Phase Equilibrium in the Y-Fe-O System at 1000℃

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Phase equilibrium was established in the Y-Fe-O system at 1000℃ with an oxygen partial pressure ranging from -log (P_{O_2}/atm) = 0 to 16.15, allowing construction of a phase diagram of the Y_2O_3-Fe-Fe_2O_3 system at 1000℃. Y_2O_3, Fe, "FeO", Fe_3O_4, Fe_2O_3, and $YFeO_3$ were found to be stable in the system. $Y_3Fe_5O_{12}$ and YFe_2O_4 were not found in the system. The present results were different from those of previous work at 1200℃, in which YFe_2O_4 and $Y_3Fe_5O_{12}$ were stable together with $YFeO_3$, and also different from those of previous work at 1100℃, in which only $Y_3Fe_5O_{12}$ was stable together with $YFeO_3$ as the ternary compounds.

Nonstoichiometric ranges were found in the FeO phase, with the composition of FeO represented as a function of log (P_{O_2}/atm), $N_O/N_{Fe} = 4.635\times10^{-2} \log P_{O_2} + 1.747$. Activities of components in the solid solution were calculated from the equation.

$YFeO_3$ lattice constants, prepared in air by the quenching method, were determined and compared with previous values. These were in good agreement with previous values. The Gibbs energy changes of the reaction 1/2 Y_2O_3 + Fe + 3/4 O_2 = $YFeO_3$, appearing in the phase diagram, were calculated from the oxygen partial pressures in equilibrium, and the value obtained was compared with previous values.

Key words: Phase equilibrium, Thermogravimetry, Yttrium-iron oxide, Gibbs energy.

INTRODUCTION

Phase relations in the Fe-O system have been reported from the standpoint of steelmaking (1,2,3). As is well known, there are three oxides," FeO" , Fe_3O_4, and Fe_2O_3 in the Fe-O system. "FeO" has a cubic structure and forms a metal defect solid solution. Fe_3O_4 has an inverse spinel structure and a short solid solution range of oxygen-rich composition side, and this range changes with temperature. Fe_2O_3 has a stoichiometric composition and rhombohedral crystal system.

From JANAF data(4), the oxygen partial pressure in equilibrium with Fe and FeO, with FeO and Fe_3O_4, and with Fe_3O_4 and Fe_2O_3 were determined to be -14.91, -13.56, and -5.16 in log (P_{O_2}/atm) at 1000℃, respectively.

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The phases in the Y-Fe-O system are of important technological interest, particularly in view of their physical properties. As is well known, $YFeO_3$ and $Y_3Fe_5O_{12}$ (yttrium iron garnet, YIG) are stable in the Y-Fe-O system as ternary compounds. Notably, YIG has been used as a magnetic material, and $YFeO_3$ and $Y_3Fe_5O_{12}$ have been used in operational memory.

Recently, a new YFe_2O_4 phase was found to be stable at 1200℃ by Kimizuka and Katsura (5), and it has a hexagonal crystal system with a = 6.090 Å and c = 24.788 Å. Piekarczyk et al. (6) have reported the YFe_2O_4 phase to be stable above 1010℃. According to Kato et al. (7), the crystal structure of this compound is a new type of AB_2X_4, where A and B are cations and X is an anion, and belongs to the trigonal system with the space group R3/m. The structure consists of alternate layers of Ln_2O_3 and Fe_4O_5, and thus anisotropies, both in the magnetic interaction and the electrical conductivity, are expected.

The crystal structure and magnetic properties of YFe_2O_4, together with $ErFe_2O_4$, have been studied by Matsumoto et al. (8), and the pressure dependence of the YFe_2O_4 magnetic phase transitions was found.

Solid electrolyte galvanic cell EMF was performed on the reaction Fe + 3/2 NiO + 1/2 Y_2O_3 = 3/2 Ni + $YFeO_3$ at 1200~1400K, and in combination with the Gibbs energy of NiO formation obtained by Charett et al.(9), Gibbs energy of the reaction, Fe +1/2 Y_2O_3 + 3/4 O_2 = $YFeO_3$, was calculated(10).

