

Calculation of the Thermodynamic Properties in the Ir-B System Based on the Known Phase Diagram

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Abstract: The results of the thermodynamic properties calculation in the binary Ir-B system is presented in this paper. Based on the known liquidus and solidus lines from the phase diagram, specific calculation procedure according to Rao and Belton was done, so activities and activity coefficients for iridium and boron were determined at the temperatures of 2800, 2900 and 3000K.

Keywords: alloy thermodynamics, phase diagram, Ir-B system

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INTRODUCTION

Several investigations on the iridium borides have been reported in literature by ARRONSON ET AL. in 1962 ^[1] and 1963 ^[2], LUNDSTRAM in 1967 ^[3], ROGL ET AL. in 1971 ^[4], as well as the

liquidus and solidus-liquidus data according to IPSE AND ROGL in 1981 ^[5] and metallographical investigation of Ir-B system by STUPAREVIĆ in 1986 ^[6].

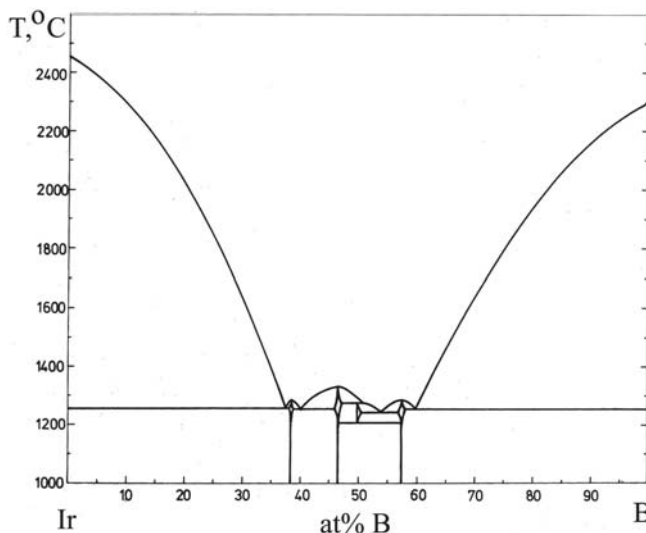


Figure 1. Phase diagram of the Ir-B system ^[5].

Table 1. Characteristic reactions in the Ir-B system according to IPSEK AND ROGL [5].

Temperature, °C	Reaction	B-content (at%)	Type of reaction
1259 ± 4	$L \rightarrow Ir + IrB_{0.7}$	37.5	eutectic
1287 ± 4	$L \rightarrow IrB_{0.7}$	38.5	congr. melt.
1258 ± 4	$L \rightarrow IrB_{0.7} + IrB_{0.9}$	40.0	eutectic
1333 ± 4	$L \rightarrow IrB_{0.9}$	46.5	congr. melt.
1274 ± 0	$L + IrB_{0.9} \rightarrow IrB$	50.0	peritectic
1209 ± 3	$IrB \rightarrow IrB_{0.9} + IrB_{1.35}$	50.0	eutectoid
1248 ± 3	$L \rightarrow IrB + IrB_{1.35}$	54.0	eutectic
1287 ± 5	$L \rightarrow IrB_{1.35}$	57.5	congr. melt.
1255 ± 0	$L \rightarrow IrB_{1.35} + B$	60.0	eutectic

Phase diagram of the Ir-B binary system is given in Fig.1, while the characteristic reactions and their type at the certain compositions and temperatures are presented in Table 1.

Concerning the thermodynamic data for this binary system, there are no adequate references in literature. The main reason for this is the high investigating temperature, which causes many difficulties in the experimental work.

So, as a contribution to the better thermodynamic knowledge of the Ir-B binary system, an analytical approach to this subject is presented in this paper. Based on the known liquidus and solidus lines from the phase diagram, specific calculation procedure according to RAO AND BELTON [7,8] was performed, which enabled the determination of the activities, activity coefficients and other partial molar quantities at the temperature of 2500 K.

THEORETICAL FUNDAMENTALS

In some binary systems it is possible to calculate the activity coefficients of components in liquid solutions from the locations of the liquidus and solidus lines on the phase diagrams. For systems of simple eutectic type, with little or no terminal solid solubility, this method offers a means of obtaining the activity coefficients with acceptable accuracy [7,8].

For illustration of this method, two examples of calculation will be given for the imaginary binary eutectic Me_1 - Me_2 system (where Me_1 and Me_2 are different metals):

- *first*, if there are no terminal solid solubility, and
- *second*, if there is little solid solubility in the investigated system.

First case: Assume that on the Me_2 -rich side of the phase diagram the liquidus descends sharply with increasing Me_1 content and terminates at the eutectic point (T_2, x_{Me_2}).

