

Standard Free Energy of Formation of YFeO_3 , $\text{Y}_3\text{Fe}_5\text{O}_{12}$, and a New Compound YFe_2O_4 in the $\text{Fe}-\text{Fe}_2\text{O}_3-\text{Y}_2\text{O}_3$ System at 1200°C

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The phase equilibria in the $\text{Fe}-\text{Fe}_2\text{O}_3-\text{Y}_2\text{O}_3$ system have been established at 1200°C . The following phases were stable: yttria, hematite, magnetite, wüstite, metallic iron, yttrium-iron perovskite, yttrium-iron garnet, and a new phase YFe_2O_4 , belonging to a rhombohedral crystal system. The YFe_2O_4 compound has a solid solution from $\text{YFe}_2\text{O}_{3.905}$ to $\text{YFe}_2\text{O}_{4.000}$. The standard free energies of formation of $\text{YFe}_2\text{O}_{3.905}$, YFeO_3 , and $\text{Y}_3\text{Fe}_5\text{O}_{12}$ have been determined to be $-96\,800 \pm 200$ cal, $-59\,800 \pm 200$ cal, and $-143\,700 \pm 600$ cal, respectively, from metallic iron, Y_2O_3 , and oxygen.

Introduction

Many works on rare earth elements-transition elements-oxygen systems have been investigated from the standpoint of crystallographic and magnetic properties. These have especially focused their attentions on the perovskite and garnet structures found in these systems. However, very few studies have been published on the thermochemical aspect in order to determine the standard free energies of formation of these complex oxides. Recently, Kimizuka and Katsura (1) determined the standard free energy of formation of LaFeO_3 from metallic iron, La_2O_3 , and oxygen after establishing the phase equilibria in the $\text{Fe}-\text{Fe}_2\text{O}_3-\text{La}_2\text{O}_3$ system.

Van Hook (2) studied the equilibria in the $\text{Fe}_2\text{O}_3-\text{FeO}-\text{Y}_2\text{O}_3$ system at elevated temperatures under varying oxygen partial pressure from oxygen to carbon dioxide, but he did not determine the phase relations in the $\text{Fe}-\text{Fe}_2\text{O}_3-\text{Y}_2\text{O}_3$ system.

In the present study, we have established the phase equilibria in the $\text{Fe}-\text{Fe}_2\text{O}_3-\text{Y}_2\text{O}_3$ system

at 1200°C under varying oxygen partial pressure from 1 to $10^{-15.80}$ atm, and found a new compound YFe_2O_4 . Based on the phase equilibria, we have determined the standard free energies of formation of YFeO_3 , YFe_2O_4 , and $\text{Y}_3\text{Fe}_5\text{O}_{12}$ from metallic iron, Y_2O_3 , and oxygen.

Experimental

1. Materials

Guaranteed reagent grade Fe_2O_3 and Y_2O_3 (99.99%) powders were employed for all starting materials. Desired ratios of $\text{Y}_2\text{O}_3/\text{Fe}_2\text{O}_3$ were obtained by mixing them in an agate mortar under ethyl alcohol. Mixtures thus obtained were heated at 1200°C for 72 hr in air. Sintered samples were pulverized in an agate mortar and heated again at 1200°C for 72 hr in air. Loosely sintered samples thus obtained, were crushed to obtain small size pieces ($3 \times 3 \times 3$ mm³).

2. Apparatus and Procedures

About 3 g of sintered pieces having a desired

ratio of Y₂O₃/Fe₂O₃ were put into a small alumina crucible which has slit-cuts on the wall in order to facilitate equilibration between gas and solid phases. The crucible was then suspended in a vertical furnace wound with 40% Rh60%Pt wire kept at 1200°C and at a desired oxygen partial pressure. Subsequent thermogravimetric procedures were the same as those described in a previous paper (3). The weight of sample in oxygen was chosen as the reference, because the weight loss due to the reduction of the Fe₂O₃ component was insignificant over all mixtures.