The objectives of the present study are to; (1) establish a detailed phase diagram of Y-Fe-O system at 1000℃ as a function of oxygen partial pressure; (2) ascertain whether YFe_2O_4 and $Y_3Fe_5O_{12}$ are stable or not ; that is, whether the phase diagram at 1000℃ is different from those at 1200℃ and 1100℃ or not; (3) determine the thermochemical properties of reactions based on the phase diagram at 1000℃.

2. EXPERIMENTAL

Analytical grade Y_2O_3 (99.9%) and Fe_2O_3 (99.9%) were used as the starting materials. Both oxides were calcined at 1000℃. Mixtures having desired ratios of Y_2O_3/Fe_2O_3 were prepared by thoroughly mixing in an agate mortar with repeated calcination during intermediate mixings. This was followed by the same procedures as described previously (11).

The desired oxygen partial pressures were obtained by using gas mixtures of CO_2 and H_2, and of CO_2 and O_2, and using individual gases O_2 and CO_2. The actual oxygen partial pressure of the gas phases was measured by means of a solid electrolytic cell composed of $(ZrO_2)_{0.85}(CaO)_{0.15}$(12).

The apparatus and procedures for controlling the oxygen partial pressure, keeping a constant temperature, the thermogravimetry method, and the criterion for the establishment of equilibrium were the same as described previously (11). The method of establishing equilibrium can be briefly described as follows. To ensure equilibrium, the equilibrium weight of each sample at a particular oxygen partial pressure was determined for both sides of the reaction; that is, as the oxygen partial pressure was increased from a low value and as it was decreased from a high value. The balance, furnace, and gas mixer are schematically shown in the previous report (13). The furnace was installed vertically, and a mullite tube wound with Pt-Rh(60%-40%) alloy wire served as the heating element. To ensure the desired oxygen partial pressures, an appropriate gas mixture was passed from the bottom of the furnace to the top.

The identification of phases and the determination of lattice constants were performed using of Rint 2500 Rigaku X-ray diffractometer, employing Ni-filterd CuKα radiation. An external standard silicon was used to calibrate 2θ.

3. RESULTS AND DISCUSSIONS

(1) Phase equilibrium

1) Fe-O system at 1000℃.

To date, three oxides are known for the Fe-O system, "FeO", Fe_3O_4, and Fe_2O_3.

In the present experiment, the Fe-O system was reinvestigated using the present apparatus and techniques at 1000℃. The results are as follows. Figure 1a shows the oxygen partial pressure, -log(P_{O_2}/atm), versus the weight changes, W_{O_2}/W_T of the Fe-O system. Here, W_{O_2} is the weight increase of a sample from the reference weight at log(P_{O_2}/atm) = -16.15, at which Fe is stable, and W_T is the total weight gain from the reference state to the state at 1 atm O_2. As shown in Fig. 1a, weight breaks are found at 15.22, 13.38, and 6.02. These values correspond to the oxygen partial pressures in equilibrium of the three reactions: 1) Fe + 1/2 O_2 = FeO, 2) 3 FeO + 1/2 O_2 = Fe_3O_4, and 3) 2/3 Fe_3O_4 + 1/6O_2 = Fe_2O_3, which are listed in Table 4. Figure 1b shows the relationship between the oxygen partial pressure and a

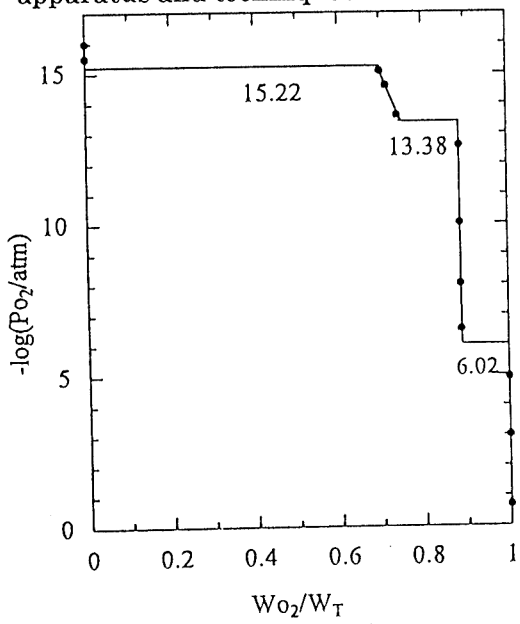

Fig. 1a. The relationship between the oxygen partial pressure, log (P_{O_2}/atm) and the weight change of samples, W_{O_2}/W_T in the Fe-O system.

composition, the N_O/N_{Fe} mole fraction ratio, of the FeO solid solution. Here, No and N_{Fe} represent the mole fraction of oxygen and iron in the FeO solid solution.