Because solid Me_2 dissolves no Me_1 , then, at any point on the liquidus curve, a liquid Me_1 - Me_2 solution of composition x_{Me_2} is in equilibrium with pure solid Me_2 , at temperature T . In other words,

$$\text{Me}_1\text{-Me}_2 \text{ (liquid alloy)} = \text{Me}_2 \text{ (pure, solid)} \text{ at } T \quad (1)$$

The partial molar free energy of Me_2 in the liquid alloy, G_{Me_2} , is equal to the molar free energy of the pure solid Me_2 , $G_{\text{Me}_2(s)}^\circ$. Thus

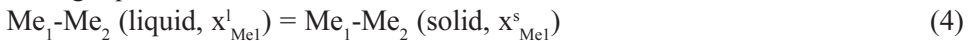
$$G_{\text{Me}_2} = G_{\text{Me}_2(l)}^\circ + RT \ln a_{\text{Me}_2} = G_{\text{Me}_2(s)}^\circ \quad (2)$$

where a_{Me_2} is the activity of Me_2 in the liquid alloy with respect to the pure liquid Me_2 standard state. Rearranging the terms,

$$RT \ln a_{\text{Me}_2} = G_{\text{Me}_2(s)}^\circ - G_{\text{Me}_2(l)}^\circ = -\Delta G_{s \rightarrow l(\text{Me}_2)}^\circ \quad (3)$$

where $\Delta G_{s \rightarrow l(\text{Me}_2)}^\circ$ is the standard free energy of fusion for Me_2 at temperature T (this quantity should be expressed as a function of temperature using data on heat of fusion and heat capacity).

Second case: In the case of eutectic systems, with little terminal solid solubility of Me_2 in Me_1 , following equilibrium reaction could be written:



which means that activity of Me_1 -component is less than 1. Further, this can be expressed as

$$G_{\text{Me}_1(l)} = G_{\text{Me}_1(l)}^\circ + RT \ln a_{\text{Me}_1(l)} = G_{\text{Me}_1(s)} = G_{\text{Me}_1(s)}^\circ + RT \ln a_{\text{Me}_1(s)} \quad (5)$$

where $a_{\text{Me}_1(l)}$ and $a_{\text{Me}_1(s)}$ are activities of Me_1 -component in liquid (related to pure liquid Me_1 in the standard state) and solid phase (related to pure solid Me_1 in the standard state), respectively. When solubility of Me_2 in the Me_1 is not too high, it can be assumed that the solid phase is amenable to Raoult law, so $a_{\text{Me}_1(s)} = x_{\text{Me}_1}^s$. Rearranging the Eq. (5) one obtains

$$\log a_{\text{Me}_1(l)} = \log x_{\text{Me}_1}^s - \Delta G_{s \rightarrow l(\text{Me}_1)}^\circ / 2.303RT \quad (6)$$

which is the basic equation for the calculation of $a_{\text{Me}_1(l)}$ at different liquidus temperatures T . When values for activities of Me_2 -component in liquid alloys of different compositions - at the liquidus temperature are calculated, the activity coefficients at the investigated temperature T' can be calculated assuming regular solution behavior for the melts as follows [8]

$$\gamma^i = \gamma_i^{(T/T')} \quad (7)$$

Systems that are amenable to this type of analysis include, for example, lead-silver, iron-silicon, magnesium-silicon, iron-copper, etc. Often, in this type of system, experimental data on activities are available for only a limited range of compositions, and these data can be combined with activity data deduced from the phase diagram [8]. For some systems, Ir-B for example, where no data are available, this method could be very useful in the thermodynamic analysis and obtaining the activity-composition relation for the investigated composition range.

RESULTS AND DISCUSSION

The Ir-B phase diagram belongs to the group of systems for which the described calculation method [7,8] could be applied. But, the characteristics of this system make it differ from the original look of the simple eutectic type diagrams: numerous iridium borides occurs in the middle region of the phase diagram [5], so concentration range with iridium molar content 0.35-0.65 was not considered.

Regions in the concentration range that were investigated are alloys with $x_{\text{Ir}} = 0-0.35$ and $0.6-1$, respectively. For the first interval, iridium-rich side was treated and thermodynamic properties for iridium were determined, and in the second interval, boron-rich side of the phase diagram was investigated and thermodynamic properties for boron were determined.

Values of chosen alloy compositions and adequate liquidus temperatures read from the Ir-B phase diagram are shown in Table 2.

Table 2. Chosen compositions and adequate liquidus temperatures.

x_{Ir}	x_{B}	T_{liq}, K
0.05	0.95	2503
0.10	0.90	2414
0.15	0.85	2310
0.20	0.80	2184
0.25	0.75	2058
0.30	0.70	1895
0.35	0.65	1732
0.65	0.35	1651
0.70	0.30	1866
0.75	0.25	2058
0.80	0.20	2236
0.85	0.15	2932
0.90	0.10	2532
0.95	0.05	2629

In further analysis, thermodynamic properties for the adequate component were calculated considering the calculation procedure given by Eq. (6). Results of this calculation, which include the value for $\Delta G^{\circ}_{s \rightarrow l}$ for boron and iridium at the corresponding liquidus temperature, the activities and activity coefficients for both components in the liquid phase at the liquidus temperature are presented in Table 3.

