Thermodynamic Study of Fe-Ta and Fe-Nb Alloys by Means of the Knudsen Cell Mass Spectrometry

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The activity of iron in the Fe-Ta and Fe-Nb alloys at 1 873 K was determined by means of the Knudsen cell mass spectrometry. A modified internal standard method was employed, in which a piece of pure iron foil placed on the sample surface in the Knudsen cell served as the internal standard material. The ion intensity of iron from the foil was first measured at several temperatures before the alloy sample and the foil melted together. The ion intensity from pure solid iron thus obtained was extrapolated to give ion intensity from pure liquid iron at higher temperatures. The temperature of the sample was then raised to form uniform liquid alloy and the ion intensity of iron from the alloy was measured. The activity of iron in the alloy was determined by comparing the ion intensities from pure iron and from alloy.

The activities of Ta and Nb were derived from that of iron by integrating the Gibbs-Duhem equation. The activity coefficients of Ta and Nb in the infinitely dilute solution with liquid pure metal as the standard state were also calculated. The interaction parameters were determined. These results were compared with those of elements adjacent to Ta and Nb in the periodic table.

Invariant reactions appeared in the Fe-Ta binary alloy system at high temperature were investigated by employing the ion intensity thermal analysis, in which the ion intensity represented the temperature of the sample. Heat treatment and metallographic study was also carried out for the identification and composition determination of phases.

KEY WORDS: Fe-Ta alloy; Fe-Nb alloy; Knudsen cell mass spectrometry; thermodynamics; activity; ion intensity thermal analysis; phase diagram.

1. Introduction

Although there have been numerous studies on the activity and activity coefficient of iron based liquid alloys, the data tend to concentrate upon some limited number of systems which naturally are important in the iron and steelmaking and are those characterized by experimental readiness in the measurements.

Iron based alloys with some of transition metals on fifth and sixth periods, such as Nb, Mo, Ta and W may be grouped into those with experimental difficulties. Measurement of thermodynamic properties of alloys of iron with these elements is important not only from the technical point of view, but also from pure scientific point of view in filling up the vacancies of knowledge.

The authors developed a Knudsen cell mass spectrometric technique of determining activities of a binary alloy, composed of a metal with high vapor pressure and a nonvolatile metal. Activities of Fe-Mo¹⁾ and Fe-W²⁾ alloys were determined by the use of this technique. In the present study, iron, volatile component in the Fe-Ta and Fe-Nb alloys as in the Fe-Mo and Fe-W alloys, served as the internal standard before it was melted in this technique.

A method of thermal analysis by the use of Knudsen cell mass spectrometer has also been developed by the authors.³⁾ In this method ion intensity of an alloy component is used as a measure of temperature of the

sample in the cell. This method enables us to perform thermal analysis at relatively high temperature with very high sensitivity.

2. Experimental

Between equilibrium partial pressure p_i of a component i of an alloy in a Knudsen cell at a temperature T and the ion intensity I_i , we have the following equation.

$$I_i = (Ap_i c_i / 4kT) g(\sigma_i(E - E_i^0)jl/c_i)\eta_i S_i \dots\dots\dots(1)$$

where, A : effective area of the orifice of the Knudsen cell

c_i : the average velocity of particles in the vapor phase

E : chamber potential of the ion source

E_i^0 : ionization potential of particle i

g : geometric factor between cell and ion source

j : intensity of ionizing electron current

k : Boltzmann's constant

l : effective length of path of the particles across the ionizing electron beam

S_i : sensitivity of the detector of the ion current.

η_i : isotopic abundance

σ_i : ionization cross section of particle i

Or simply,

$$I_i = hk_i p_i / T \quad \text{.....(2)}$$

where, h : apparatus constant including g which varies run to run

k_i : constant which depends on the characteristics of the particle i .