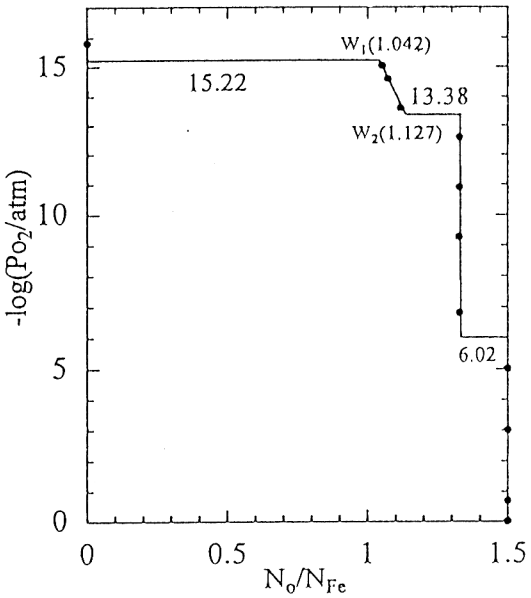

Fig. 1b. The relationship between the oxygen partial pressure, log (P_{O_2}/atm), and the N_O/N_{Fe} mole fraction ratio in the Fe-O system.

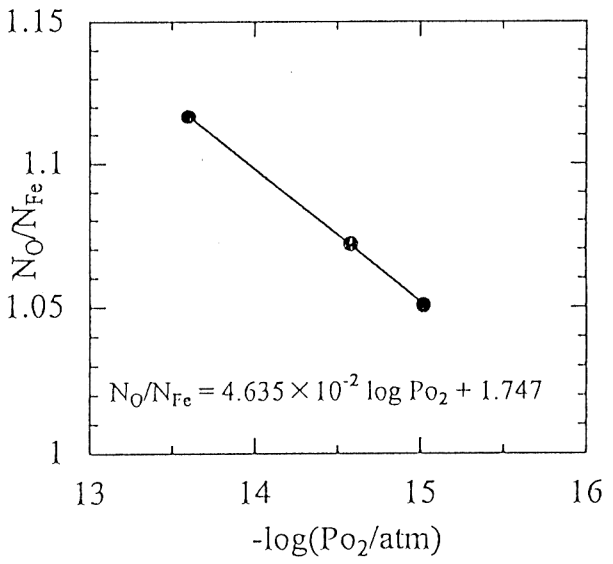

Fig. 1c. The relationship between the oxygen partial pressure, log (P_{O_2}/atm) and N_O/N_{Fe} in the FeO solid solution.

It is apparent that the FeO solid solution is stable in the oxygen partial pressure -log P_{O_2} = 13.38 ~15.22, and that the composition of FeO in equilibrium with metallic iron is 1.042 of the N_O/N_{Fe} mole ratio at log (P_{O_2}/atm) = -15.22 and the composition of FeO in equilibrium with Fe_3O_4 is 1.127 of the N_O/N_{Fe} mole ratio at log (P_{O_2}/atm) = -13.38, respectively. The log (P_{O_2}/atm) versus the N_O/N_{Fe} mole ratio of FeO solid solution is shown in Fig. 1c, and is represented by an equation: $N_O/N_{Fe} = 4.635\times10^{-2}$ logP_{O_2} + 1.747. This equation will be used to obtain the activities of the iron and FeO components in the solid solution by the Gibbs-Duhem equation(1,14).

A slight weight increase might be observed from –log(P_{O_2}/atm)= -13.38 to 6.02 for Fe_3O_4, as is well known, although it is not evident from Fig. 1a or b because of the scale of abscissa.

2) Y_2O_3-Fe-Fe_2O_3 system.

