

## "حساب مخطط اطوار الهافنيوم -تنتالوم باستخدام الطريقة النظرية"

### "Calculation of Phase Diagram of Hafnium-Tantalum System by using The Theoretical Method"

زينب فاضل كاظم

هندسة المعادن- كلية هندسة المواد

جامعة بابل

لينا فاضل كاظم

هندسة المواد اللا معدنية- كلية هندسة المواد

جامعة بابل

#### Abstract:-

In this research the phase diagram of (Hf-Ta)binary system has been evaluated through (CALPHAD)[calculation of phase diagrams] method by using the experimental data of phases equilibria and thermodynamic properties. The computer programs in the language of quick basic have been formulated for the calculation of stable phases relations with mole fraction as a function of temperature, the basis of these programs is the approximate representation of free energy-mole fraction curves. The Gibbs free energy of the liquid , body centered cubic and hexagonal closed packed were calculated by the regular solution model. The present results were shown a good agreement between the theoretical and experimental diagrams . The maximum temperature difference between the theoretical and experimental phase diagrams was 243. The eutectoid point in the theoretical diagram was  $X_{Ta}=0.24$  and  $T_{th}=1609.4^{\circ}K$  while the eutectoid point in the experimental diagram was  $X_{Ta}=0.2$  and  $T_{ex}=1366^{\circ}K$ .

#### الخلاصة:

في هذا البحث تم الحصول على مخطط الاطوار للنظام الثنائي (هافنيوم - تنتالوم) من خلال طريقة CALPHAD النظرية لحساب مخططات الاطوار باستخدام القيم التجريبية لاتزان الاطوار و الخواص الترموديناميكية. تمت صياغة برامج بلغة البيسك السريع لحساب علاقات الاطوار المستقرة مع الكسر المولي كدالة لدرجة الحرارة ، ويعتبر التمثيل التقريبي لمنحنيات الطاقة الحرة-الكسر المولي كأساس لهذه البرامج. لقد تم حساب طاقة كبس الحرة للسائل و المكعب المتمركز الجسم و السداسي المكتظ من خلال نموذج المحلول النظامي، وقد اظهرت النتائج توافق جيد بين مخططي الاطوار النظري و العملي. عند نقطة اليوتكتويد ظهر اكبر فرق في درجات الحرارة وهو  $243^{\circ}K$  بحيث كانت نقطة اليوتكتويد عند الكسر المولي للتنتالوم 0.24 ودرجة الحرارة  $1609.4^{\circ}K$  في المخطط النظري بينما في المخطط التجريبي كانت نقطة اليوتكتويد عند الكسر المولي للتنتالوم 0.2 ودرجة الحرارة  $1366^{\circ}K$ .

#### Introduction:

The phase diagrams are visual representation of the material state as a function of temperature, pressure and concentrations of the constituent components. There are two approaches in phase diagrams investigations and thermodynamic properties of multi-component systems were studied, these approaches were: experimental and theoretical methods.[ Udovsky ,2002]

Phase diagrams are critical research tools for many scientific disciplines, including material science, ceramics ,geology, physics, metallurgy, chemical engineering, and chemistry. So phase diagrams can be regarded as “road maps” for materials processing because they contain important information for the development

of new materials, control of structure and composition of critical phases, and improvement properties of technologically important materials. The applications of phase diagrams ranging from the preparation of, single-phase bulk materials, deliberate precipitation of second phases, to the formation of melts.[Wong2001, Liu2004]

Over the past decades, CALPHAD (CALculation of PHase Diagrams) thermodynamic modeling has been widely recognized as a powerful tool in predicting multi- component phase diagrams and guiding new materials development. CALPHAD modeling begins with the evaluation of descriptions of pure elements and binary systems. By combining the constitutive binary systems and ternary experimental data, ternary interactions and Gibbs energy of ternary phases have been obtained. Thermodynamic databases thus developed cover the whole composition and temperature ranges, including experimentally uninvestigated regions. It is based on the fact that a phase diagram is a manifestation of the equilibrium thermodynamic properties of the system, which are the sum of the properties of the individual phases. [Noirfontaine2012, Liu2004]

