Phase Equilibrium in the Y·Fe·O System at 1000°C

Kenzo Kitayama*, Miyuki Takano, Kozo Eitaki, and Akihiro Hoshina

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Phase equilibrium was established in the Y·Fe·O system at 1000°C with an oxygen partial pressure ranging from \( \log (P_{O_2}/\text{atm}) = 0 \) to 16.15, allowing construction of a phase diagram of the \( Y_2O_3 \cdot Fe \cdot Fe_2O_3 \) system at 1000°C. \( Y_2O_3, Fe, "FeO", Fe_3O_4, \) 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°C, 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°C, 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 \( \log (P_{O_2}/\text{atm}) \), \( Na/Na_x = 4.635 \times 10^2 \cdot \log P_{O_2} + 1.747 \). 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 \( \log (P_{O_2}/\text{atm}) \) at 1000°C, respectively.

* Professor, Department of Applied Chemistry and Biotechnology
The phases in the Y·Fe·O system are of important technological interest, particularly in view of their physical properties. As is well known, YFeO₃ and Y₃Fe₂O₁₂ (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 YFeO₃ and Y₃Fe₂O₁₂ have been used in operational memory.

Recently, a new YFe₂O₄ phase was found to be stable at 1200°C 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 YFe₂O₄ phase to be stable above 1010°C. According to Kato et al. (7), the crystal structure of this compound is a new type of AB₂X₄, 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 Ln₂O₃ and Fe₄O₅, and thus anisotropies, both in the magnetic interaction and the electrical conductivity, are expected.

The crystal structure and magnetic properties of YFe₂O₄, together with ErFe₂O₄, have been studied by Matsumoto et al. (8), and the pressure dependence of the YFe₂O₄ magnetic phase transitions was found.

Solid electrolyte galvanic cell EMF was performed on the reaction Fe + 3/2 NiO + 1/2 Y₂O₃ = 3/2 Ni + YFeO₃ 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 Y₂O₃ + 3/4 O₂ = YFeO₃, was calculated(10).

The objectives of the present study are to: (1) establish a detailed phase diagram of Y·Fe·O system at 1000°C as a function of oxygen partial pressure; (2) ascertain whether YFe₂O₄ and Y₃Fe₂O₁₂ are stable or not; that is, whether the phase diagram at 1000°C is different from those at 1200°C and 1100°C or not; (3) determine the thermochemical properties of reactions based on the phase diagram at 1000°C.

2. EXPERIMENTAL

Analytical grade Y₂O₃ (99.9%) and Fe₂O₃ (99.9%) were used as the starting materials. Both oxides were calcined at 1000°C. Mixtures having desired ratios of Y₂O₃/Fe₂O₃ 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 CO₂ and H₂, and of CO₂ and O₂, and using individual gases O₂ and CO₂. The actual oxygen partial pressure of the gas phases was measured by means of a solid electrolytic cell composed of (ZrO₂)₀.₈₆(CaO)₀.₁₄(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-filtered CuKα radiation. An external standard silicon was used to calibrate 2θ.

3. RESULTS AND DISCUSSIONS

(1) Phase equilibrium

1) Fe·O system at 1000°C.

To date, three oxides are known for the Fe·O system, "FeO", Fe₂O₄, and Fe₂O₃.

In the present experiment, the Fe·O system was reinvestigated using the present apparatus and techniques at 1000°C. The results are as follows. Figure 1a shows the oxygen partial pressure, -log(Po₂/atm), versus the weight changes, W₀₂/W₇, of the Fe·O system. Here, W₀₂ is the weight increase of a sample from the reference weight at log(Po₂/atm) = -16.15, at which Fe is stable, and W₇ is the total weight gain from the reference state to the state at 1 atm O₂. 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 O₂ = FeO, 2) 3 FeO + 1/2 O₂ = Fe₂O₄, and 3) 2/3 Fe₃O₄ + 1/6O₂ = Fe₂O₃, which are listed in Table 4. Figure 1b shows the relationship between the oxygen partial pressure and a
composition, the \( \text{NO}/\text{N}_{\text{Fe}} \) mole fraction ratio, of the FeO solid solution. Here, \( \text{NO} \) and \( \text{N}_{\text{Fe}} \) represent the mole fraction of oxygen and iron in the FeO solid solution.