Four samples, having Y_2O_3/Fe_2O_3 molar ratios of 0.7/0.3, 0.6/0.4, 0.4/0.6, and 0.2/0.8, were prepared for thermogravimetric analysis. Figure 2 shows the oxygen partial pressure, -log(P_{O_2}/atm), versus the weight changes, W_{O_2}/W_T, for three representative samples: 0.6/0.4 (Fig. 2a), 0.4/0.6 (Fig. 2b), and 0.2/0.8 (Fig. 2c). Here also, W_{O_2} is the weight increase of a sample from the reference weight at log (P_{O_2}/atm) = -16.15, at which Y_2O_3 and Fe are stable, and W_T is the total weight-gain from the reference state

to the state at 1 atm O_2, at which Y_2O_3 and $YFeO_3$, and $YFeO_3$ and Fe_2O_3 were stable, depending upon the total compositions of samples, as shown in Fig. 3. These phases

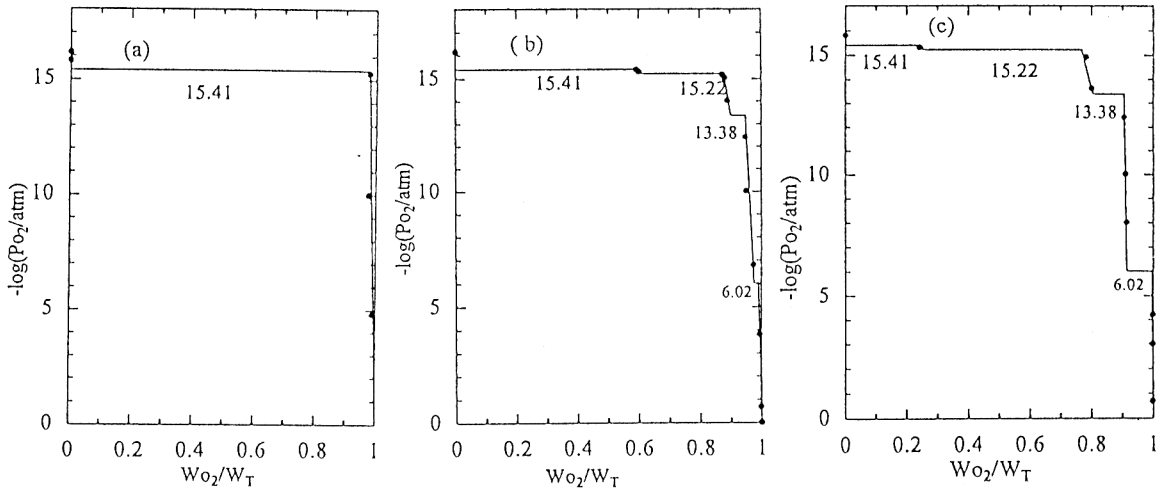

Fig. 2. The relationship between the oxygen partial pressure, log (P_{O_2}/atm), and the weight change of the samples, W_{O_2}/W_T. (a) Y_2O_3/Fe_2O_3 = 0.6/0.4, (b) Y_2O_3/Fe_2O_3 = 0.4/0.6, and (c) Y_2O_3/Fe_2O_3 = 0.2/0.8.

were ascertained by an identification of phase. As is evident from Fig. 2, weight breaks are found at 15.41, 15.22, 13.38, and 6.02 in -log (P_{O_2}/atm). These values correspond to the oxygen partial pressure in equilibrium with the three solid phases, Y_2O_3 + $YFeO_3$ + Fe, $YFeO_3$ + FeO + Fe, $YFeO_3$ + FeO + Fe_3O_4, and $YFeO_3$ + Fe_3O_4 + Fe_2O_3, respectively.

