

## Phase Equilibria in the Fe-Nb-O System at 1200°C

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Received May 12, 1986; in revised form November 3, 1986

Phase equilibria in the system Fe-Nb-O at 1200°C are established by changing the oxygen partial pressure from 0 to  $-15.00$  in  $\log(P_{O_2}/\text{atm})$  and are represented in the  $\text{Nb}_2\text{O}_5$ -Fe- $\text{Fe}_2\text{O}_3$  system. In this system,  $\text{FeNbO}_4$ ,  $\text{FeNb}_2\text{O}_6$ ,  $\text{Fe}_4\text{Nb}_2\text{O}_9$ , niobium-iron spinel, and  $\text{NbO}_2$  phases appear and have non-stoichiometric compositions. Lattice constants of the compounds and the solid solutions are determined and discussed with respect to the oxygen partial pressure dependency and to the coexistence of the other compounds. The lattice constant of the spinel solid solution increases with the increasing of the content of " $\text{Fe}_7\text{Nb}_2\text{O}_{12}$ ." The standard Gibbs energies of the reactions appearing in the phase diagram are calculated. © 1987 Academic Press, Inc.

### Introduction

Subsolidus phase equilibria of the oxides in the system Fe-Nb-O were experimentally determined at 1180°C, 1 atm, and variable oxygen partial pressures by Turnock (1). As the quenched method was adopted, details of the phase diagram were not clear and the oxygen partial pressures in equilibrium with three solid phases still had large errors. No thermochemical data were given either.

The objectives of the present study are to establish the phase diagram at 1200°C by the thermogravimetry and to calculate the standard Gibbs energy of the reactions found in the diagram. The  $\text{NbO}_2$ - $\text{Nb}_2\text{O}_5$  system is reinvestigated at 1200°C in relation to the Fe-Nb-O system.

### Experimental

Analytical-grade  $\text{Fe}_2\text{O}_3$  (99.9%) and  $\text{Nb}_2\text{O}_5$  (99.9%) are used as starting mate-

rials. Both oxides were previously dried at 900° and 1200°C in air, respectively.

Desired ratios of  $\text{Nb}_2\text{O}_5/\text{Fe}_2\text{O}_3$  are obtained by mixing thoroughly in an agate mortar under ethyl alcohol. The mixtures thus obtained are calcined at 1200°C at several times during the intermediate mixing and are treated by the same procedures as in the previous paper (2). A 2- to 6-g sample is used considering the content of the  $\text{Fe}_2\text{O}_3$  in the mixtures. The apparatus and procedures for controlling the oxygen partial pressures and keeping a constant temperature, the method of the thermogravimetry, and the criterion for the establishment of equilibrium are the same as those described in the previous papers (2-4).

The chemical composition of the niobium-iron spinels is volumetrically determined.  $\text{Fe}^{2+}$  and total iron content are determined by  $\text{KMnO}_4$  standard solution.  $\text{Nb}_2\text{O}_5$  content is indirectly obtained as the difference between the weight of  $\text{FeO} + \text{Fe}_2\text{O}_3$  and the total weight.

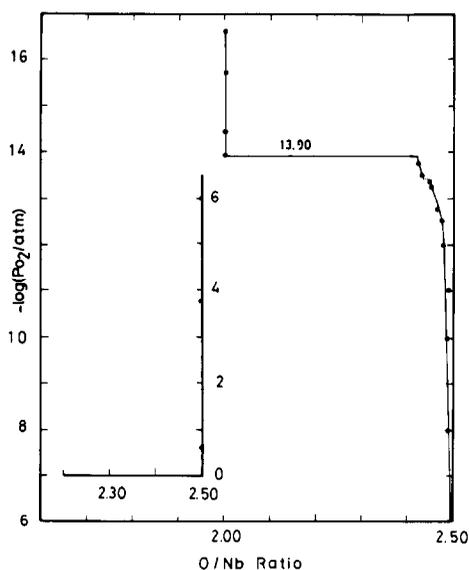


FIG. 1. The relationship between the composition, O/Nb, and the oxygen partial pressure in the  $\text{Nb}_2\text{O}_4$ - $\text{Nb}_2\text{O}_5$  system at 1200°C.