[Figure 1b] The relationship between the oxygen partial pressure, \( \log (\text{PO}_2/\text{atm}) \), and the \( \text{NO}/\text{N}_{\text{Fe}} \) mole fraction ratio in the FeO system.

It is apparent that the FeO solid solution is stable in the oxygen partial pressure \( \log \text{PO}_2 = 13.38 \sim 15.22 \), and that the composition of FeO in equilibrium with metallic iron is 1.042 of the \( \text{NO}/\text{N}_{\text{Fe}} \) mole ratio at \( \log (\text{PO}_2/\text{atm}) = 15.22 \) and the composition of FeO in equilibrium with Fe\(_2\)O\(_4\) is 1.127 of the \( \text{NO}/\text{N}_{\text{Fe}} \) mole ratio at \( \log (\text{PO}_2/\text{atm}) = 13.38 \), respectively. The \( \log (\text{PO}_2/\text{atm}) \) versus the \( \text{NO}/\text{N}_{\text{Fe}} \) mole ratio of FeO solid solution is shown in Fig. 1c, and is represented by an equation: \( \text{NO}/\text{N}_{\text{Fe}} = 4.635 \times 10^{-2} \log \text{PO}_2 + 1.747 \). 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 \( \log (\text{PO}_2/\text{atm}) = 13.38 \) to 6.02 for Fe\(_2\)O\(_4\), as is well known, although it is not evident from Fig. 1a or b because of the scale of abscissa.

2) \( \text{Y}_2\text{O}_3 \cdot \text{Fe} \cdot \text{Fe}_2\text{O}_5 \) system.

Four samples, having \( \text{Y}_2\text{O}_3/\text{Fe}_2\text{O}_3 \) 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, \( \log (\text{PO}_2/\text{atm}) \), versus the weight changes, \( \text{Wo}/\text{W}_0 \), 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, \( \text{Wo} \) is the weight increase of a sample from the reference weight at \( \log (\text{PO}_2/\text{atm}) = -16.15 \), at which \( \text{Y}_2\text{O}_3 \) and Fe are stable, and \( \text{W}_0 \) is the total weight gain from the reference state.
to the state at 1 atm O₂, at which Y₂O₃ and YFeO₃, and YFeO₃ and Fe₂O₃ were stable, depending upon the total compositions of samples, as shown in Fig. 3. These phases 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 (P₀₂/ atm). These values correspond to the oxygen partial pressure in equilibrium with the three solid phases, Y₂O₃ + YFeO₃ + Fe, YFeO₃ + FeO + Fe, YFeO₃ + FeO + Fe₂O₄, and YFeO₃ + Fe₂O₄ + Fe₂O₃, respectively.

<table>
<thead>
<tr>
<th>Y₂O₃ Mol</th>
<th>Fe₂O₃ ratio</th>
<th>-log P₀₂ atm</th>
<th>Time hr</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
<td>15.80</td>
<td>6.7</td>
<td>Fe</td>
</tr>
<tr>
<td>0.2</td>
<td>0.8</td>
<td>15.30</td>
<td>6.9</td>
<td>Fe + Y₂O₃</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6</td>
<td>15.80</td>
<td>6.7</td>
<td>Fe + Y₂O₃</td>
</tr>
<tr>
<td>0.6</td>
<td>0.4</td>
<td>15.80</td>
<td>6.7</td>
<td>Fe + Y₂O₃</td>
</tr>
</tbody>
</table>

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, Y₂O₃, Fe, FeO, Fe₂O₄, Fe₂O₃, and YFeO₃ were evaluated by powder X-ray analysis and were found to be stable under the experimental conditions, whereas Y₃Fe₂O₁₂ (YIG) and YFe₂O₄ were not found to be stable.