Table 1 Identification of Phase

Y_2O_3 Mol	Fe_2O_3 ratio	-log P_{O_2} atm	Time hr	Phase
0	1.0	15.80	6.7	Fe
		14.60	7.3	FeO
		13.60	7.6	FeO
		12.50	7.4	Fe_3O_4
		8.50	20.9	Fe_3O_4
		5.00	21.0	Fe_2O_3
		0.68	16.0	Fe_2O_3
0.2	0.8	15.80	6.7	Fe + Y_2O_3
		15.30	6.9	Fe + $YFeO_3$
		14.60	7.2	FeO + $YFeO_3$
		13.60	6.8	FeO + $YFeO_3$
		12.50	8.0	Fe_3O_4 + $YFeO_3$
		8.50	22.4	Fe_3O_4 + $YFeO_3$
		5.00	22.0	Fe_2O_3 + $YFeO_3$
		0.68	75.0	Fe_2O_3 + $YFeO_3$
0.4	0.6	15.80	6.7	Fe + Y_2O_3
		15.30	6.9	Fe + $YFeO_3$
		14.60	7.2	FeO + $YFeO_3$
		13.60	6.8	FeO + $YFeO_3$
		12.50	8.0	Fe_3O_4 + $YFeO_3$
		8.50	22.4	Fe_3O_4 + $YFeO_3$
		5.00	22.0	Fe_2O_3 + $YFeO_3$
		0.68	75.0	Fe_2O_3 + $YFeO_3$
0.6	0.4	15.80	6.7	Fe + Y_2O_3
		8.50	22.4	$YFeO_3$ + Y_2O_3
		0.68	75.0	$YFeO_3$ + Y_2O_3

Table 1 shows the results of phase identification for the Y-Fe-O system, along with the experimental conditions.

Samples of about 500mg were prepared for the phase identification by means of the quenching method. Six phases, Y_2O_3, Fe, FeO, Fe_3O_4, Fe_2O_3 ,and $YFeO_3$ were evaluated by powder X-ray analysis and were found to be stable under the experimental conditions, whereas $Y_3Fe_5O_{12}$ (YIG) and YFe_2O_4 were not found to be stable.

From the above thermogravimetric results and phase identification, a phase diagram

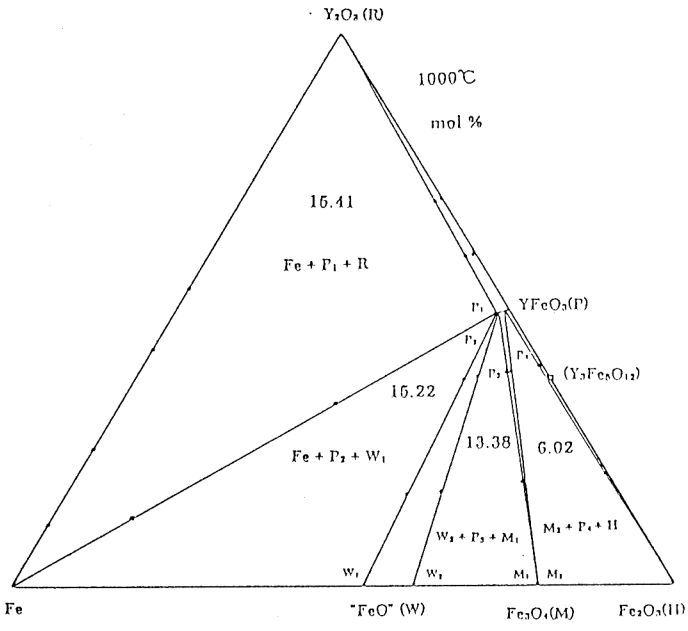

Fig. 3. Phase equilibrium in the Y_2O_3-Fe-Fe_2O_3 system at 1000℃. Numerical values indicated in the three phase regions are the oxygen partial pressures in -log(P_{O_2}/atm) in equilibrium with the solid phases shown in each region. Abbreviations are the same as those in Table 2.

for the Y_2O_3-Fe-Fe_2O_3 system was constructed. The numerical values of the three solid fields in Fig. 3 are the values of -log P_{O_2} in equilibrium with the three solid phases described above. As described above, $Y_3Fe_5O_{12}$ and YFe_2O_4 were not stable under the present experimental conditions. Piekarczyk et al.(6) reported that "the phase diagram analysis shows for the entire temperature range investigated, from 900 to 1250℃, that the garnet $Y_3Fe_5O_{12}$ can coexists with Fe_3O_4 and Fe_2O_3". This shows a striking difference between the Y-Fe-O phase diagram of the present results and that of other author's results. The nonstoichiometry of $YFeO_3$ was also determined, but the composition range was small. The relationship between the oxygen partial pressure and the composition No/N_{YFeO3} of the $YFeO_3$ solid solution could be represented by an equation: $No/N_{YFeO3} = -1.426\times10^{-4}(\log P_{O_2})^2 - 1.379\times10^{-4}(\log P_{O_2})$, obtained by the least-squares method. Here, No and N_{YFeO3} represent the mole fraction of oxygen and $YFeO_3$ in the $YFeO_3$ solid solution. This equation can be solved to show that yttrium-iron perovskite would be stoichiometric ($YFeO_{3.00}$(P)) at 0 and $YFeO_{2.97}$(P_1) at - 15.41 in terms of log(P_{O_2}/atm).