## Results and Discussion

### (1) Phase Equilibria

#### $\text{NbO}_2$ - $\text{Nb}_2\text{O}_5$ System

Many investigations of the binary system  $\text{NbO}_2$ - $\text{Nb}_2\text{O}_5$  at high temperatures have been published (5-12). Kovba *et al.* (5) reported the existence of a single phase between  $\text{NbO}_{2.454}$  and  $\text{NbO}_{2.474}$  at 1100°-1200°C, and only  $\text{Nb}_2\text{O}_{5-x}$  was found at 900°-1200° (6). At 1300° and 1400°C five discrete compounds,  $\text{Nb}_{12}\text{O}_{29}$ ,  $\text{Nb}_{22}\text{O}_{54}$ ,  $\text{Nb}_{47}\text{O}_{116}$ ,  $\text{Nb}_{25}\text{O}_{62}$ , and  $\text{Nb}_{53}\text{O}_{132}$ , were observed (11).

In Fig. 1 the relationships between the composition of the sample, O/Nb ratio, and the oxygen partial pressure,  $\log(P_{\text{O}_2}/\text{atm})$ , are shown. The  $\text{Nb}_2\text{O}_5$  phase shows nonstoichiometric compositions. The composition  $\text{Nb}_2\text{O}_5$  is maintained by keeping  $-\log P_{\text{O}_2}$  between 0 and 4.00. From  $-\log P_{\text{O}_2} = 4.00$  to 12.00, the composition is represented by the equation  $X_{\text{O}}/X_{\text{Nb}_2\text{O}_5} = 0.0045$

$\log P_{\text{O}_2} + 0.018$ . Here,  $X_{\text{O}}$  and  $X_{\text{Nb}_2\text{O}_5}$  are the mole fractions of the subscripted species in the solid solution. From 12.00 to 13.40 in  $-\log P_{\text{O}_2}$ , the composition is represented by the equation  $X_{\text{O}}/X_{\text{Nb}_2\text{O}_5} = -0.02667(\log P_{\text{O}_2})^2 - 0.6334 \log P_{\text{O}_2} - 3.811$ .

The existence of a nonstoichiometric intermediate phase,  $\text{Nb}_2\text{O}_{4.84}$ , is found from 13.40 to 13.90 in  $-\log P_{\text{O}_2}$ . This phase already has been seen at higher temperatures (7-10). The composition is represented  $X_{\text{O}}/X_{\text{Nb}_2\text{O}_{4.84}} = 0.05 \log P_{\text{O}_2} + 0.695$ . The powder X-ray patterns of the samples which are made at  $\log P_{\text{O}_2} = -13.00$  and  $-13.75$  are very similar. This was already pointed out at 1350° to 1400°C by Brauer (13) and at 1300°C by Lavrent'ev *et al.* (14).

As shown in Fig. 1, the  $\text{NbO}_2$  phase is stoichiometric within experimental errors. But Schäffer *et al.* (7) and Marucco *et al.* (9) reported  $\text{NbO}_{2.024}$  at 1300°C and  $\text{NbO}_{2.0060}$  at 1100°C, respectively.

#### $\text{Fe-Nb-O}$ System

Ten samples with  $\text{Nb}_2\text{O}_5/\text{Fe}_2\text{O}_3$  mole ratios of 85/15, 8/2, 75/25, 7/3, 1, 45/55, 3/7, 2/8, 1/9, and 5/95 were prepared for use in thermogravimetry.

In Fig. 2 the relationships between the oxygen partial pressure,  $-\log(P_{\text{O}_2}/\text{atm})$ , on the ordinate and the weight change,  $W_{\text{O}_2}/W_{\text{T}}$ , on the abscissa are shown with six representative samples, 8/2 (a), 7/3 (b), 1 (c), 2/8 (d), 1/9 (e), and 5/95 (f). Here,  $W_{\text{O}_2}$  is the weight decrease of the samples from the reference weight in 1 atm  $\text{O}_2$  and  $W_{\text{T}}$  is the total weight decrease of the sample which might be expected if all the  $\text{Fe}_2\text{O}_3$  in the sample changed into Fe metal. From Fig. 2, abrupt weight changes are observed at 14.13, 12.53, 12.27, (11.94), 11.00, 8.17, 6.22, 3.83, and 3.50 in  $-\log P_{\text{O}_2}$ . These values correspond to the oxygen partial pressures in equilibrium with the three solid phases and are shown in Fig. 3. The value in parentheses, which is that in equilibrium

with Fe + "FeO" at 1200°C, is tentative. Turnock already pointed out that a liquid phase appears in this region. As the exact isothermal section including the liquid phase could not be established, discussion about this region will be omitted.

