A + \frac{q}{p+q} {}^0G_B + \Delta G_{A_p B_q}^f + {}^{mag}G_{A_p B_q}$$

$\Delta G_{A_p B_q}^f = a + bT$  where the parameters  $a$  and  $b$  were evaluated in the present work.

## RESULTS AND DISCUSSION

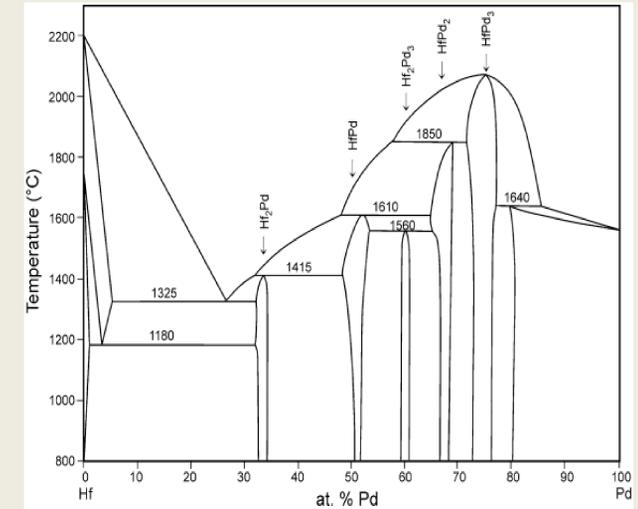


Fig. 2 Hf-Pd phase diagram modified according to newly acquired data by [8].

The calculated phase diagram shown in Fig. 3 is very similar to the experimental one shown in Fig. 2.

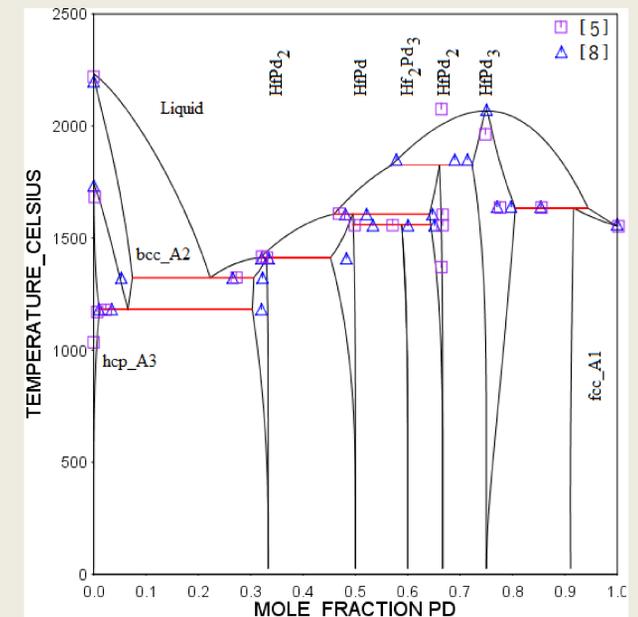


Fig. 3 Calculated Hf-Pd phase diagram during this work.

## CONCLUSIONS

Both calculated phase diagram and thermodynamic properties agree well with those of most relative experimental data.

## REFERENCES

- [1] K. Yaqoob, Université Paris-Est Créteil (2013).
- [2] Redlich O., Kister A., Ind. Eng. Chem., 40 (1948) 345-348.
- [3] Jansson B., PhD Thesis. Royal Institute of Technology, Stockholm, Sweden (1984).
- [4] Sundman B., et al., Calphad, 12 (1985) 153-90.
- [5] Shurin, A.K., Petkov, V.V.: Russ. Metall. (1972) 122.
- [6] S.N. Tripathi and S.R. Bharadwaj, J. Phase Equilib., 1995, 16, p 527-531.
- [7] Selhaoui, N., Gachon, J.C., Hertz, J.: J. Alloys Compounds 204 (1994) 157.
- [8] J.K. Stalick, &R.M. Waterstrat, Journal of Phase Equilibria and Diffusion, 37(4), 2016, 416-422.
- [9] Gachon, J.C., Charles, J., Hertz, J.: Calphad 9 (1985) 29
- [10] Topor, L., Kleppa, O.J.: Metall. Trans. A 18 (1987) 1989
- [11] Dinsdale AT, CALPHAD, 15-4 (1991) 317-425.