As described above(1-3), the Fe_3O_4 phase has a small nonstoichiometry, although this is not explicitly shown in Fig. 3 because of the figure's scale.

The compositions, symbols, compounds stability ranges in oxygen partial pressures and activities of components in the solid solutions are tabulated in Table 2. In the next section, these activities will be used in the calculation of the Gibbs energy changes of

Table 2. Compositions, Symbols, Stability Ranges of Oxygen Partial Pressures, and Activities of Components in Solid Solutions.

Component	Compositions	Symbols	-log(P_{O_2}/atm)	log a_i
FeO	$FeO_{1.042}$	W_1	15.22	0
	$FeO_{1.127}$	W_2	13.38	−0.0628
$YFeO_3$	$YFeO_{2.96}$	P_1	5.41	0
	$YFeO_{2.98}$	P_2	13.38	0.0280
	$YFeO_{2.99}$	P_3	6.02	0.0749
	$YFeO_{3.00}$	P	0.00	0.0788

reactions.

The lattice constants of $YFeO_3$ perovskite were determined to be orthorhombic using the $0.6Y_2O_3/0.4Fe_2O_3$ mole ratio sample which was made at 0.68 in -log P_{O_2}. The results are tabulated in Table 3, together with the previously reported values (15). Slight differences were found in the lattice constants.

(2) Standard Gibbs Energy Change of Reaction

On the basis of the established phase diagram, Gibbs energy changes of reactions were determined by the equation, $\triangle G^\circ = -RT \ln K$. Here, R is the gas constant, T the absolute temperature, and K the equilibrium constant of the reaction.

Table 3. Lattice constants of quenched $YFeO_3$

Sample		-log P_{O_2}/atm	Time/h	Coexisting Phase	a/A	b/A	c/A	V/A^3
Y_2O_3	Fe_2O_3							
0.6	0.4	0.68	70	Y_2O_3	5.592(2)	7.609(4)	5.288(2)	225.0(2)
Ref. 15)					5.5946	7.6053	5.2817	

Four chemical reactions were found in the established phase diagram, as represented in Table 4. In calculation of the Gibbs energy changes of reactions the activity of each component has to be used. For example, as is apparent from the phase diagram, the activity of FeO in reaction 1) is different from that of reaction 2). That is, the activity of the FeO component at the composition W_1 in Fig. 1b, which is in equilibrium with Fe should be different from that of FeO at the composition W_2,

Table 4. The Gibbs Energy Change of Reactions at 1000℃

Reaction	−log(P_{O_2}/atm)	$-\Delta G^0$/kJmol^{-1}
1) Fe + 1/2 O_2 = FeO	15.22	185.6
	(14.91)	181.8*
	(14.94)	182.1**
2) 3 FeO + 1/2 O_2 = Fe_3O_4	13.38	165.5
	13.38	168.8[a]
	(13.56)	165.3*
	(13.22)	161.2**
3) 2/3 Fe_3O_4 + 1/6 O_2 = Fe_2O_3	6.02	24.5
	(5.16)	21.0*
	(5.33)	21.7**
4) Fe + 1/2 Y_2O_3 + 3/4O_2 = $YFeO_3$	15.41	281.8
	(15.07)	275.7***
	(15.15)	277.1****

* These values were calculated from the Gibbs energy data of JANAF Table (4).

** These values were calculated from the data of Ref. 16

*** This value was calculated by combining the value of Ref. 10 and the value of the formation of NiO in Ref. 16.

**** This value was calculated based on the data of 1/2 Fe_2O_3 + 1/2 Y_2O_3 = $YFeO_3$ (Ref. 17) and the value of the reaction Fe + 3/4 O_2 = 1/2 Fe_2O_3, which was calculated based on JANAF Table (4).

a) This value was calculated based on the activity of FeO(W_2) in Table 2.

which is in equilibrium with Fe_3O_4.