The thermocouple, Pt-13%Rh87%Pt, was calibrated against the melting point of gold, and the fluctuation of temperature was within ±2°C. The oxygen partial pressure was measured by means of a solid electrolyte cell composed of (ZrO₂)_{0.85}(CaO)_{0.15}. The difference between measured and calculated oxygen partial pressures was within ±0.01 in terms of log P_{O₂} in the range from 1 to 10^{-15.80} atm. The procedure to measure the

oxygen partial pressure has been described in a previous paper (4). The equilibrium among condensed and gaseous phases was certified by oxidation and reduction reactions.

Phases in quenched samples were identified by the powder X-ray diffraction method with Mn-filtered FeK α radiation.

3. Chemical Analysis

In addition to the analysis by the thermogravimetric method, the FeO/Fe₂O₃ ratios in several quenched samples were determined by the wet chemical method described by Iwasaki *et al.* (5).

Results and Discussion

1. Phase Equilibria

Figure 1 shows the phase equilibria in the Fe-Fe₂O₃-Y₂O₃ system at 1200°C. The following phases were stable in the present experimental conditions: Yttria (Y₂O₃), hematite (Fe₂O₃), magnetite (Fe₃O₄), wüstite (FeO),

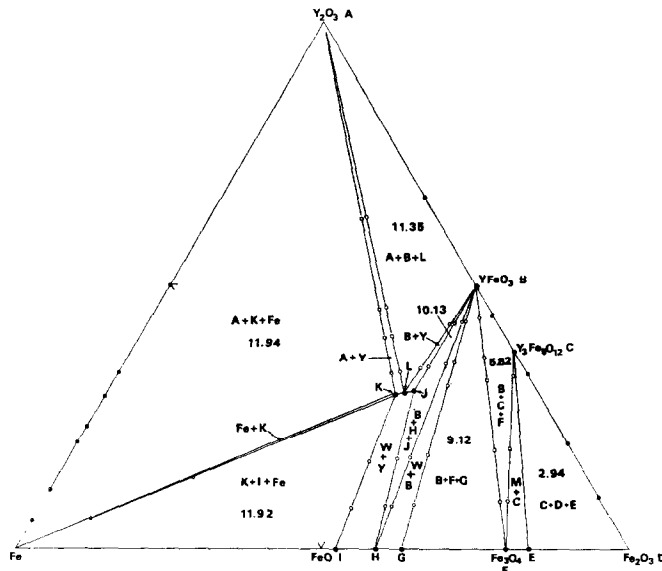


FIG. 1. The phase diagram of the Fe-Fe₂O₃-Y₂O₃ system at 1200°C (mole%). Numbers mean values of $-\log P_{O_2}$ in fields equilibrated with three solid phases. Letters A, B, C, D, F, and J represent stoichiometric compositions of Y₂O₃, YFeO₃, Y₃Fe₄O₁₂, Fe₂O₃, Fe₃O₄, and YFe₂O₄ phases, respectively. M means the magnetite solid solution from E to F, W means the partial solid solution of wüstite from G to H, and W' means the partial solid solution of wüstite from H to I. Y means the solid solution of YFe₂O₄ from K to J, Y' means the partial solid solution of YFe₂O₄ from K to L, and Y'' means the partial solid solution of YFe₂O₄ from L to J. Chemical composition of each letter is as follows: E. Fe_{2.957}O₄, G. Fe_{0.862}O, H. Fe_{0.894}O, I. Fe_{0.953}O, K. YFe₂O_{3.905}, L. YFe₂O_{3.944}. The composition of the point K should have a very small interval, but we could not determine its variation.