2.1. Apparatus

A Knudsen cell mass spectrometer, which consisted of a single focusing mass spectrometer and a Knudsen cell furnace, was used in the present study. The Knudsen cell furnace chamber was placed below the ion source so that particles from the cell could enter upwards the ionizing zone of the ion source through a small hole on the wall separating the ion source and the cell chambers. This hole could be closed by a shutter manipulated from the outside of the chamber. The ion source and the cell chamber were pumped separately by oil diffusion pumps. Pressures in the ion source and the cell chambers were maintained respectively about 5×10^{-5} and 1×10^{-4} Pa.

A tantalum Knudsen cell holder was heated by electron bombardment from two ring filaments which were controlled separately. The temperature was measured at upper side and bottom center of the cell holder with W/W-26%Re thermocouples. Electron currents from upper and lower ring filaments were adjusted separately to yield uniform temperature profile inside the Knudsen cell. The temperature measured was calibrated by separate experiments in which ion intensity thermal analysis of pure metals with known melting point such as iron and palladium was carried out.

A sintered alumina crucible of 9 mm in diameter and 11 mm in height and a lid with an orifice of 0.4 mm in diameter were used as a Knudsen cell.

2.2. Sample Preparation

The chemical compositions of iron, tantalum and niobium used in the present study are as follows.

1) Pure iron (mass %)

Fe: 99.94, C: 0.002, Si: 0.005, Mn: 0.001, P: 0.005, Cu: 0.005, Ni: 0.004, S: 0.005, Cr: 0.003, N: 0.002, Co: 0.013, Ti: 0.003, Al: 0.003, V: 0.001, O: 0.004

2) Tantalum

Ta: 99.90, Nb: 0.06, Fe: 0.003, W: 0.028, Ni: 0.001, Ti: 0.001, Si: 0.005, C: 0.003, N: 0.003, O: 0.009, H: 0.001

3) Niobium

Nb: 99.90, Ta: 0.07, Ni: 0.003, Cr: 0.001, Fe: 0.003, C: 0.008, O: 0.009

These materials were melted together to give desired composition in a vacuum arc furnace under argon atmosphere of $5-8 \times 10^{-4}$ Pa. The compositions of alloys were determined by atomic absorption spectrometry.

2.3. Activity Determination

The apparatus constant h may take different values on each setting of the Knudsen cell in the furnace. However, this constant may be eliminated when ac-

tivity is the subject of the study where not the value of the pressure of alloy component but the ratio of the pressure of the component is to be measured. In this case, the constants h and k_i in Eq. (2) can be canceled by taking the ion intensity ratio.⁴⁾ If ion intensities of iron from pure iron and from the alloy could be measured with the same cell in a single run, the constants may be canceled out by taking the ratio of these ion intensities in deriving the activity of iron. This was done as follows.

A certain volume of an alloy sample was charged in a Knudsen cell and a piece of iron foil was placed on the surface of the sample to cover the entire top surface of the sample.

Ion intensity of iron from the solid iron foil, I_{Fe}^o (foil), was measured at several temperatures below the melting points of iron and the alloy. These values for I_{Fe}^o (foil) were extrapolated to give the ion intensity I_{Fe}^o of iron at any temperature. This extrapolation was made on the basis of linear relation of $\ln(I_{Fe}T)$ vs. $1/T$ plot and by the use of heats of sublimation and vaporization of pure iron. After the ion intensity measurements from the foil, the temperature of the cell was raised to melt the alloy and the foil together to form an uniform liquid alloy. Then ion intensity of iron from the alloy, $I_{Fe}(\text{alloy})$, was measured at temperatures where the activity was to be determined. Thus obtained I_{Fe}^o and $I_{Fe}(\text{alloy})$ can be regarded as measured in the same cell and under the same condition, therefore values for h are the same in the following equations.

$$p_{Fe}^o = k_{Fe} h I_{Fe}^o T \quad \text{.....(3)}$$

$$p_{Fe}(\text{alloy}) = k_{Fe} h I_{Fe}(\text{alloy}) T \quad \text{.....(4)}$$

Hence, we have

$$a_{Fe} = p_{Fe}(\text{alloy}) / p_{Fe}^o = I_{Fe}(\text{alloy}) / I_{Fe}^o \quad \text{.....(5)}$$

The activities of Ta and Nb in the alloys can be derived by the integration of the Gibbs-Duhem equation.