From the above thermogravimetric results and phase identification, a phase diagram
for the Y₂O₃·Fe₂O₃·Fe₃O₅ system was constructed. The numerical values of the three solid fields in Fig. 3 are the values of -log P⁰₂ in equilibrium with the three solid phases described above. As described above, Y₃Fe₅O₁₂ and YFe₂O₅ 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°C, that the garnet Y₃Fe₅O₁₂ can coexist with Fe₃O₄ and Fe₂O₅". 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 YFe₂O₅ was also determined, but the composition range was small. The relationship between the oxygen partial pressure and the composition No/N₃Fe₂O₅ of the YFe₂O₅ solid solution could be represented by an equation: $\frac{No}{N₃Fe₂O₅} = -1.426 \times 10^4(log P⁰₂)^2 - 1.379 \times 10^4(log P⁰₂)$, obtained by the least-squares method. Here, No and N₃Fe₂O₅ represent the mole fraction of oxygen and YFe₂O₅ in the YFe₂O₅ solid solution. This equation can be solved to show that yttrium-iron perovskite would be stoichiometric (YFe₂O₅·(P), at 0 and YFe₂O₅·(P) a at 15.41 in terms of log(P⁰₂/atm).

As described above (1-3), the Fe₅O₄ 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 solid solutions are tabulated in Table 2.

<table>
<thead>
<tr>
<th>Component</th>
<th>Compositions</th>
<th>Symbols</th>
<th>log P⁰₂/atm</th>
<th>log a₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>FeO₁.₀₄₂</td>
<td>W₁</td>
<td>15.22</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>FeO₁₁.₇₀₂</td>
<td>W₂</td>
<td>13.38</td>
<td>-0.0628</td>
</tr>
<tr>
<td>YFe₂O₅</td>
<td>YFe₂O₂.₅₆</td>
<td>P₁</td>
<td>5.41</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>YFe₂O₂.₅₆</td>
<td>P₂</td>
<td>13.38</td>
<td>0.0280</td>
</tr>
<tr>
<td></td>
<td>YFe₂O₂.₉₉</td>
<td>P₃</td>
<td>6.02</td>
<td>0.0749</td>
</tr>
<tr>
<td></td>
<td>YFe₂O₅.₀₀</td>
<td>P</td>
<td>0.00</td>
<td>0.0788</td>
</tr>
</tbody>
</table>

In the next section, these activities will be used in the calculation of the Gibbs energy changes of
reactions.

The lattice constants of YFeO₃ perovskite were determined to be orthorhombic using the 0.6Y₂O₃/0.4Fe₂O₃ mole ratio sample which was made at 0.68 in \log P_0₂. 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, \[ \Delta G^\circ = -RT \ln K \]. Here, \( R \) is the gas constant, \( T \) the absolute temperature, and \( K \) the equilibrium constant of the reaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>\log P_{0₂}/atm</th>
<th>Time/h</th>
<th>Coexisting Phase</th>
<th>( a/A )</th>
<th>( b/A )</th>
<th>( c/A )</th>
<th>( V/A^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y₂O₃ Fe₂O₃</td>
<td>0.6</td>
<td>0.4</td>
<td>0.68</td>
<td>70</td>
<td>( Y₂O₃ )</td>
<td>5.532(2)</td>
<td>7.609(4)</td>
</tr>
<tr>
<td>Ref. 15)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.5946</td>
<td>7.6053</td>
</tr>
</tbody>
</table>