metallic iron (γ -iron), yttrium-iron perovskite (YFeO_3), yttrium-iron garnet ($\text{Y}_3\text{Fe}_5\text{O}_{12}$), and a new phase (YFe_2O_4). Each phase containing the Y_2O_3 component has the following characteristics. (a) Pure yttrium oxide was stable in the range of P_{O_2} from 1 to 10^{-16} atm. Cassedanne (6) reported the Y_2O_3 - Fe_2O_3 solid solution at temperatures from 800 to 1600°C in air. In the present study, however, it was hard to recognize the existence of the Y_2O_3 -iron oxide solid solution at oxygen partial pressures below $10^{-11.35}$ atm. (b) It was ascertained that the yttrium-iron perovskite phase, YFeO_3 , may have no significant deviation from the stoichiometric composition, on the basis that the lattice constants of yttrium-iron perovskite equilibrated with Y_2O_3 , with $\text{Y}_3\text{Fe}_5\text{O}_{12}$, and with YFe_2O_4 are identical within experimental error. (c) Yttrium-iron garnet had an insignificant solubility of Y_2O_3 and of Fe_2O_3 , respectively, though Van Hook (2) pointed out that the garnet phase in equilibrium with oxide liquid deviates from the ideal formula composition $\text{Y}_3\text{FeO}_{12}$ with changes in temperature and in oxygen partial pressure. Stoichiometric yttrium-iron garnet decomposed to form stoichiometric yttrium-iron perovskite and stoichiometric magnetite at an oxygen partial pressure of $10^{-5.82}$ atm. (d) As seen in Fig. 1, the solid solution of the new phase ranged from $\text{YFe}_2\text{O}_{3.905}$ to $\text{YFe}_2\text{O}_{4.000}$. After quenching the composition of YFe_2O_4 obtained by the thermogravimetric method at an oxygen partial pressure of $10^{-10.14}$ atm, ferrous and ferric irons were analyzed by the wet chemical method. The result showed an identical composition, $\text{Y}_{1.004}\text{Fe}_{2.002}\text{O}_{4.000}$ (based on 4 O) with that obtained by thermogravimetry. The YFe_2O_4 solid solution is black and dissolves easily in aqueous acid solutions. It is not attracted by a hand magnet at room temperature. This solid solution decomposes to form wüstite and yttrium-iron perovskite under high pressure of 50 kbar at temperatures from 900 to 1100°C (Professor S. Akimoto, University of Tokyo, kindly studied this by using the tetrahedral anvil type high pressure apparatus). The X-ray powder diffraction data of the composition YFe_2O_4 are given in Table I. In the present experiment, we found that a series of AFe_2O_4

TABLE I
SPACINGS AND INDICES OF THE YFe_2O_4 CRYSTAL^a

No.	Indices	Observed spacings (Å)	Observed intensities	Calculated spacings (Å)
1	0 0 3	8.248	20	8.263
2	0 0 6	4.128	30	4.131
3	2 1 1	3.0199	100	3.0223
4	1 1 $\bar{2}$	2.9538	10	2.9571
5	0 0 9	2.7525	50	2.7543
6	2 1 4	2.7334	80	2.7329
7	1 2 5	2.5930	90	2.5947
8	2 1 $\bar{8}$	2.1717	20	2.1718
9	2 1 10	1.9223	40	1.9224
10	3 0 0	1.7580	60	1.7581
11	3 0 6	1.6171	20	1.6177
12	2 1 $\bar{14}$	1.5307	10	1.5306
13	$\bar{4}$ $\bar{2}$ 1	1.5199	10	1.5197
14	3 0 9	1.4820	30	1.4819
15	4 2 5	1.4554	10	1.4554
16	$\bar{4}$ 2 10	1.2976	10	1.2973

^a Space group: $R3m$, $R\bar{3}$, or $R32$; extinction law: $-h + k + l = 3n$. $a = 6.090 \pm 0.004$ Å; $c = 24.788 \pm 0.004$ Å as a hexagonal crystal system.

type of compounds where A includes Ho^{3+} , Er^{3+} , Yb^{3+} , Tm^{3+} , and Lu^{3+} were synthesized similarly under lower oxygen partial pressures at 1200°C (7). These compounds all have the same X-ray powder diffraction patterns. Of these compounds, a plate-like single crystal of YbFe_2O_4 has been successfully grown from melt at 1400°C, and we could obtain Precession and Weissenberg photographs. On the basis of these photographs, we could determine the space group and the lattice parameters of YFe_2O_4 as given in Table I. The detailed results of the crystal structure analysis of AFe_2O_4 will be published elsewhere in the near future.