Fernandez A.[1996] studied phase diagram of Hf-Nb by applying a theoretical method which relies on the coupling between thermochemistry and phase diagrams. The approach involves the analysis and synthesis of selected phase equilibrium data using models for  $G_m$  of bcc, hcp and liquid, and the evaluation of a set of optimum model parameters through a computer optimization technique. The  $G_m$  functions arrived at in this way are used in constructing, by calculation, a phase diagram for the Hf-Nb system, and in analysing the composition and structure dependence of the enthalpy of formation. Detailed comparisons are reported with estimates from the Miedema method and other predictive approaches, and with the behavior of the related systems Hf-Ta, Zr-Nb and Zr-Ta, which have recently been analyzed.

Wanga Y.and others [2004]studied systematic first-principles calculation for the total energies of 78 pure elemental solids has been performed at zero Kelvin using the projector augmented-wave method within the generalized gradient approximation. The total energy differences, i.e. lattice stabilities, among the face-centered-cubic (fcc), body-centered-cubic (bcc), and hexagonal-close-packed (hcp) crystal structures are studied and compared with the Scientific Group ThermoData Europe (SGTE) database developed by the CALPHAD method. For non-transitional elements, favorable comparison is observed, while for the majority of transition elements, particularly the V, Cr, Mn, Fe, and Co group elements, significant discrepancies exist. The Bain/tetragonal distortion analysis between fcc and bcc structures shows that when one structure is stable, the other is unstable, and the higher the energy of the unstable structure, the larger the discrepancy. Through analysis of the alloying effect in binary systems. They concluded that the lattice stability of unstable structures obtained through extrapolation of first-principles calculations in binary systems is close to the SGTE lattice stability obtained by the CALPHAD method.

Noirfontaine M. [2012] discussed the distinct approaches of the method for the calculation of multi-component systems for Portland cement elaboration. The article gives a state of the art of the most recent experimental data and the various calculations for the CaO-

Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase diagram. The predictive feature of the CALPHAD method is illustrated using the CaOAl<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system with the two-sublattices model: extrapolated (predicted) and fully-assessed phase diagrams are compared in the clinkering zone of interest. The recent application of the predictive method for the calculations of high-order systems (taking into account Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>, CaF<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>) shows that the databases developed with the two-sublattices model and the modified quasichemical model are no longer equivalent.

In this research ,the theoretical phase diagram of two refractory metals (Hf-Ta)has been calculated, because there are two main difficulties in developing phase diagrams of refractory alloys: lack of basic experimental data on thermodynamics, mechanical, and physical properties of most of these alloy systems, and difficulties associated with processing of these alloys. In order to avoid traditional trial-and error experiments that are also time consuming and expensive, it has become essential to develop theoretical modeling to guide experimental alloy development.

### **Thermodynamic model:**

The phase stability in a system ,as normally presented on an isobaric phase diagram, can be determined from the knowledge of the variations of the Gibbs free energy variations for various possible phases with respect to composition and temperature. [Gaskell,2003]

Consider the binary system of (Hf-Ta) forms regular liquid solution and regular solid solution. [Gaskell,2003] The Gibbs free energy of mixing depends on the temperature up or below melting temperature of the two metals. To calculate Gibbs free energy of mixing at temperature above melting temperatures of two metals using:

$$\Delta G_L^M = X_{Ta}\Delta G_{m(Ta)} + RT(X_{Ta}\ln(X_{Ta}) + X_{Hf}\ln(X_{Hf}))$$

$$\Delta G_S^M = -X_{Hf}\Delta G_{m(Hf)} + RT(X_{Ta}\ln(X_{Ta}) + X_{Hf}\ln(X_{Hf}))$$

The entropy of mixing= $-R((X_{Ta}\ln(X_{Ta}) + X_{Hf}\ln(X_{Hf}))$ )

The previous equations using to draw figs(1a-1c) .

