Thermodynamic Study of Spinel Type Solid Solutions of the Fe_3O_4 - ZnFe_2O_4 System by E.M.F. Measurements using the Solid Electrolyte*

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The e.m.f. of the following galvanic cells with a $\text{ZrO}_2 + \text{CaO}$ solid electrolyte has been measured in the temperature range of 850–1050°C in the whole composition range of spinel type solid solutions of Fe_3O_4 - ZnFe_2O_4 .

The activities of Fe_3O_4 were derived from the e.m.f. according to a new analytical method. In the solid solutions coexisting with the Fe_2O_3 , $a_{\text{Fe}_3\text{O}_4}$ curve shows a small positive deviation from Raoult's law in the ZnFe_2O_4 -rich range, and obeys Raoult's law in the Fe_3O_4 -rich range. In the solid solutions coexisting with ZnO , the $a_{\text{Fe}_3\text{O}_4}$ curve shows a large positive deviation from Raoult's law in the whole composition range and $a_{\text{Fe}_3\text{O}_4}$ has a finite non-zero value in pure ZnFe_2O_4 . Equilibrium oxygen partial pressures for the solid solutions coexisting with Fe_2O_3 or ZnO were calculated from the experimental results. These results were compared with published data.

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I. Introduction

Thermodynamic properties of some double oxides with spinel-type structure have been presented. Kleppa *et al.*⁽¹⁾ have determined the enthalpies of formation of many simple spinels by oxide melt solution calorimetry. Schmalzried and Tretyakov⁽²⁾ have determined the standard free energies of formation of spinels by an e.m.f. method using the solid electrolyte. Recently, Jacob and Alcock⁽³⁾ measured the oxygen potentials over the systems $\text{Fe} + \text{FeCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3$ and $\text{Fe} + \text{FeV}_2\text{O}_4 + \text{V}_2\text{O}_3$ by an e.m.f. method using the solid electrolytes. Muan *et al.*⁽⁴⁾ and Schmahl *et al.*⁽⁵⁾ have

determined thermodynamic properties of solid solutions with spinel-type structure by a gas equilibrium method.

Thermodynamic properties of the system Fe_3O_4 - ZnFe_2O_4 have attracted much interest because the differences in oxygen parameters and lattice parameters between Fe_3O_4 and ZnFe_2O_4 are very small⁽⁶⁾, and the solid solution is considered as a product of mixing of an inverse spinel and a normal spinel.

Benner and Kenworthy⁽⁷⁾ investigated the ZnO - Fe_2O_3 - Fe_3O_4 system at 1100, 1300 and 1400°C with oxygen pressures between 1.0 and 1×10^{-4} atm, and used the results to calculate the activities of ZnO , Fe_2O_3 and Fe_3O_4 in the single phase region of spinel solid solution of the ternary system and the activities of components in the pseudobinary system Fe_3O_4 and ZnFe_2O_4 . The activities of Fe_3O_4 and ZnFe_2O_4 show large positive deviations from Raoult's law. Tretyakov⁽⁸⁾ measured the oxygen pressures for the solid solutions coexisting with Fe_2O_3 or ZnO by an e.m.f. method using the solid electrolyte with air as a reference, and calculated the activity of Fe_3O_4 . According to his data, the

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activity of Fe_3O_4 shows a negative deviation from Raoult's law in the solid solutions coexisting with Fe_2O_3 and a positive deviation in the solid solutions coexisting with ZnO .

This study was carried out to determine the activities of Fe_3O_4 in the system Fe_3O_4 – ZnFe_2O_4 at 850–1050°C by the e.m.f. method using the solid electrolyte according to the following new calculating method.

II. Experimental Principles

1. Solid solutions of Fe_3O_4 – ZnFe_2O_4 coexisting with Fe_2O_3

In the galvanic cell,

where x represents the mole fraction of Fe_3O_4 in the Fe_3O_4 – ZnFe_2O_4 system, passing of two Faradays of electricity, there are the following charge transfer operations:

at the left electrode

at the right electrode

Under the condition that the mutual solubility of the solid solution and Fe_2O_3 is negligibly small, the over-all cell reaction is:

The cell potential E for reaction (3) is given by the well-known expression:

$$\Delta \bar{G}_{\text{Fe}_3\text{O}_4} = -EF = RT \ln a_{\text{Fe}_3\text{O}_4}, \quad (4)$$

$$\int_{X(\text{Fe}_3\text{O}_4)=1}^{X(\text{Fe}_3\text{O}_4)} d\mu_{(\text{Fe}_3\text{O}_4)} = \int_{\mu_{\text{O}_2}(X_{\text{Fe}_3\text{O}_4}=1)}^{\mu_{\text{O}_2}(X_{\text{Fe}_3\text{O}_4})} - \frac{X_{(\text{ZnFe}_2\text{O}_4)}}{4X_{(\text{ZnFe}_2\text{O}_4)} + 6X_{(\text{Fe}_3\text{O}_4)}} d\mu_{\text{O}_2} \quad (10)$$