Figures 2a, b, and c show the relationship between the weight-change of starting mixtures and the oxygen partial pressure in order to determine the boundary lines of each assembly. As clearly seen, the new phase YFe_2O_4 is in equilibrium with the Y_2O_3 phase as a distinctive step (2) in Fig. 2a, and is in equilibrium with the YFeO_3 phase as a step (4) and with the Y_2O_3 phase as a step (5) both in

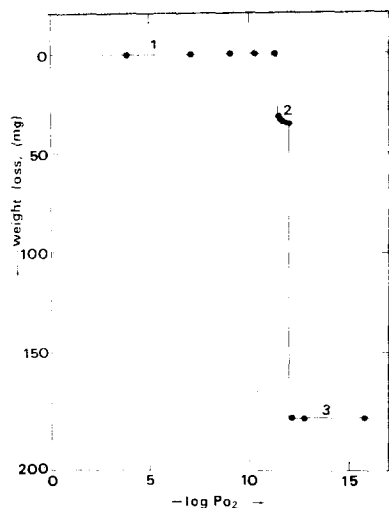


FIG. 2 (all parts). The relationship between weight loss and $\log P_{O_2}$. a. Starting conditions, $Y_2O_3/Fe_2O_3 = 2/1$, sample weight 2 207.0 mg. The equilibrated solid phases in each step are as follows: 1. $Y_2O_3 + YFeO_3$, 2. $Y_2O_3 +$ partial solid solution of YFe_2O_4 from L to K , 3. $Y_2O_3 +$ metallic iron.

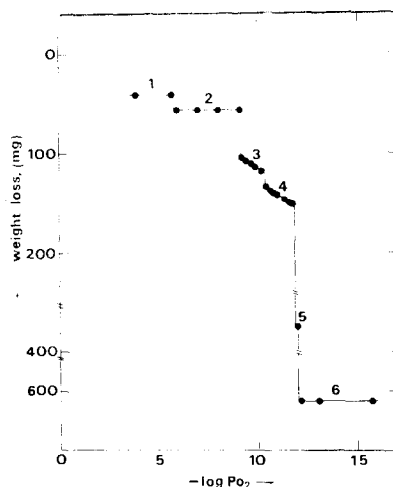


FIG. 2c. Starting conditions, $Y_2O_3/Fe_2O_3 = 1/4$, sample weight 2759.5 mg. The equilibrated solid phases in each step are as follows: 1. $Y_3Fe_5O_{12} + Fe_3O_4$, 2. $YFeO_3 + Fe_3O_4$, 3. $YFeO_3 +$ partial solid solution of wüstite from G to H , 4. solid solution of YFe_2O_4 from J to $K +$ partial solid solution of wüstite from H to I , 5. $YFe_2O_{3.905}(K) +$ metallic iron, and 6. $Y_2O_3 +$ metallic iron.

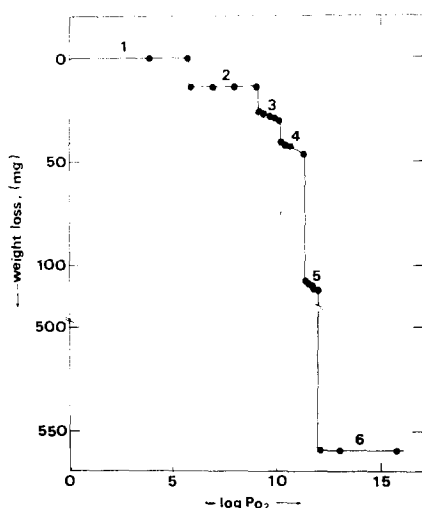
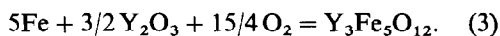
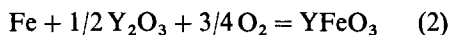
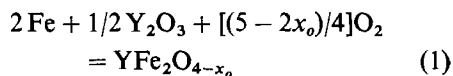


FIG. 2b. Starting conditions, $Y_2O_3/Fe_2O_3 = 4/5$, sample weight 3986.7 mg. The equilibrated solid phases in each step are as follows; 1. $YFeO_3 + Y_3Fe_5O_{12}$, 2. $YFeO_3 + Fe_3O_4$, 3. $YFeO_3 +$ partial solid solution of wüstite from G to H , 4. $YFeO_3 +$ partial solid solution of YFe_2O_4 from J to L , 5. $Y_2O_3 +$ partial solid solution of YFe_2O_4 from L to K , and 6. $Y_2O_3 +$ metallic iron.