The identification of phases is carried out with samples of different starting materials at different conditions of oxygen pressure. Some of these results, obtained by powder X-ray diffractometry with  $\text{FeK}\alpha$  radiation, are shown in Table I. Tokizaki *et al.* (15) reported that the crystal form of  $\text{FeNb}_2\text{O}_6$  depends upon the conditions of the preparation,  $\log(\text{CO}_2/\text{H}_2)$ , and temperature. The quench samples prepared at the different conditions of oxygen partial pressure show the same columbite-type pattern in the present study.

Based upon the above results from the thermogravimetry and the phase identification, a phase diagram was drawn and is shown in Fig. 3. The diagram is similar to that of Turnock (1) at 1180°C. Dashed lines are the iso-oxygen partial pressure lines in two-phase fields and values are indicated on each line. There are eight phases,  $\text{Nb}_2\text{O}_5$  (E),  $\text{Nb}_2\text{O}_4$  (F),  $\text{FeNbO}_4$  (B),  $\text{FeNb}_2\text{O}_6$  (C),  $\text{Fe}_4\text{Nb}_2\text{O}_9$  (D), "FeO" (W), niobium-iron spinel (M), and  $\alpha$ -Fe. These all have nonstoichiometric compositions except for  $\alpha$ -Fe and  $\text{Fe}_2\text{O}_3$ . The composition of  $F_2$ , being richest in  $\text{FeNb}_2\text{O}_6$ , is  $\text{Fe}_{0.28}\text{Nb}_{0.72}\text{O}_2$ , which is comparable to  $\text{Fe}_{0.27}\text{Nb}_{0.73}\text{O}_2$  at 1180°C. The niobium-iron spinel solid solution also has a wide range of composition, its end composition being  $\text{Fe}_{2.43}\text{Nb}_{0.54}\text{O}_{4.00}$ ,  $\sim 80$  mole% " $\text{Fe}_7\text{Nb}_2\text{O}_{12}$ ," which is also identical to that at 1180°C. The small difference in temperatures does not affect these compositions.

Turnock (1) showed that  $\text{Fe}_2\text{O}_3$  has a nonstoichiometric range, but it cannot be found explicitly because of the sluggish reaction and  $\log P_{\text{O}_2} = -3.50$  is different from  $-2.94$  at which  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  coexist in equilibrium at 1200°C. Compositions of  $C_4$

TABLE I  
IDENTIFICATION OF PHASE

$\text{Nb}_2\text{O}_5/\text{Fe}_2\text{O}_3$ (mole ratio)	$-\log P_{\text{O}_2}$ (atm)	Time (hr)	Phase
85/15	15.00	8	$\text{NbO}_2$
8/2	12.50	8	$\text{NbO}_2$ + $\text{Nb}_2\text{O}_5$
75/25	14.50	10	$\text{NbO}_2$
	13.00	14	$\text{NbO}_2$
	12.20	15	$\text{Nb}_2\text{O}_5$ + $\text{FeNb}_2\text{O}_6$
	4.00	21	$\text{Nb}_2\text{O}_5$ + $\text{FeNb}_2\text{O}_6$
	3.60	19	$\text{Nb}_2\text{O}_5$ + $\text{FeNbO}_4$
	0.68	7	$\text{Nb}_2\text{O}_5$ + $\text{FeNbO}_4$
7/3	14.00	7	$\text{Nb}_2\text{O}_5$ + $\text{FeNb}_2\text{O}_6$
45/55	15.00	8	Fe + $\text{NbO}_2$
	14.50	10	Fe + $\text{NbO}_2$
	14.00	7	Fe + $\text{FeNb}_2\text{O}_6$
	13.00	14	Fe + $\text{FeNb}_2\text{O}_6$
	12.00	15	$\text{Fe}_4\text{Nb}_2\text{O}_9$ + $\text{FeNb}_2\text{O}_6$
	8.30	22	$\text{Fe}_4\text{Nb}_2\text{O}_9$ + $\text{FeNb}_2\text{O}_6$
	8.00	18	Sp + $\text{FeNb}_2\text{O}_6$
	6.50	23	Sp + $\text{FeNb}_2\text{O}_6$
	6.00	23	Sp + $\text{FeNbO}_4^a$
	3.60	19	Sp + $\text{FeNbO}_4$
	2.60	12	$\text{FeNbO}_4$ + $\text{Fe}_2\text{O}_3$
	0.68	7	$\text{FeNbO}_4$ + $\text{Fe}_2\text{O}_3$
3/7	12.30	15	Fe + $\text{Fe}_4\text{Nb}_2\text{O}_9$
	11.90	15	FeO + $\text{Fe}_4\text{Nb}_2\text{O}_9$
	11.20	14	FeO + $\text{Fe}_4\text{Nb}_2\text{O}_9$
	10.90	15	Sp + $\text{Fe}_4\text{Nb}_2\text{O}_9$
	8.30	22	Sp + $\text{Fe}_4\text{Nb}_2\text{O}_9$
1/9	12.30	15	Fe + $\text{Fe}_4\text{Nb}_2\text{O}_9$
	11.90	15	FeO + $\text{Fe}_4\text{Nb}_2\text{O}_9$
5/95	9.50	15	FeO + Sp