From Eq. (4), we have

$$\ln(I_i T) = -\Delta H_i^o / RT + C \quad \text{.....(6)}$$

where, ΔH_i^o : enthalpy of vaporization of i
 C : a constant.

The plot of $\ln(I_i T)$ against $1/T$ yielded an almost straight line.

In all these measurements of ion intensity, the attainment of the equilibrium in the cell was confirmed by observing constant ion intensity lasting at least 10 min after the temperature was fixed.

2.4. Ion Intensity Thermal Analysis

Differentiation of Eq. (6) gives

$$dI_i / I_i = (\Delta H_i^o / RT - 1) dT / T \quad \text{.....(7)}$$

This equation relates the relative change in the temperature to the relative change in the ion intensity. In the case of iron, for instance, ΔH_{Fe}^o is nearly equal to 380 kJ/mol and at about 1 900 K, the value in the

parentheses in the right hand side of the Eq. (7) made about 23. That is the relative change in the ion intensity is 23 times larger than the relative change in the temperature. On the other hand, the relative change in the electromotive force of a thermocouple is only 1.4(W/W-26%Re), 1.8(Pt-6%Rh/Pt-30%Rh) and 1.4(Pt/Pt-13%Rh) times larger than the relative temperature change. This means that the ion intensity is as more than ten times sensitive as the thermocouple. Ion intensity can be used in thermal analysis of alloys. Continuous recording of the ion intensity of iron, during heating or cooling of the cell at a constant rate, yields a heating or cooling curve of the ion intensity. On the ion intensity curve, suspension of temperature change during a transformation is reflected clearly.

In case that a sample undergoes a transformation in the experimental temperature range, it is obvious from Eq. (6) that the value of the slope, $-\Delta H_i^*/R$, of the $\ln(I_{Fe}T)$ vs. $1/T$ plot is different with different phases. Thus in principle, it is possible to determine the transformation temperature from the intersection of two lines, but this method is sensitive to the error in the determination of slopes of two lines.

2.5. Metallographic Study

Samples of several compositions, about 2 g each, contained respectively in alumina crucibles were heated in purified Ar+5% H_2 atmosphere for 21.6 to 43.2 ks and quenched into water. The samples were studied with microscope, EPMA and X-ray diffractometry.

Phases exist between liquid iron and solid Ta were also confirmed with a Fe-Ta diffusion couple. A Ta rod was inserted in the liquid iron contained in an alumina crucible, heated for 32.4 ks at 1873 K and quenched into water. The interface of liquid iron and solid Ta was examined with EPMA.

3. Experimental Results

3.1. Fe-Ta Alloys

An example of the results of the ion intensity measurements is given in the form of $\ln(I_{Fe}T)$ vs. $1/T$ in Fig. 1. A relation for pure solid iron is drawn through the data obtained from the measurements with iron foil at lower temperatures and is extrapolated to higher temperature. Linear behavior of the $\ln(I_{Fe}T)$ vs. $1/T$ relations for pure iron and alloy is observed in every single-phase or two-phase region. The breaks on the curve correspond to the invariant reactions. Typical behavior of the ion intensity of iron with time during the ion intensity thermal analysis is shown in Fig. 2. It is clear in Fig. 2 that when the alloy undergoes an invariant reaction, although the heating power increases steadily, the ion intensity holds constant value until the reaction finishes, indicating that the temperature of the sample does not change.

The results of the ion intensity measurements and the activity of iron derived at 1873 K are shown in Table 1. Ion intensity data are given in the form of

Heat No. 27

Fig. 1. Relation between $\ln(I_{Fe}T)$ and $1/T$ for the Fe-Ta alloy.

Heat No. 21

Fig. 2. Ion intensity thermal analysis for the Fe-Ta alloy.