Fig. 2b, and also is in equilibrium with wüstite as a step (4) in Fig. 2c. The composition $YFe_2O_{3.905}$ [point (K) in Fig. 1] is in equilibrium with metallic iron in the range of oxygen partial pressures only from $10^{-11.92}$ to $10^{-11.94}$ atm as pointed out in Fig. 2c.

2. Calculations of the Standard Free Energy of Formation of YFe_2O_4 , $YFeO_3$, and $Y_3Fe_5O_{12}$

On the basis of the present phase equilibria, we will determine the following three standard free energies of formation from metallic iron, Y_2O_3 , and oxygen:



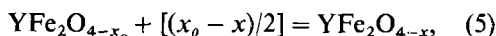
In Eq. (1), $YFe_2O_{4-x_o}$ was in equilibrium with metallic iron and Y_2O_3 , and the value of x_o was determined to be 0.095. In the present paper, we choose this composition as the standard of the activity of YFe_2O_4 . The standard free energy of formation, $\Delta G^o(I)$, referred to

Eq. (1) was thus calculated to be $-96\,800 \pm 200$ cal, because the equilibrated oxygen partial pressure was $10^{-11.94}$ atm. Based on $\Delta G^\circ(1)$, we obtain the following equation involving activities of both metallic iron and $\text{YFe}_2\text{O}_{4-x_0}$:

$$\Delta G^\circ(1) = -2.303RT[\log a_{\text{YFe}_2\text{O}_{4-x_0}} - 2 \log a_{\text{Fe}} - (5 - 2x_0)/4 \log P_{\text{O}_2}], \quad (4)$$

where R , T , and a_i mean gas constant, absolute temperature, and the activity of each component, respectively. Equation (3) is applicable when the YFe_2O_4 solid solution is in equilibrium with pure Y_2O_3 .

In order to determine the activity of $\text{YFe}_2\text{O}_{4-x_0}$ at the point (L) in Fig. 1 where the YFe_2O_4 solid solution is in equilibrium with both Y_2O_3 and YFeO_3 , we will apply the following reaction between $\text{YFe}_2\text{O}_{4-x_0}$ and oxygen:

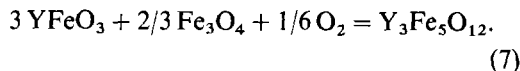


where x means any value from x_0 to the point (L) in Fig. 1. The value of x at the point (L) was determined experimentally to be 0.056. Applying Gibbs–Duhem equation to Eq. (5), we may calculate the activity of $\text{YFe}_2\text{O}_{4-x_0}$ at the point (L) as follows:

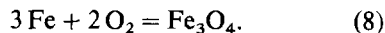
$$\log a_{\text{YFe}_2\text{O}_{4-x_0}}(L) = \frac{\log P_{\text{O}_2}(L)}{\log P_{\text{O}_2}(K)} - 1/2 \int_{\log P_{\text{O}_2}(K)}^{\log P_{\text{O}_2}(L)} (x_0 - x) d \log P_{\text{O}_2} \quad (6)$$

where $\log P_{\text{O}_2}(K)$ and $\log P_{\text{O}_2}(L)$ were determined to be -11.94 and -11.35 , respectively. Since the relationship between $(x_0 - x)$ and $\log P_{\text{O}_2}$ in the solid solution from (K) to (J) was substantially linear within the present experimental errors, the integration was readily obtained. The value of $\log a_{\text{YFe}_2\text{O}_{4-x_0}}$ at the point (L) was calculated to be -0.007 . Substituting this value into Eq. (4), we obtain the value -0.358 as an activity of metallic iron in the solid solution (L). By using this activity of metallic iron, we may calculate the standard free energy of formation of YFeO_3 , $\Delta G^\circ(2)$, referred to Eq. (2), because the activity of Y_2O_3 is unity. The value thus obtained, $-59\,800 \pm 200$ cal, is smaller than that of LaFeO_3 , $-68\,700 \pm 200$ cal, determined by the present authors (I).