Using the well-known relation, $d\mu = RT d \ln a$, one obtain,

$$\log a_{\text{Fe}_3\text{O}_4} = \int_{\log P_{\text{O}_2}(X_{\text{Fe}_3\text{O}_4}=1)}^{\log P_{\text{O}_2}(X_{\text{Fe}_3\text{O}_4})} - \frac{X_{(\text{ZnFe}_2\text{O}_4)}}{4X_{(\text{ZnFe}_2\text{O}_4)} + 6X_{(\text{Fe}_3\text{O}_4)}} d \log P_{\text{O}_2}. \quad (11)$$

$a_{\text{Fe}_3\text{O}_4}$ can be calculated from eq. (11) if the equilibrium oxygen partial pressure is known in the whole composition range of the Fe_3O_4 – ZnFe_2O_4 system. In this study the following cell was used to obtain $\log P_{\text{O}_2}$;

where $\Delta \bar{G}_{\text{Fe}_3\text{O}_4}$: partial molar free energy of formation of Fe_3O_4 – ZnFe_2O_4 solid solution; F : Faraday's constant; R : universal gas constant; T : absolute temperature; $a_{\text{Fe}_3\text{O}_4}$: activity of Fe_3O_4 in the solid solution. The reference state is Fe_3O_4 in equilibrium with Fe_2O_3 in the binary system Fe – O . One can calculate the activity of Fe_3O_4 using the measured e.m.f. of cell [I] and eq. (4).

2. Solid solutions of Fe_3O_4 – ZnFe_2O_4 coexisting with ZnO

Consider the equilibrium reaction between a spinel solid solution of Fe_3O_4 – ZnFe_2O_4 and ZnO . Let the parentheses represent the component in the solid solutions.

From eqs. (5) and (6), one can get eq. (7) describing the equilibrium relation in the whole range of Fe_3O_4 – ZnO – ZnFe_2O_4 .

Using the chemical potentials for eq. (7) and $\mu_{(\text{ZnO})} = \mu_{\text{ZnO}}^0$, eq. (8) can be obtained.

$$\frac{2}{3}d\mu_{(\text{Fe}_3\text{O}_4)} + \frac{1}{6}d\mu_{\text{O}_2} = d\mu_{(\text{ZnFe}_2\text{O}_4)} \quad (8)$$

where μ_{ZnO}^0 : chemical potential of pure ZnO . We assume that the Fe_3O_4 – ZnFe_2O_4 system can be treated like a binary system and apply the Gibbs-Duhem equation to the system,

$$X_{(\text{Fe}_3\text{O}_4)}d\mu_{(\text{Fe}_3\text{O}_4)} + X_{(\text{ZnFe}_2\text{O}_4)}d\mu_{(\text{ZnFe}_2\text{O}_4)} = 0. \quad (9)$$

Then the following equation can be obtained.

III. Experimental Procedure

Materials: In order to form ZnFe_2O_4 , equal molar proportions of reagent-grade ZnO and Fe_2O_3 powders were mixed, and heated in air at 900°C for 7 d. In order to prepare Fe_3O_4 , Fe (99.5% purity) and Fe_2O_3 powders were mixed in a desired ratio, pressed into pellets, and heated in argon atmosphere at 1000°C for 24 h. After Fe_3O_4 and ZnFe_2O_4 were finely ground, they were mixed in desired ratios. The mixtures were compacted into pellets and heated in argon atmosphere at 900°C for 5 d to form the spinel solid solutions. After each heat-treatment, the formation of the desired phases was confirmed by an X-ray diffractometer. ZnO or Fe_2O_3 powders were mixed with the solid solutions in the molar ratio (1:2), and they were pressed into pellets and heated in argon at 950°C for 2 d before e.m.f. measurements. The reference electrode, $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$, was prepared in a similar way to Fe_3O_4 . $\text{Ni} + \text{NiO}$ electrode was prepared from reagent-grade NiO and Ni (99.98% purity) powders. They were mixed, pressed and heated at 1000°C for 24 h in argon atmosphere.

Apparatus and Procedure: The apparatus and cell arrangements were similar to those used in an earlier study of solid Co-Mo alloys⁽⁹⁾. The e.m.f. of cells [I] and [II] was measured for increasing and decreasing temperatures between 850 and 1050°C . The time required to reach the equilibrium varied at first from 10 to 20 h and from 2 to 10 h after the temperature was settled to the next one. The e.m.f. was measured with a digital voltmeter. The cell temperature was measured with a Pt-Pt-13Rh thermocouple. It was confirmed that the compositional change in the solid solution during the experiments was negligibly small, when examining the peak (731) in the diffraction pattern for the spinel solid solution.