Eq. (6) for a temperature range including 1873 K. In Table 1, the temperatures of an invariant reaction detected through the ion intensity thermal analysis are indicated in the last column when they were observed.

An invariant reaction was detected with alloys below 29.7 at% Ta and the reaction temperature was found to be 1714 ± 2 K. This temperature is in good agreement with the $L = \delta\text{-iron} + \epsilon\text{-Fe}_2\text{Ta}$ eutectic temperature given in the Kubaschewski's phase diagram.⁵⁾ In runs with alloys over 29.7 at% Ta, no invariant reactions were detected in the experimental temperature range up to about 1890 K.

The secondary electron images of some of Fe-Ta alloys quenched from 1873 K are shown in Fig. 3. As to the sample shown by Fig. 3(a), deformation of shape of the specimen was observed after the heat treatment, which indicated the alloy melted partially. Fig. 3(d) shows the interface of the Fe-Ta diffusion couple. Phases of liquid iron alloy L , ϵ -Fe₂Ta, μ -FeTa and Ta solid solution (Ta) appeared in the above named order. Phases appeared in the alloys at 1873 K which were identified through heat treatment and metallographic study are shown in Table 2. The compositions obtained with EPMA of phases observed in the two-phase samples are shown in Table 3. These values give the equilibrium phase boundaries at 1873 K. The composition of the liquid iron alloy in equilibrium with ϵ phase could not be determined because of microsegregation observed in the liquid phase.

Activity of iron at 1873 K determined through Eq. (5) is shown in Fig. 3. As no bending was observed on the $\ln(I_{Fe}T)$ vs. $1/T$ lines for first 6 runs in Table 1, alloys below 0.156 at% Ta were liquid at 1873 K. Judging from the precision of the data, the liquid iron solution was assumed to obey Raoult's law. The liquidus composition of ϵ -phase at 1873 K was determined as the intersection of the Raoult's line and a horizontal activity line for the $L+\epsilon$ two-phase region at $a_{Fe}=0.832$, which is the mean value of next four

Heat No.	Molar fraction of Ta	Temp. range (K)	Relation	
			Pure	
			Solid	
			-A	B
9	0.048	1746-1921	4.679	36.63
34	0.054	1625-1875	4.534	36.31
12	0.094	1751-1927	4.675	36.64
32	0.152	1610-1899	4.593	36.36
21	0.153	1630-1942	4.585	36.11
31	0.156	1650-1898	4.698	36.63
25	0.239	1640-1966	4.684	37.49
22	0.244	1658-1980	4.677	37.07
27	0.255	1639-1989	4.614	36.64
33	0.297	1626-1904	4.627	36.83
17	0.319	1629-1868	4.734	37.17
50	0.404	1752-1879	4.654	37.11
49	0.406	1736-1909	4.642	36.96
47	0.436	1751-1859	4.639	36.11
51	0.444	1769-1900	4.554	35.60
48	0.606	1774-1915	4.674	36.90
53	0.727	1746-1909	4.509	35.88
55	0.775	1706-1877	4.757	37.96
54	0.810	1762-1905	4.667	37.46
56	0.828	1701-1866	4.565	36.28

Ion intensity equation is given only for the phases stable at

A: Fe B: ϵ (Fe₂Ta)
C: μ (FeTa) D: Ta
(a) 25 at% Ta (8 h + W.Q.)
(b) 46 at% Ta (10 h + W.Q.)
(c) 64 at% Ta (10 h + W.Q.)
(d) Diffusion couple (9 h + W.Q.)

Fig. 3. Microstructure of the Fe-Ta alloys at 1873 K.