At temperature below melting temperature of Tantalum and above melting temperature of Hf the Gibbs free energy for mixing of liquid and solid phases:

$$\Delta G_L^M = X_{Ta}\Delta G_{m(Ta)} + RT(X_{Ta}\ln(X_{Ta}) + X_{Hf}\ln(X_{Hf})) + LX_{Hf}X_{Ta}$$

$$\Delta G_S^M = -X_{Hf}\Delta G_{m(Hf)} + RT(X_{Ta}\ln(X_{Ta}) + X_{Hf}\ln(X_{Hf})) + BX_{Hf}X_{Ta}$$

Where:

L=interaction parameter for liquid phase,B= interaction parameter for bcc phase. These equations using to draw figs.(1d-2e).

At temperatures below melting temperatures of two metals the Gibbs free energies for mixing of solid and liquid phases are:

$$\Delta G_L^M = X_{Ta} \Delta G_{m(Ta)} + X_{Hf} \Delta G_{m(Hf)} + RT (X_{Ta} \ln(X_{Ta}) + X_{Hf} \ln(X_{Hf})) + LX_{Hf}X_{Ta}$$

$$\Delta G_S^M = RT (X_{Ta} \ln(X_{Ta}) + X_{Hf} \ln(X_{Hf})) + BX_{Hf}X_{Ta}$$

The previous equations using to draw figs.(2f-3b).

To calculate the curve of Gibbs free energy against composition at constant temperature between  $\beta$  (*body centered cubic*) and  $\epsilon$  (closed packed hexagonal) that represent solid phases and the temperature above  $T_0^{\beta\epsilon}$  for Hf, the Gibbs free energy of mixing for  $\beta$  phase and  $\epsilon$  phase are:-

$$\Delta G_\beta^M = -X_{Hf} \Delta G_{(Hf)}^{\beta \rightarrow \epsilon} + RT (X_{Ta} \ln(X_{Ta}) + X_{Hf} \ln(X_{Hf}))$$

$$\Delta G_\epsilon^M = X_{Ta} \Delta G_{Ta}^{\beta \rightarrow \epsilon} + RT (X_{Ta} \ln(X_{Ta}) + X_{Hf} \ln(X_{Hf}))$$

The concluded figures are 3c.3d and 3e.

At temperature below  $T_0^{\beta\epsilon}$  for Hf and above  $T_0^{\beta\epsilon}$  for Ta the equations are:

$$\Delta G_\beta^M = -X_{Hf} \Delta G_{(Hf)}^{\beta \rightarrow \epsilon} + RT (X_{Ta} \ln(X_{Ta}) + X_{Hf} \ln(X_{Hf})) + BX_{Ta}X_{Hf}$$

$$\Delta G_\epsilon^M = X_{Ta} \Delta G_{Ta}^{\beta \rightarrow \epsilon} + RT (X_{Ta} \ln(X_{Ta}) + X_{Hf} \ln(X_{Hf})) + EX_{Ta}X_{Hf}$$

**Where:** E= interaction parameter for hcp phase. The concluded figures are 3f to 5b.

Don't take temperature below  $T_0^{\beta\epsilon}$  Because it in the minus charge. Five programs have been used to calculate the above equations and draw the curves between Gibbs free energy and mole fraction for several temperatures and use the data from the following table[Kaufman ,1970]:

Metal	Gibbs free energy difference (cal/g-atom)	Temperature(° K)
Hf	$\Delta G^{\beta \rightarrow L} = 4990 - 2.0T$	$T_m^\beta = 2495^\circ K$
	$\Delta G^{\beta \rightarrow \epsilon} = -1830 + 0.9T$	$T_0^{\beta\epsilon} = 2033^\circ K$
Ta	$\Delta G^{\beta \rightarrow L} = 6540 - 2T$	$T_m^\beta = 3270^\circ K$
	$\Delta G^{\beta \rightarrow \epsilon} = 1500 + 0.8T$	$T_0^{\beta\epsilon} = -1875^\circ K$