<sup>a</sup> Tetragonal.

and  $C_5$  and of  $B_2$  and  $B_3$  are not identical, while those in Turnock (1) were illustrated as if these pairs were identical. A compound  $\text{FeNb}_{11}\text{O}_{29}$ , of orthorhombic type, has been reported by Turnov *et al.* (16) and Brunner and Gruhn (17). According to the present results, the  $\text{Nb}_2\text{O}_5$  phase has nonstoichiometric composition not only on the  $\text{Nb}_2\text{O}_4$  side but also on the  $\text{FeNbO}_4$  side, where the end composition is  $\text{FeNb}_{11}\text{O}_{29}$  ( $E_1$ ).

In Table II the compositions, symbols, and stability ranges in the oxygen partial pressure of the solid solutions, are tabulated together with activities of each component in the solid solution. The activity of the  $\text{Fe}_4\text{Nb}_2\text{O}_9$  component in the solid solution is calculated using the Gibbs-Duhem equation, giving  $X_{\text{O}}/X_{\text{Fe}_4\text{Nb}_2\text{O}_9} = 0.0596 \log$

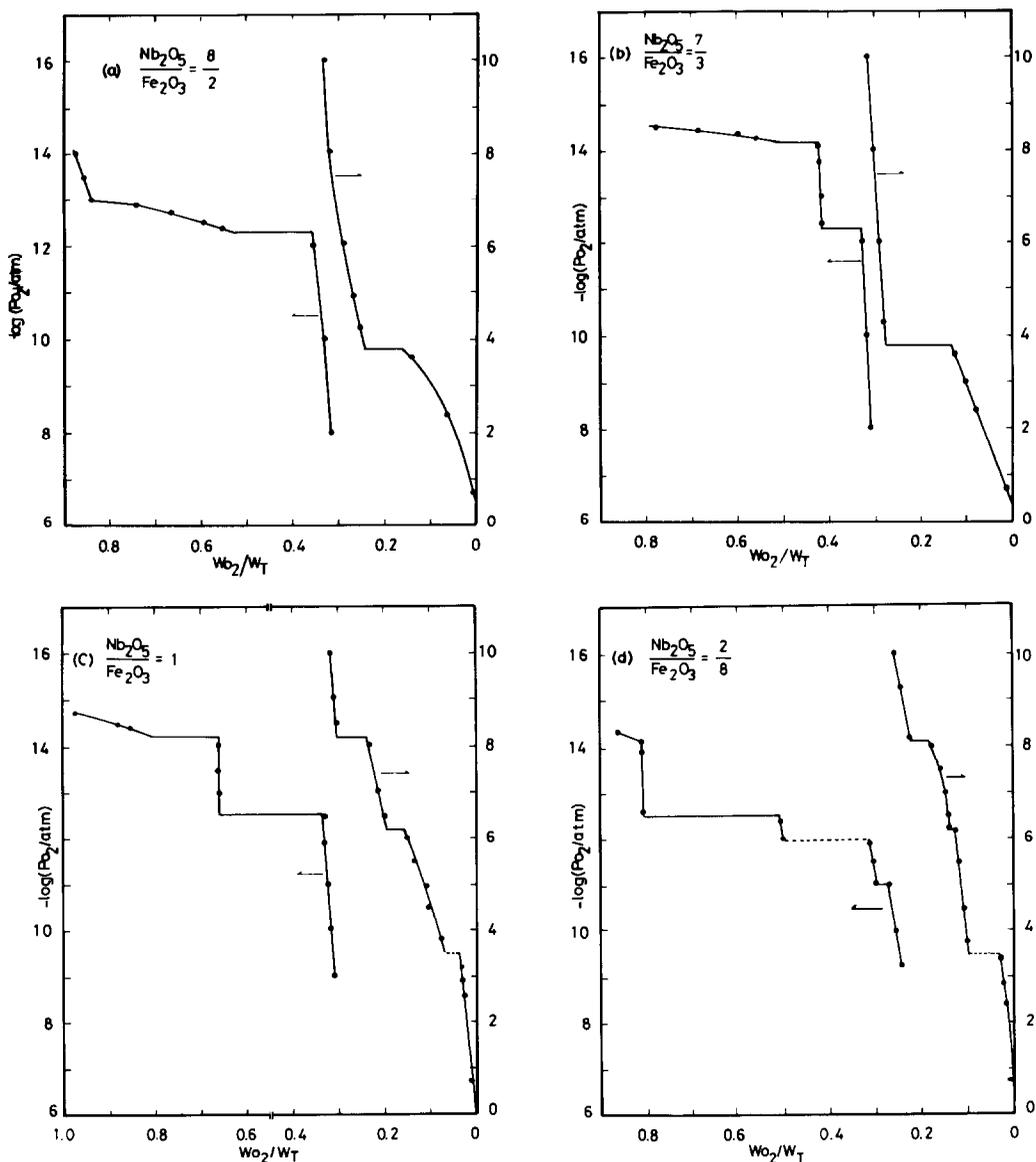


FIG. 2. The relationship between the composition,  $W_{O_2}/W_T$ , and the oxygen partial pressure in the system Fe-Nb-O at 1200°C with ratios of  $Nb_2O_5/Fe_2O_3$  of (a) 8/2, (b) 7/3, (c) 1, (d) 2/8, (e) 1/9, and (f) 5/95.

$P_{O_2} + 0.756$ . The latter equation is derived assuming that the oxygen content in the solid solution changes with the change of the oxygen partial pressure as shown in Table II.

Lattice constants of the compounds are

determined with the aid of the previous data. The values of  $FeNb_2O_6$  still have large errors compared with the previous data; therefore, they are not included in Table III. The lattice constants of  $FeNbO_4$  prepared in air are almost the same and are



TABLE II  
COMPOSITIONS, SYMBOLS, STABILITY RANGES IN  
THE OXYGEN PARTIAL PRESSURES, AND ACTIVITIES  
OF SOLID SOLUTIONS