Table 1. Experimental results for Fe-Ta alloy.

between ion intensity of iron I_{Fe} and temperature T . $\ln(I_{Fe}T)=A\ 10^4/T+B$										Activity of iron at 1 873 K	Temp. of reaction $\delta+\epsilon=L$ (K)
iron		Alloy									
Liquid		Liquid		Liq. + ϵ		$\epsilon + \mu$		$\mu + (Ta)$			
$-A$	B	$-A$	B	$-A$	B	$-A$	B	$-A$	B		
4.334	34.73	4.308	34.56							0.969	
4.334	35.21	4.310	35.03							0.949	1 713
4.334	34.76	4.326	34.63							0.916	
4.334	34.93	3.987	32.91							0.846	1 713
4.334	34.72	4.407	34.90							0.811	1 715
4.334	34.61	4.102	33.25							0.886	1 717
4.334	35.56			4.515	36.33					0.822	1 716
4.334	35.17			4.231	34.46					0.852	1 713
4.334	35.09			4.326	34.32					0.797	1 713
4.334	35.21			4.375	35.28					0.862	
<div><div>ϵ</div><div>4.22234.09</div></div>											
4.328	34.93									0.760	
4.335	35.35					5.282	39.52			0.412	
4.335	35.27					6.106	43.86			0.421	
4.335	34.44					5.743	41.09			0.420	
4.335	34.39					5.350	39.03			0.459	
4.335	35.03							4.653	35.01	0.179	
4.335	34.92							4.927	36.44	0.194	
4.335	35.63							4.879	37.14	0.248	
4.335	35.63							4.817	35.99	0.109	
4.328	34.97							4.915	36.44	0.189	

Ta as the standard state is 0.75 ± 0.15 . A value of 0.31 ± 0.07 for the activity coefficient of Ta, $\gamma_{\text{Ta}}^{\circ}(l)$, with liquid Ta as the standard is calculated by using the entropy of melting $\Delta S_m = 9.6 \text{ J/(mol K)}$ and melting point $T_m = 3278 \text{ K}$ of Ta.⁶⁾

Thermodynamic values for Fe-Ta alloy are tabulated in Table 4.

3.2. Fe-Nb System

An example of the ion intensity measurement of a Fe-Nb alloy is given in the form of $\ln(I_{\text{Fe}}T)$ vs. $1/T$ in Fig. 5. As the eutectic temperature of Fe-Nb alloy is at 1643 K which is 70 K below the eutectic point of Fe-Ta alloy, the iron foil was kept away from

the alloy specimen by a step in the cell in order to raise the upper limit of the temperature range for the measurements with the foil. This is shown schematically in Fig. 5. The experimental results and the activity of iron calculated at 1873 K are given in Table 5.

The temperatures of invariant reactions studied by the ion intensity thermal analysis agreed with the phase diagram given by Kubaschewski.⁵⁾ The activity curves were drawn according to the phase boundaries given in the Kubaschewski's phase diagram in Fig. 6. The standard states for activities are liquid iron and solid Nb, respectively. Slight negative deviation is observed on the activity of iron in

Table 4. Thermodynamics of Fe-Ta alloy at 1873 K .

X_{Ta}	Phase	Fe(l)=Fe(in alloy)			Ta(s)=Ta(in alloy)		
		a_{Fe}	γ_{Fe}	$\Delta G_{\text{Fe}}^{\text{M}}$ (J/mol)	a_{Ta}	γ_{Ta}	$\Delta G_{\text{Ta}}^{\text{M}}$ (J/mol)
0	L	1	1	0	0	0.75	—
0.1		0.9	1	-1 630	0.075	0.75	-40 200
0.168		0.832 ± 0.04	1	-2 850	0.126 ± 0.025	0.75	-32 200
0.294	ϵ	0.832 ± 0.04	1.18	-2 850	0.126 ± 0.025	0.43	-32 200
0.405		0.427 ± 0.03	0.72	-13 300	0.457 ± 0.029	1.13	-12 100
0.503	μ	0.427 ± 0.03	0.86	-13 300	0.457 ± 0.029	0.91	-12 100
0.591		0.183 ± 0.07	0.45	-26 500	0.936 ± 0.006	1	-1 050
0.936	(Ta)	0.183 ± 0.07	2.84	-26 500	0.936 ± 0.006	1	-1 050
1		0	2.84	—	1	1	0

Table 5. Experimental results for Fe-Nb alloy.