Since stoichiometric $\text{Y}_3\text{Fe}_5\text{O}_{12}$ was in equilibrium with both stoichiometric YFeO_3 and Fe_3O_4 at an oxygen partial pressure of $10^{-5.82}$ atm as seen in Fig. 1, the standard free energy change, $\Delta G^\circ(7)$, referred to the following Eq. (7) may be obtained to be -6500 ± 600 cal,

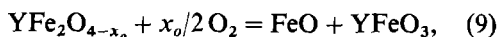


According to Darken and Gurry (8), the activity of metallic iron in stoichiometric Fe_3O_4 which is in equilibrium with wüstite is $10^{-1.545}$, and the oxygen partial pressure at which stoichiometric Fe_3O_4 is in equilibrium with wüstite is $10^{-9.14}$ atm at 2100°C . Thus, the standard free energy of formation of Fe_3O_4 , $\Delta G^\circ(8)$, referred to the following equation is calculated to be $-154\,500 \pm 300$ cal at 1200°C ,



Adding $\Delta G^\circ(7) + 2/3 \Delta G^\circ(8) + 3 \Delta G^\circ(2)$, we obtain the standard free energy of formation of $\text{Y}_3\text{Fe}_5\text{O}_{12}$, $\Delta G^\circ(3)$, referred to Eq. (3) to be $-288\,900 \pm 600$ cal. Numerical values described above are summarized in Table II.

In addition, we may calculate the standard free energy of reaction, $\Delta G^\circ(9)$, referred to the following equation:



where the YFe_2O_4 phase was in equilibrium with both wüstite and YFeO_3 as seen in Fig. 1. In the present experiments, we determined the activity of FeO at the point (H) in Fig. 1 to be $10^{-0.070}$ on the basis of the following stoichiometric reaction



This value is identical with that obtained by Darken and Gurry (8), $10^{-0.0703}$. The activity of $\text{YFe}_2\text{O}_{4-x_0}$ is calculated by adopting Eq. (6), and we obtain the value $10^{-0.0430}$ for the point (J) in Fig. 1. Since the activity of YFeO_3 and the equilibrated oxygen partial pressure were 1 and $10^{-10.13}$ atm, respectively, $\Delta G^\circ(9)$, referred to Eq. (9) is calculated to be -3100 cal. By summing up $\Delta G^\circ(1) + \Delta G^\circ(9) - \Delta G^\circ(10)$, we obtain $-59\,700$ cal which should be identical with $\Delta G^\circ(2)$, $-59\,800$ cal.

TABLE II
THE STANDARD FREE ENERGIES OF FORMATION OF YFe₂O_{4-x_o}, YFeO₃, AND Y₃Fe₅O₁₂ AT 1200°C

Equation	-Log P _{O₂}	ΔG° (cal)	-Log a _i other than unity
(1) 2 Fe + 1/2 Y ₂ O ₃ + [(5 - 2x _o)/4] O ₂ = YFe ₂ O _{4-x_o} (x _o = 0.095)	11.94	-96 800 ± 200	
(2) Fe + 1/2 Y ₂ O ₃ + 3/4 O ₂ = YFeO ₃	11.35	-59 800 ± 200	Fe: 0.358
(3) 5 Fe + 2/3 Y ₂ O ₃ + 15/4 O ₂ = Y ₃ Fe ₅ O ₁₂ [ΔG°(7) + 2/3 ΔG°(8) + 3 ΔG°(2)]	—	-288 900 ± 600	
(7) 3 YFeO ₃ + 2/3 Fe ₃ O ₄ + 1/6 O ₂ = Y ₃ Fe ₅ O ₁₂	5.82	-6500 ± 600	
(8) 3 Fe + 2 O ₂ = Fe ₃ O ₄	9.14	-154 500 ± 300	FeO: 1.545
(9) YFe ₂ O _{4-x_o} + x _o /2 O ₂ = FeO + YFeO ₃ (x _o = 0.095)	10.13	-3100 ± 200	FeO: 0.070 YFe ₂ O _{4-x_o} : 0.0430
(10) Fe + 1/2 O ₂ = FeO	11.92	-40 200 ± 200	

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