Component	Composition	Symbol	$-\log P_{O_2}$ (atm)	$\log a_i$
Nb <sub>2</sub> O <sub>5</sub>	Nb <sub>2</sub> O <sub>5,00</sub>	E	0-4.00	0
	FeNb <sub>11</sub> O <sub>29</sub>	E <sub>1</sub>	3.83	—
FeNbO <sub>4</sub>	Nb <sub>2</sub> O <sub>4,95</sub>	E <sub>2</sub>	12.27	-0.079
	FeNbO <sub>4,00</sub>	B	0	—
	Fe <sub>0,95</sub> Nb <sub>1,05</sub> O <sub>4,00</sub>	B <sub>1</sub>	3.50	—
	Fe <sub>0,81</sub> Nb <sub>1,19</sub> O <sub>4,00</sub>	B <sub>2</sub>	3.83	0
FeNb <sub>2</sub> O <sub>6</sub>	Fe <sub>0,79</sub> Nb <sub>1,21</sub> O <sub>4,00</sub>	B <sub>3</sub>	6.22	—
	FeNb <sub>2</sub> O <sub>6,00</sub>	C	14.13	0
	FeNb <sub>2</sub> O <sub>6,00</sub>	C <sub>1</sub>	12.53	0
	FeNb <sub>2</sub> O <sub>6,00</sub>	C <sub>2</sub>	12.27	0
	Fe <sub>1,02</sub> Nb <sub>1,99</sub> O <sub>6,00</sub>	C <sub>3</sub>	8.15	—
	Fe <sub>1,08</sub> Nb <sub>1,95</sub> O <sub>6,00</sub>	C <sub>4</sub>	3.83	—
Fe <sub>4</sub> Nb <sub>2</sub> O <sub>9</sub>	Fe <sub>1,11</sub> Nb <sub>1,90</sub> O <sub>6,00</sub>	C <sub>5</sub>	6.22	—
	Fe <sub>4</sub> Nb <sub>2</sub> O <sub>9,00</sub>	D	12.53	0
	Fe <sub>4</sub> Nb <sub>1,99</sub> O <sub>9,07</sub>	D <sub>1</sub>	(11.94)	-0.0079
	Fe <sub>4</sub> Nb <sub>1,99</sub> O <sub>9,10</sub>	D <sub>2</sub>	11.00	-0.042
	Fe <sub>4</sub> Nb <sub>2,01</sub> O <sub>9,27</sub>	D <sub>3</sub>	8.15	-0.306
Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>2,97</sub> O <sub>4,00</sub>	M <sub>1</sub>	3.50	—
	Fe <sub>2,99</sub> O <sub>4,00</sub>	M <sub>2</sub>	6.22	-0.014
	Fe <sub>3,00</sub> O <sub>4,00</sub>	M	9.14	0
	Fe <sub>2,85</sub> Nb <sub>0,09</sub> O <sub>4,00</sub>	M <sub>3</sub>	8.15	—
	Fe <sub>2,43</sub> Nb <sub>0,54</sub> O <sub>4,00</sub>	M <sub>4</sub>	11.00	—
NbO <sub>2</sub>	Fe <sub>0,28</sub> Nb <sub>0,72</sub> O <sub>2</sub>	F <sub>2</sub>	14.13	—
	Fe <sub>0,28</sub> Nb <sub>0,72</sub> O <sub>2</sub>	F <sub>1</sub>	12.27	—

independent of the coexistence of other compounds, Fe<sub>2</sub>O<sub>3</sub> and FeNb<sub>11</sub>O<sub>29</sub>. This might mean that FeNbO<sub>4</sub> has no large non-stoichiometric range on the FeNb<sub>11</sub>O<sub>29</sub> and Fe<sub>2</sub>O<sub>3</sub> sides. Values for FeNbO<sub>4</sub> prepared at -3.62 atm from the 75/25 sample and at -6.00 atm from the 3/7 sample are well fit not to an orthorhombic but to a rutile structure. Also, values of Fe<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub> and niobium-iron spinel are not affected by the coexistence of another phase at any oxygen partial pressure.

In Table IV the relationship between the lattice constant and the composition of the spinel solid solution is shown together with the conditions of preparation, starting materials, and lattice constants of tantalum-iron spinel. Here,  $X$  means the mole fraction of the assumed Fe<sub>7</sub><sup>2+</sup>Nb<sub>2</sub><sup>5+</sup> (or Ta<sup>5+</sup>)O<sub>12</sub>. These data are plotted in Fig. 4 together with the niobium-iron spinel data reported by Turnock. The present values change linearly with  $X$  up to 0.5 and then slightly