Heat No.	Molar fraction of Nb	Temp. range (K)	Relation between ion intensity of iron I_{Fe} and temperature T .								
			Pure Fe						Alloy		
			Solid		Liquid				L		$\epsilon +$
			-A	B	-A	B	-A	B	-A	B	
8	0.048	1 613-1 884	4.960	37.92	4.479	35.26	4.490	35.28			
4	0.091	1 568-1 864	4.442	35.26	4.006	32.70	3.961	32.32			
31	0.094	1 570-1 884	4.538	35.48	4.328	34.31	4.220	33.63			
59	0.139	1 573-1 874	4.610	37.05	4.335	35.53	4.204	34.64			
58	0.144	1 558-1 853	4.616	37.23	4.335	35.69	4.222	34.92			
11	0.192	1 634-1 888	4.743	36.19	4.379	34.18	3.816	30.94			
14	0.234	1 593-1 878	4.712	36.90	4.328	34.78	3.969	32.55			
12	0.242	1 601-1 893	4.510	35.14	4.328	34.13	3.666	30.35			
32	0.298	1 592-1 873	4.660	35.77	4.328	33.94			4.199	32.90	
											ϵ
											4.410
											33.14
15	0.320	1 680-1 887	4.608	34.86	4.328	33.31					3.897
30	0.370	1 720-1 871	4.619	35.06	4.328	33.45					4.467
29	0.384	1 722-1 870	4.556	35.04	4.328	33.78					3.188
20	0.388	1 684-1 916	4.514	36.02	4.328	34.99					3.626
19	0.394	1 716-1 886	4.527	36.84	4.328	35.74					
16	0.502	1 708-1 915	4.702	35.99	4.328	33.92					
26	0.548	1 697-1 879	4.645	36.75	4.328	35.00					
23	0.596	1 744-1 858	4.682	37.16	4.328	35.21					
24	0.671	1 748-1 900	4.731	37.30	4.328	35.07					
25	0.760	1 778-1 891	4.698	36.73	4.328	34.68					
27	0.856	1 753-1 859	4.609	36.44	4.328	34.89					

Ion intensity equation is given only for the phases stable at 1873 K .

the liquid iron alloy. For the sake of analytical expression, quadratic formalism was assumed through experimental points in the liquid iron alloy. The

activity coefficient γ_{Fe} was given by

$$\ln \gamma_{\text{Fe}} = -0.71(1-x_{\text{Fe}})^2 \quad \text{.....(8)}$$

where, x_{Fe} : atomic fraction of iron.

Data in the two-phase regions were averaged respectively and these values were connected by straight lines in the single-phase regions. Henry's law was assumed for Nb solid solution (Nb).

The activity coefficient of Nb in the infinitely dilute solution in liquid iron with solid Nb as the standard $\gamma_{\text{Nb}}^{\circ}(\text{s})$ is 0.44 ± 0.06 . A value of 0.26 ± 0.03 for the activity coefficient with liquid Nb as the standard $\gamma_{\text{Nb}}^{\circ}(\text{l})$ is calculated by using melting point of Nb, 2740 K and entropy of melting ΔS_m 9.6 J/(mol K).⁶⁾ The interaction parameter $\epsilon_{\text{Nb}}^{\text{Nb}}$ derived from the quadratic formalism assumption is 1.42.

Thermodynamic values are tabulated in Table 6.

4. Discussion

Several phase diagrams have been reported of Fe-Ta alloy.^{5,7,8)} The eutectic reaction, $L = \delta\text{-Fe} + \epsilon\text{-Fe}_2\text{Ta}$ is almost confirmed to occur at about 1700 K, while the types and temperatures of reaction among $\epsilon\text{-Fe}_2\text{Ta}$, $\mu\text{-FeTa}$ and (Ta) are left undefined.