## **Results and Discussion:-**

Fig.(1a-1f) have been represented the calculated Gibbs free energy of liquid and solid solutions. From fig(1a-1c) the liquid solution is more stable than the solid solution in all temperatures and in fig(1d) the liquid solution is more stable from  $X_{Ta}=0$  to 0.99 and at  $X_{Ta}=1$  Gibbs free energy of the liquid and solid solutions are equal at melting temperature of tantalum ( $T_{Ta}^m = 3270^\circ K$ ). In figs.(1e-1f) at  $T=3159.2^\circ K$  and  $T=3048.5^\circ K$  there is intersection between two curves of liquid and solid solution, by drawing a line tangent to the point of intersection of the two curves and this site of intersection means there is a mixture of liquid and solid solution in this place.

In figs.(2a-2d) there is intersection between Gibbs free energy of liquid and solid solution from  $T=2937.8^\circ K$  to  $T=2605.7^\circ K$ . By drawing a tangent at the point of intersection between liquid and solid curves, then the vertical lines have been drawn from the point of tangencies of the two curves to the horizontal line that represents the mole fraction of tantalum. The distance between these two lines exhibits the range of mole fraction of the mixture between liquid and solid solution. In figs.(2e-2f) the solid solution is more stable than the liquid solution because the decreasing in temperature less the melting point of hafnium ( $T_{Hf}^m = 2495^\circ K$ ).

In figs.(3a) and(3b) the solid solution of body center cubic (bcc) crystal structure more stable than the liquid solution. In figs.(3c,3d,3e) the Gibbs free energy of (bcc) is lower than the Gibbs free energy of the hexagonal closed packed (hcp) which means bcc is more stable than hcp phase at all mole fractions of Ta. In fig.(3c) the shape of Gibbs free energy curve of bcc phase was curved line downward at  $(0-0.4)X_{Ta}$  and straight line in mole fractions  $(0.4-0.6)X_{Ta}$  and curved upward at  $(0.6-1)X_{Ta}$ , which means there is a miscibility gap of two solid solutions. In first part a solid solution of bcc is more stable, in second part a mixture of two solid solutions is more stable and a new solid solution is stable at part three. The similar behavior in figs.(3d) and(3e).

In fig.(3f) and (4a),(4b), and(4c) there are five portions in curves of hcp and bcc. In first portion a phase of hcp is more stable, after that there is intersection between free energy curve of hcp and bcc which means there is a mixture of hcp and bcc. In other portions the same behavior in fig.(3c) presented. From fig(4d) to fig(5b) which have been represented by temperature from  $T=1498.8^\circ K$  to  $T=1055.9^\circ K$ , a mixture of hcp and s.s is more stable in all mole fractions of Ta.

All the previous figures are used to conclude theoretical phase diagram as in fig.(6). In site that Gibbs free energy of liquid solution less than Gibbs free energy of solid solution means the site above liquidus line in phase diagram where the phase is liquid for all mole fractions. The place of liquid and solid solution means there is intersection between Gibbs free energy of liquid and solid solution. In the site the

solid solution more stable than liquid solution this means places under the solidus line. The same manner is used to detect under solidus line in the phase diagram.

Fig.(6) represents the theoretical and experimental phase diagrams of Hf-Ta system. The experimental phase diagram from [the phase diagram web] and the liquidus line in experimental and theoretical diagrams have been coincide from (0.54 to 1)  $X_{Ta}$ . The liquidus line in theoretical diagram above liquidus line in experimental diagram and the maximum difference in temperature has been occurred at  $X_{Ta}=0.32$ , where  $T_{th}=2605^{\circ}K$  and  $T_{ex}=2500^{\circ}K$ . The experimental diagram represents diagram with minimum point while the theoretical diagram represents diagram with two metal completely soluble in liquid and solid state without minimum point.