TABLE III  
THE LATTICE CONSTANTS OF THE COMPOUNDS

Compound	Nb <sub>2</sub> O <sub>5</sub> /Fe <sub>2</sub> O <sub>3</sub> (mole ratio)	$-\log P_{O_2}$ (atm)	Coexisting phase	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	Ref.
FeNbO <sub>4</sub>	75/25	0.68	FeNb <sub>11</sub> O <sub>29</sub>	5.004 ± 0.008	5.622 ± 0.006	4.657 ± 0.007	131.1 ± 0.3	Present
	45/55	0.68	Fe <sub>2</sub> O <sub>3</sub>	5.007 ± 0.001	5.622 ± 0.001	4.654 ± 0.001	131.0 ± 0.1	Present
	75/25	3.62	FeNb <sub>11</sub> O <sub>29</sub>	4.723 ± 0.001		3.063 ± 0.003	68.32 ± 0.07	Present
	45/55	3.80	Sp	5.032 ± 0.001	5.647 ± 0.001	4.669 ± 0.001	132.7 ± 0.1	Present
	3/7	6.00	Sp	4.738 ± 0.002		3.058 ± 0.003	68.65 ± 0.09	Present
FeNb <sub>11</sub> O <sub>29</sub>				5.005	5.613	4.647		(16)
	75/25	3.62		28.70 ± 0.03	3.828 ± 0.001	20.618 ± 0.001	2266 ± 3	Present
				28.70	3.829	20.61		(17)
Fe <sub>4</sub> Nb <sub>2</sub> O <sub>9</sub>	45/55	8.50	FeNb <sub>2</sub> O <sub>6</sub>	5.221 ± 0.003		14.245 ± 0.013	336.3 ± 0.5	Present
	2/8	8.50	Sp	5.216 ± 0.003		14.206 ± 0.020	334.7 ± 0.6	Present
	3/7	11.90	FeO	5.224 ± 0.002		14.211 ± 0.007	335.9 ± 0.3	Present
	45/55	12.00	FeNb <sub>2</sub> O <sub>6</sub>	5.221 ± 0.002		14.238 ± 0.009	336.1 ± 0.3	Present
Sp				5.233		14.236		(18)
	3/7	6.00	FeNbO <sub>4</sub>	8.404 ± 0.001			593.5 ± 0.2	Present
	3/7	8.00	FeNb <sub>2</sub> O <sub>6</sub>	8.459 ± 0.001			605.3 ± 0.3	Present
	5/95	8.00	FeNb <sub>2</sub> O <sub>6</sub>	8.451 ± 0.001			603.5 ± 0.1	Present
	2/8	9.50	Fe <sub>4</sub> Nb <sub>2</sub> O <sub>9</sub>	8.551 ± 0.008			625.2 ± 1.8	Present
	5/95	9.50	FeO	8.479 ± 0.001			609.5 ± 0.2	Present
	5/95	10.90	FeO	8.593 ± 0.002			634.5 ± 0.3	Present
2/8	10.90	Fe <sub>4</sub> Nb <sub>2</sub> O <sub>9</sub>	8.592 ± 0.001			634.2 ± 0.1	Present	

TABLE IV  