The temperature 1714 ± 2 K of the eutectic reaction $L = \delta + \epsilon$ obtained in the present study agrees well with the reported values. In the runs with alloys of which composition was in the two-phase regions, $\epsilon + \mu$ and $\mu + (\text{Ta})$, no invariant reactions were detected within the experimental temperature range. This means that neither eutectic reaction shown by dashed lines at about 1820 K for ϵ and μ nor that at about 1950 K for μ and (Ta) in the Kubaschewski's diagram occur at least up to about 1890 K. The composition 40.5 and 59.1 at% Ta of the phase boundaries of ϵ with μ and μ with (Ta) found in the present study are a little higher than those shown in the Kubaschewski's diagram.

From the composition dependence of activities shown in Fig. 4, it is obvious that there are two intermediate phases. Thermodynamic property measured at high temperature supported the results obtained from the quenched sample.

The value for $\gamma_{\text{Ta}}^{\circ}(\text{l})$ at 1873 K was reported by

Heat No. 14

Fig. 5. Relation between $\ln(I_{\text{Fe}}T)$ and $1/T$ for the Fe-Nb alloy.

$\ln(I_{\text{Fe}}T)=A\ 10^4/T+B$					Activity of iron at 1 873 K				
L'		$L'+\zeta$		$\zeta+(\text{Nb})$					
B	$-A$	B	$-A$	B					
					0.962				
					0.869				
					0.902				
					0.826				
					0.846				
					0.791				
					0.731				
					0.782				
					0.704				
					0.545				
30.20					0.387				
33.52					0.367				
27.88					0.359				
30.97					0.360				
<table><tr><th colspan="2">L'</th></tr><tr><td>4.704</td><td>34.85</td></tr></table>					L'		4.704	34.85	0.340
L'									
4.704	34.85								
	4.348	33.82			0.276				
		<table><tr><th colspan="2">ζ</th></tr><tr><td>4.271</td><td>32.55</td></tr></table>		ζ		4.271	32.55		0.258
ζ									
4.271	32.55								
		3.819	30.76	0.203					
		3.870	30.61	0.197					
		4.050	31.90	0.222

Fig. 6. Activities in the Fe-Nb alloy at 1873 K.

Table 6. Thermodynamics of Fe-Nb alloy at 1873 K.

X_{Nb}	Phase	Fe(l)=Fe(in alloy)			Nb(s)=Nb(in alloy)		
		a_{Fe}	γ_{Fe}	$\Delta G_{\text{Fe}}^{\text{M}}$ (J/mol)	a_{Nb}	γ_{Nb}	$\Delta G_{\text{Nb}}^{\text{M}}$ (J/mol)
0	L	1	1	0	0	0.435	—
0.1		0.894	0.993	-1760	0.050	0.498	-46650
0.2		0.777	0.972	-3930	0.113	0.565	-33900
0.265		0.700 ± 0.010	0.953	-5560	0.160 ± 0.024	0.604	-28500
0.32	ϵ	0.700 ± 0.010	1.029	-5560	0.160 ± 0.024	0.500	-28500
0.36		0.369 ± 0.010	0.577	-15500	0.585 ± 0.022	1.63	-8370
0.45	L'	0.369 ± 0.010	0.671	-15500	0.585 ± 0.022	1.30	-8370
0.54		0.278 ± 0.010	0.604	-19900	0.785 ± 0.043	1.45	-3770
0.57	ζ	0.278 ± 0.010	0.647	-19900	0.785 ± 0.043	1.38	-3770
0.64		0.208 ± 0.011	0.578	-24400	0.95 ± 0.011	1.48	-790
0.95	(Nb)	0.208 ± 0.011	4.16	-24400	0.95 ± 0.011	1	-790
1		0	4.16	—	1	1	0

Morita *et al.*⁹⁾ as 0.04, and by Buzek¹⁰⁾ as 0.025. Disagreement between these values and the present result is rather large. Morita *et al.* who studied the solubility of nitrogen in liquid Fe-Ta alloys and the precipitation of TaN, calculated the value for $\gamma_{\text{Ta}}^{\circ}(l)$ combining their value for the standard free energy of precipitation of TaN with several known free energy data. Morita *et al.* pointed out in their paper that combination of several thermodynamic values may cause accumulation of errors and the precision of the obtained value might be poor.