Table 3. Results of the thermodynamic calculation at the liquidus temperature.

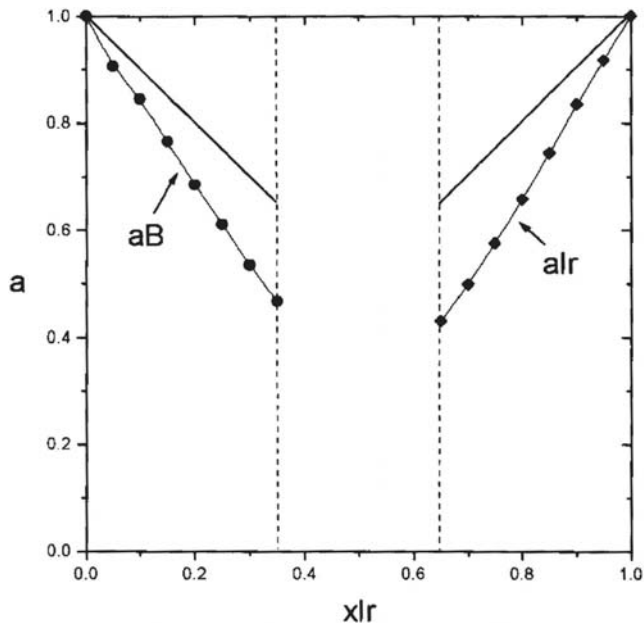
x_{Ir}	$\Delta G^{\circ}_{s \rightarrow l} (\text{B})$	$\log a_{\text{B}}$	a_{B}	γ_{B}
0.05	0	-0.04576	0.900	0.947
0.10	331	-0.07774	0.836	0.929
0.15	1289	-0.12605	0.748	0.880
0.20	2448	-0.18348	0.655	0.819
0.25	3605	-0.24639	0.567	0.756
0.30	5095	-0.32751	0.470	0.672
0.35	6570	-0.41996	0.380	0.585
x_{Ir}	$\Delta G^{\circ}_{s \rightarrow l} (\text{Ir})$	$\log a_{\text{Ir}}$	a_{Ir}	γ_{Ir}
0.65	9608	-0.49102	0.323	0.497
0.70	7877	-0.37537	0.421	0.602
0.75	6201	-0.28231	0.522	0.696
0.80	4573	-0.20372	0.626	0.782
0.85	3106	-0.12591	0.748	0.880
0.90	1770	-0.08227	0.827	0.919
0.95	838	-0.03892	0.914	0.962

The calculation of activities and activity coefficients at the investigated temperatures of 2800, 2900 and 3000K, was done according to Eq. (7), assuming regular solution behavior for the melts. As for the illustration, dependencies of iridium and boron activities on composition at the temperature of 3000K are shown in Fig. 2.

Negative deviation from the Raoult law in the investigated composition ranges could be noticed for both components ($\gamma_{\text{Ir}} < 1$ and $\gamma_{\text{B}} < 1$), which means that good miscibility between

Table 4. Thermodynamic properties for iridium and boron at the investigated temperature.

Temp.	2800K		2900K		3000K	
xIr	γ_B	aB	γ_{Ir}	aIr	γ_B	aB
0.05	0.953	0.905	0.954	0.907	0.956	0.908
0.1	0.938	0.845	0.941	0.846	0.942	0.848
0.15	0.900	0.765	0.903	0.768	0.906	0.770
0.2	0.856	0.685	0.861	0.688	0.865	0.692
0.25	0.814	0.611	0.820	0.615	0.825	0.619
0.3	0.764	0.535	0.771	0.540	0.778	0.545
0.35	0.718	0.467	0.726	0.472	0.734	0.477
0.4	0.924	0.554	0.927	0.556	0.929	0.557
xIr	γ_{Ir}	aIr	γ_{Ir}	aIr	γ_{Ir}	aIr
0.65	0.662	0.430	0.671	0.436	0.680	0.442
0.7	0.713	0.499	0.721	0.505	0.729	0.510
0.75	0.766	0.575	0.773	0.580	0.780	0.585
0.8	0.822	0.657	0.827	0.662	0.833	0.666
0.85	0.875	0.744	0.879	0.747	0.883	0.750
0.9	0.927	0.834	0.929	0.836	0.932	0.838
0.95	0.965	0.916	0.966	0.918	0.967	0.919

**Figure 2.** Dependencies of iridium and boron activities on the composition at 3000K.

constitutional components in the iridium-boron system exists. This fact is in agreement with the phase diagram type, in which numerous iridium borides are formed. Also,

it could be noticed that the activity value increases with increasing temperature, coming closer to the Raoult line.

Having in mind that, up to now, there were no thermodynamic properties on this system, as well as the fact that extremely high temperatures were taken into the consideration, the application of the Rao and Belton's calculation procedure could be very useful and adequate methodology for thermodynamic investigation of such systems.

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