THE COMPOSITIONS OF NIOBIUM-IRON SPINEL AND TANTALUM-IRON SPINEL AND LATTICE CONSTANTS

Nb <sub>2</sub> O <sub>5</sub> /Fe <sub>2</sub> O <sub>3</sub>	-log P <sub>O<sub>2</sub></sub> (atm)	X <sup>a</sup>	a (Å)	Ta <sub>2</sub> O <sub>5</sub> /Fe <sub>2</sub> O <sub>3</sub>	-log P <sub>O<sub>2</sub></sub> (atm)	X <sup>a</sup>	a (Å)
0/1	9.00	0	8.395	5/95	9.00	(0.22 ± 0.01)	8.456
5/95	9.00	0.21 ± 0.01 (0.22 ± 0.01) <sup>b</sup>	8.450	1/9	9.00	(0.43 ± 0.02)	8.517
1/9	9.00	0.43 ± 0.03 (0.44 ± 0.01)	8.515	15/85	11.00	(0.73 ± 0.04)	8.601
5/95 <sup>c</sup>	10.90	(0.77 ± 0.04)	8.593	2/8 <sup>d</sup>	11.90	(0.80 ± 0.08)	8.635

<sup>a</sup> XFe<sub>7</sub>Z<sub>2</sub>O<sub>12</sub> · 3(1 - X)Fe<sub>3</sub>O<sub>4</sub> [Z = Nb or Ta]

<sup>b</sup> Values in parentheses were calculated from the thermogravimetric data.

<sup>c</sup> "FeO" coexists.

<sup>d</sup> Fe<sub>4</sub>Ta<sub>2</sub>O<sub>9</sub> coexists.

curve convexly, while those of Turnock's change linearly but are smaller than the present values. The values of tantalum-iron spinel change linearly, too.

From Fig. 3 the lattice constants of the spinel solid solution are expected to be different if the different starting materials were used at the same oxygen partial pressure. In Fig. 5 the lattice constants of the spinel solid solution of different starting

mixtures are shown in relation to the oxygen partial pressure.

(2) The Standard Gibbs Energy of Reactions

On the basis of the established phase diagram, the standard Gibbs energies of reactions which appear in the diagram can be calculated from the equation  $\Delta G^\circ = -RT \ln K$ . Here,  $R$  is the gas constant,  $T$  the abso-

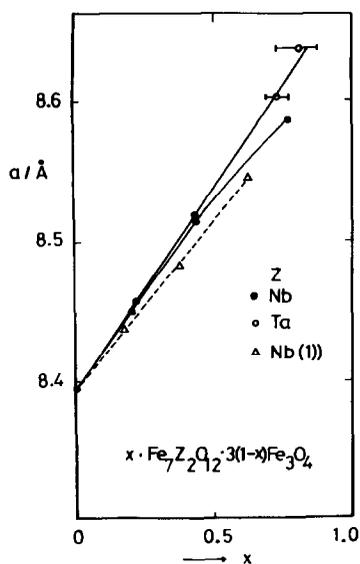


FIG. 4. The relationship between the lattice constant and the composition, X, of the spinel solid solutions.