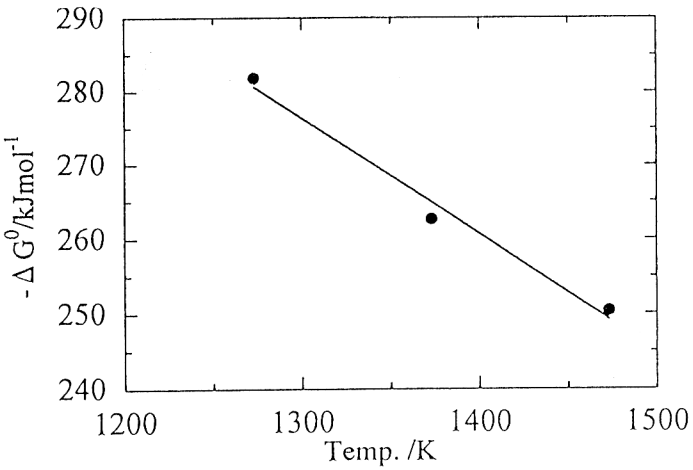

Fig. 4 The relationship between ΔG^0 for reaction4) and the temperature.

The Gibbs-Duhem equation was used to calculate the activities of Fe and FeO components in the FeO solid solution from the obtained No/N_{Fe} relation. The details of the calculation can be found in the report of Darken and Gurry (1), and in the book by Wagner (14). In Table 4, values obtained in the present experimental conditions are shown. The values of log (Po_2/atm) in parentheses were calculated from the corresponding ΔG^0 values.

The ΔG^0 value of −185.6 kJmol^{-1} for reaction 1) determined in the present investigation agrees well with the values −181.8 and −182.1 kJmol^{-1} calculated from the values of JANAF (4) and those of Robie et al.(16), respectively. Also, values for reactions 2) and 3), in the present study are in fairly good agreement with those calculated from JANAF (4) and (16).

The value −275.7kJmol^{-1} for the reaction 4) was calculated by combining the value of a reaction, Fe + 3/2 NiO + 1/2 Y_2O_3 = 3/2 Ni + $YFeO_3$, of Yamauchi et al. (10), and the value of the formation of NiO with the value compiled by Robie et al. (16). Also, the value −277.1 kJmol^{-1} for the reaction 4) wais calculated based on the data (17) of the reaction 1/2 Fe_2O_3 + 1/2 Y_2O_3 = $YFeO_3$, and the value of the reaction Fe + 3/4 O_2 = 1/2 Fe_2O_3, which was calculated based on JANAF Table (4).

The Present ΔG^0 value for reaction 4) is in fairly good agreement with the above previous values.

In Fig. 4, the relationship between the ΔG^0 for the reaction 4) and the temperature is shown. Values obtained at 1100℃ and 1200℃ were quoted from 18) and 5), respectively. A reasonable linear equation, $\Delta G^0 = -4.811\times10^2 + 1.575\times10^{-1}T$, was obtained by means of the least-squares method.

4. Conclusion

(1) Phase equilibrium in the Y-Fe-O system at 1000℃ was established under an oxygen partial pressure from 0 to -16.15 in log (Po_2/atm).

(2) Under the present experimental conditions, Y_2O_3, Fe, "FeO", Fe_3O_4, Fe_2O_3, and

$YFeO_3$ phases were stable, whereas YFe_2O_4 and $Y_3Fe_5O_{12}$(YIG) were not stable. This is a striking contrast to the previous results obtained at 1100℃ and 1200℃.

(3) Fe_3O_4 and $YFeO_3$ were nonstoichiometric, but the range of the nonstoichiometry of Fe_3O_4 was too small to be seen in Fig. 1a , b, and Fig. 3.

(4) The lattice constants of $YFeO_3$ were determined and compared with previous values. The values obtained are comparable to the previous values.

(5) The Gibbs energies changes of reactions found in the phase diagram were calculated with the oxygen partial pressures in equilibirium with three solid phases.

(6) The relationship between ΔG^0 and the temperature for reaction 4) was obtained.

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