The values 0.20,¹¹⁾ 0.33,¹²⁾ 0.24,¹³⁾ 0.175¹⁰⁾ and 0.92¹⁴⁾ were reported for the activity coefficient of Nb, $\gamma_{\text{Nb}}^{\circ}(l)$ at 1873 K. These values were determined in the studies on Nb-O and Nb-N saturated or non-saturated equilibrium in the liquid iron. The present result is well in accord with the previous values within the experimental precision. The values for the activity coefficient $\gamma^{\circ}(l)$ are shown for the elements in the IV-th to VI-th groups and 4th to 6th periods in the periodic table in Fig. 7. Above quoted data for Ta and Nb are all plotted, data for W and Mo were determined with the Knudsen cell mass spectrometry²⁾ and the other data are given in the Steelmaking Data Sourcebook.¹⁵⁾ From the position of the data, present result for $\gamma_{\text{Ta}}^{\circ}(l)$ is more acceptable.

As to the interaction parameter, for $\epsilon_{\text{Ta}}^{\text{Ta}}$, values 1.8,¹⁰⁾ 14.9⁹⁾ and 71¹³⁾ and for $\epsilon_{\text{Nb}}^{\text{Nb}}$, values 3.2,¹¹⁾ 1.0,¹²⁾ -0.7¹⁶⁾ and -85¹⁴⁾ were reported at 1873 K. As the data scatter very widely, comparison among these data is difficult to be made.

In addition to the runs shown in Table 1, several runs were made on the samples of which composition was thought to be in a solid single-phase region. These runs turned out to give scattering results. It was found that the equilibrium in the sample of which composition was in a liquid phase region or liquid-solid two-phase region was attainable rather quickly. Even without liquid phase, provided the sample is in a two-phase region, for instance $\epsilon + \mu$ or $\mu + (\text{Ta})$, phase equilibrium turned out to be attainable within relatively short time and reproducible measurements were possible. On the other hand, with samples of

Fig. 7. Periodicity of the activity coefficient.

single solid phase, it was difficult to carry out reproducible measurements. This was observed also in the study on the Fe-W alloys.²⁾ This is because any change in the composition of the two-phase alloy may be buffered by the change in the amount of the co-existing phases in the surface layer of the sample and the composition of the respective phases do not have to change. In addition, the activity changes rather steeply in a single-phase region, while the activity is constant in the two-phase region. The upright phase boundaries may also contribute to the stability of the measurements in the two-phase region.

5. Conclusion

The activity of iron in the Fe-Ta and Fe-Nb alloys at 1873 K was determined by means of the Knudsen cell mass spectrometer. A modified internal standard method was utilized, in which a piece of iron foil placed on the surface of the sample in the cell served

as an internal standard. The activities of Ta and Nb were derived from that of iron by integrating the Gibbs–Duhem equation. The activity coefficients in the infinitely dilute solution and the interaction parameters are as follows.

$$\gamma_{\text{Ta}}^{\circ}(s) = 0.75 \pm 0.15, \gamma_{\text{Ta}}^{\circ}(l) = 0.31 \pm 0.06, \epsilon_{\text{Ta}}^{\text{Ta}} = 0$$

and

$$\gamma_{\text{Nb}}^{\circ}(s) = 0.44 \pm 0.06, \gamma_{\text{Nb}}^{\circ}(l) = 0.26 \pm 1.03, \epsilon_{\text{Nb}}^{\text{Nb}} = 1.42$$

at 1 873 K.

Invariant reactions appeared in the Fe–Ta alloy system were investigated by means of the ion intensity thermal analysis, in which the ion intensity represents the temperature of the sample. Heat treatment and metallographic study of Fe–Ta alloys was also carried out. The existence of two intermediate phases ϵ -Fe₂Ta and μ -FeTa was confirmed. Neither the invariant reaction $L = \epsilon + \mu$ nor $L = \mu + (\text{Ta})$ was detected within the experimental temperature range up to 1 890 K.

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