**Table 4. The Gibbs Energy Change of Reactions at 1000°C**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \log(P_{0₂}/atm) )</th>
<th>( \Delta G^\circ/\text{kJ/mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Fe + 1/2 O₂ = FeO</td>
<td>15.22</td>
<td>185.6</td>
</tr>
<tr>
<td>      (14.91)</td>
<td>      181.8*</td>
<td></td>
</tr>
<tr>
<td>      (14.94)</td>
<td>      182.1**</td>
<td></td>
</tr>
<tr>
<td>2) 3 FeO + 1/2 O₂ = Fe₃O₄</td>
<td>13.38</td>
<td>165.5</td>
</tr>
<tr>
<td>      (13.56)</td>
<td>      165.3*</td>
<td></td>
</tr>
<tr>
<td>      (13.22)</td>
<td>      161.2**</td>
<td></td>
</tr>
<tr>
<td>3) 2/3 Fe₃O₄ + 1/6 O₂ = Fe₂O₃</td>
<td>6.02</td>
<td>24.5</td>
</tr>
<tr>
<td>      (5.16)</td>
<td>      21.0*</td>
<td></td>
</tr>
<tr>
<td>      (5.33)</td>
<td>      21.7**</td>
<td></td>
</tr>
<tr>
<td>4) Fe + 1/2 Y₂O₃ + 3/4 O₂ = YFeO₃</td>
<td>15.41</td>
<td>281.8</td>
</tr>
<tr>
<td>      (15.07)</td>
<td>      275.7***</td>
<td></td>
</tr>
<tr>
<td>      (15.15)</td>
<td>      277.1****</td>
<td></td>
</tr>
</tbody>
</table>

* 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 Fe₂O₃ + 1/2 Y₂O₃ = YFeO₃ (Ref. 17) and the value of the reaction Fe + 3/4 O₂ = 1/2 Fe₃O₄, which was calculated based on JANAF Table (4).
a) This value was calculated based on the activity of FeO(W₂) in Table 2.

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 W₁ in Fig. 1b, which is in equilibrium with Fe should be different from that of FeO at the composition W₂.
which is in equilibrium with Fe₃O₄.

![Graph showing the relationship between ΔG° for reaction 4 and temperature.](image)

The Gibbs-Duhem equation was used to calculate the activities of Fe and FeO components in the FeO solid solution from the obtained No/NFe 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 (P₀₂/atm) in parentheses were calculated from the corresponding ΔG° values.

The ΔG° 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 −275.7 kJmol⁻¹ for the reaction 4 was calculated by combining the value of a reaction, Fe + 3/2 NiO + 1/2 Y₂O₃ = 3/2 Ni + YFeO₃, 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 was calculated based on the data (17) of the reaction 1/2 Fe₂O₃ + 1/2 Y₂O₃ = YFeO₃, and the value of the reaction Fe + 3/4 O₂ = 1/2 Fe₂O₃, which was calculated based on JANAF Table (4).

The present ΔG° value for reaction 4 is in fairly good agreement with the above previous values.

In Fig. 4, the relationship between the ΔG° for the reaction 4 and the temperature is shown. Values obtained at 1100°C and 1200°C were quoted from 18 and 5, respectively. A reasonable linear equation, ΔG° = −4.811 × 10² + 1.575 × 10⁻¹T, was obtained by means of the least-squares method.

4. Conclusion

(1) Phase equilibrium in the Y-Fe-O system at 1000°C was established under an oxygen partial pressure from 0 to -16.15 in log (P₀₂/atm).

(2) Under the present experimental conditions, Y₂O₃, Fe, "FeO", Fe₃O₄, Fe₂O₃, and
YFeO₃ phases were stable, whereas YFe₂O₄ and Y₃Fe₉O₁₂(YIG) were not stable. This is a striking contrast to the previous results obtained at 1100°C and 1200°C.

3) Fe₃O₄ and YFeO₃ were nonstoichiometric, but the range of the nonstoichiometry of Fe₃O₄ was too small to be seen in Fig. 1a, b, and Fig. 3.

4) The lattice constants of YFeO₃ 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 equilibrium with three solid phases.

6) The relationship between ΔG° and the temperature for reaction 4) was obtained.

Reference

15) JCPDS Card No. 39-1489.