For solidus line that starts from the melting temperature of tantalum, there is small difference between the solidus line in experimental diagram upper the theoretical diagram where  $T_{ex}=3100^{\circ}K$ ,  $T_{th}=3050^{\circ}K$ , and  $X_{Ta}=0.93$ . The solidus line for experimental and theoretical diagrams have been coincide at (0.54-0.6)  $X_{Ta}$  while the experimental solidus line lower than the theoretical solidus line at  $X_{Ta}=0.2$  where  $T_{ex}=2400^{\circ}K$  and  $T_{th}=2510^{\circ}K$ .

Under  $T=2033^{\circ}K$ , the hcp phase appears with maximum amount of tantalum in theoretical diagram is 0.08% at  $T=1609.4^{\circ}K$  but for experimental diagram is 0.05% at  $T=1366^{\circ}K$ . Eutectoid reaction happens at  $X_{Ta}=0.24$ ,  $T_{th}=1609.4^{\circ}K$ , but for experimental diagram at  $X_{Ta}=0.2$ ,  $T_{ex}=1366^{\circ}K$ . Maximum temperature appears mixture of bcc and s.s is  $2052.2^{\circ}K$  for theoretical but for experimental is  $1941^{\circ}K$  and the miscibility gap of bcc and s.s ended at  $X_{Ta}=0.9\%$  for theoretical but at  $X_{Ta}=0.83$  for experimental.

These differences between experimental and theoretical diagram because the theoretical model depends on mole fraction and the experimental data of Gibbs free energy. Assumption the solid and liquid solutions as regular solution, the excess entropy is zero, and the nature of statistical entropy of mixing depending on the mole fractions. There are some parameters such as free mean path which represent the distance between the electron and the lattice do not calculate in theoretical method.

### **Conclutions:**

1. New phase of (s.s) has been observed in the curve of Gibbs free energy of bcc with composition of Ta and the theoretical phase diagram of Hf-Ta at temperatures from  $2052.2^{\circ}K$  to  $1055.9^{\circ}K$ .
2. The eutectoid point in theoretical phase diagram is  $1609.4^{\circ}K$  at  $X_{Ta}=0.24$ .

## **References:** -

- Fernández A. Guillermet [1999]" Gibbs energy coupling of phase stability and thermochemistry in the Hf-Nb system",Jou. Alloys and Compounds, Vol.234,Issue1, P.(111-118)
  
- Gaskell R.David,[2003],"**Thermodynamics of Materials**", United States, library of congress, fourth edition.
  
- Kaufman L. and Bernstein H.,[1970]"**Computer Calculation of Phase Diagrams**", Academic Press Inc.,U.S.A.
  
- Liu Z. K. , Chen L.-Q., and others[2004],"**An Integrated Framework for Multi-Scale Materials Simulation and Design**",  
[www.cse.psu.edu/raghavan/jcad](http://www.cse.psu.edu/raghavan/jcad).
- Noirfontaine N.M. ,Tusseau-S., and Pontikis V.[2012]"**CALPHAD formalism for Portland clinker:thermodynamic models and databases**",Jou. Materials Science,Vol.43,No.3,P(1471-1479).
  
- Udovsky L.A.[2002],"**Computation Thermodynamics and Informational Technologies in the Field of Computer Design of Materials**",Jou. Mining and metallurgy, Vol.38,P(189-196).
  
- Wang Y, Curtarolo S.[2004]"**Ab initio lattice stability in comparison with CALPHAD lattice stability**",Jou. Computer Coupling of Phase Diagrams and Thermochemistry ,Vol.28,P (79–90)
  
- Wong-Ng W.,Roth S.R. &Vanderah A.T.[2001],"**Phase Equilibria and Crystallography of Ceramics Oxides**",Jou. Research of national institute of standards and technology,Vol.106.,No.6,P(1097-1134).
  
- "**The Phase Diagram Web**"<http://www.crct.polymtl.ca/fact/pdweb.php>.