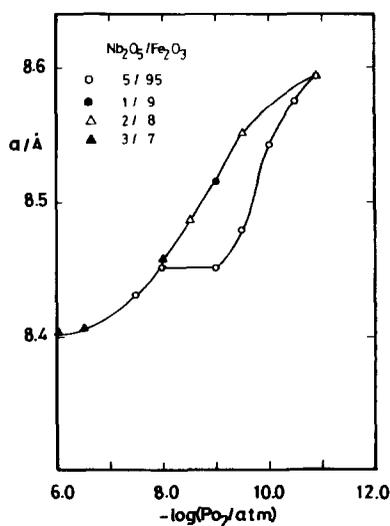


FIG. 5. The relationship between the oxygen partial pressure and the lattice constant of samples which were made from different starting compositions.

TABLE V  
 THE STANDARD GIBBS ENERGIES OF REACTIONS

Reaction	$-\log P_{O_2}^a$ (atm)	$-\Delta G^\circ$ (kJ)	Correction term
(1) $Nb_2O_4 + 0.42O_2 = Nb_2O_{4.84}$	13.90	164.6	—
(2) $Nb_2O_{4.84} + 0.08O_2 = Nb_2O_5$	13.40	26.9	—
(3) $Fe + 2NbO_2 + O_2 = FeNb_2O_6$	14.13	398.5	$a_{NbO_2}(F_2)$
(4) $3Fe + FeNb_2O_6 + \frac{3}{2}O_2 = Fe_4Nb_2O_9$	12.53	530.1	—
(5) $Fe_{0.28}Nb_{0.72}O_2 + 0.04O_2 = 0.08Nb_2O_5 + 0.28FeNb_2O_6$	12.27	14.0	—
(6) $1.35FeO + 0.27Fe_4Nb_2O_9 + 0.11O_2 = Fe_{2.43}Nb_{0.54}O_{4.00}$	11.00	35.6	—
(7) $Fe_4Nb_2O_9 + \frac{1}{2}O_2 = FeNb_2O_6 + Fe_3O_4$	8.15	123.5	$\left\{ \begin{array}{l} a_{FeNb_2O_6}(C_3) \\ a_{Fe_3O_4}(M_3) \end{array} \right.$
(8) $FeNb_2O_6 + \frac{1}{3}Fe_3O_4 + \frac{1}{2}O_2 = 2FeNbO_4$	6.22	14.2	$\left\{ \begin{array}{l} a_{FeNb_2O_6}(C_5) \\ a_{FeNbO_4}(B_3) \end{array} \right.$
(9) $2FeNb_2O_6 + \frac{1}{2}O_2 = 2FeNbO_4 + Nb_2O_5$	3.83	54.0	$\left\{ \begin{array}{l} a_{FeNb_2O_6}(C_4) \\ a_{Nb_2O_5}(E_1) \end{array} \right.$

<sup>a</sup>  $\pm 0.05$ .

lute temperature, and  $K$  the equilibrium constant of a reaction. The standard state of the activity can be chosen arbitrarily in each solid solution, and the necessary activities of the components for the calculations are tabulated in Table II. Results are shown in Table V. In the last column in the table the "correction term" is listed which needs to be determined in the future in order to calculate  $\Delta G^\circ$  values accurately. Here,  $a_{NbO_2}(F_2)$ , for example, means the activity of the  $NbO_2$  component at the composition  $F_2$ . Therefore,  $\Delta G^\circ$  values in Table V imply the energies which were obtained assuming that the activities of the "correction term" are unity. The  $\Delta G^\circ$  value for the reaction  $Nb_2O_4 + \frac{1}{2}O_2 = Nb_2O_5$  is calculated as the sum of those for reactions (1) and (2) and is  $-191.5$  kJ/mole. This value is in fairly good agreement with  $-194.8$  kJ/mole, as calculated from the data of Elliott and Gleiser (18).

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