IV. Results

1. Solid solutions of Fe_3O_4 - ZnFe_2O_4 coexisting with Fe_2O_3

The variation in e.m.f. of cell [I] with tempera-

ture is shown in Fig. 1. A long time was required to get the equilibrium values of e.m.f. on decreasing the temperature of the cell, and sometimes steady values of e.m.f. could not be obtained when the cell temperature was decreased too fast. The temperature dependence of the values of e.m.f. can be represented experimentally by the equations shown in Table 1. These e.m.f.'s are related to the activities of Fe_3O_4 by eq. (4). The activity curves are shown in Fig. 2. Activities

Fig. 1 Temperature dependence of the e.m.f. of the cell $(-)\text{Fe}_3\text{O}_4, \text{Fe}_2\text{O}_3/\text{ZrO}_2 + \text{CaO}/(\text{Fe}_3\text{O}_4)_x (\text{ZnFe}_2\text{O}_4)_{1-x}, \text{Fe}_2\text{O}_3(+)$.

Table 1 Temperature dependence of the e.m.f. of the cell $(-)\text{Fe}_3\text{O}_4, \text{Fe}_2\text{O}_3/\text{ZrO}_2 + \text{CaO}/(\text{Fe}_3\text{O}_4)_x (\text{ZnFe}_2\text{O}_4)_{1-x}, \text{Fe}_2\text{O}_3(+)$.

$X_{\text{Fe}_3\text{O}_4}$	E.M.F. (mV)	Temperature ($^\circ\text{C}$)
0.1	$29.6 + 0.15307(T) \pm 2.4$	731–963
0.2	$-74.7 + 0.18557T \pm 1.4$	803–1001
0.3	$-12.9 + 0.1079T \pm 1.4$	833–1016
0.4	$-29.4 + 0.09457T \pm 1.2$	840–1002
0.5	$-20.3 + 0.07437T \pm 1.2$	854–1091
0.6	$5.6 + 0.03917T \pm 1.2$	850–1097
0.7	$6.8 + 0.02597T \pm 1.1$	855–1091
0.8	$9.0 + 0.01097T \pm 0.8$	841–1138
0.9	$2.9 + 0.00657T \pm 0.7$	863–1118

Fig. 2 Activity-composition curves for magnetite and zincferrite in Fe_3O_4 - ZnFe_2O_4 spinel solid solutions coexisting with Fe_2O_3 .

of ZnFe_2O_4 were calculated by the following equations:

$$\ln a_{\text{ZnFe}_2\text{O}_4} = \ln X_{\text{ZnFe}_2\text{O}_4} - X_{\text{Fe}_3\text{O}_4} X_{\text{ZnFe}_2\text{O}_4} \alpha_{\text{Fe}_3\text{O}_4} + \int_0^{X_{\text{Fe}_3\text{O}_4}} \alpha_{\text{Fe}_3\text{O}_4} dX_{\text{Fe}_3\text{O}_4}, \quad (12)$$

$$\alpha_{\text{Fe}_3\text{O}_4} = \frac{\ln \gamma_{\text{Fe}_3\text{O}_4}}{(1 - X_{\text{Fe}_3\text{O}_4})^2}. \quad (13)$$

Here X_i : mole fraction of the i component, γ_i : activity coefficient of the i component. The $a_{\text{Fe}_3\text{O}_4}$ curve obeys Raoult's law on the Fe_3O_4 -rich side and shows a positive deviation from Raoult's law on the ZnFe_2O_4 -rich side. Activities derived by Benner and Kenworthy⁽⁷⁾ using the gas equilibrium method and those derived by Tretyakov⁽⁸⁾ using the e.m.f. method are also shown in Fig. 2. Molar free energies of formation of Fe_3O_4 - ZnFe_2O_4 solid solutions from the components Fe_3O_4 and ZnFe_2O_4 at 900°C are shown in Fig. 3. The integral free energy of formation of the solid solutions has a minimum near $X_{\text{Fe}_3\text{O}_4} = 0.5$.

2. Solid solutions of Fe_3O_4 - ZnFe_2O_4 coexisting with ZnO

The variation of the e.m.f. of cell [II] with temperature is shown in Fig. 4. The temperature dependence of the observed e.m.f. can be represented by the equations shown in Table 2. From the results shown in Table 2,

Fig. 3 Partial and integral free energies of formation of Fe_3O_4 - ZnFe_2O_4 solid solutions from the components Fe_3O_4 and ZnFe_2O_4 at 900°C.

Fig. 4 Temperature dependence of the e.m.f. of the cell $(-)\text{Ni}, \text{NiO}/\text{ZrO}_2 + \text{CaO}/(\text{Fe}_3\text{O}_4)_x (\text{ZnFe}_2\text{O}_4)_{1-x}, \text{ZnO}(+)$.

the equilibrium oxygen pressures for the spinel solid solutions coexisting with ZnO are calculated using the available values of P_{O_2} for the reference electrode $\text{Ni} + \text{NiO}$.

Table 2 Temperature dependence of the e.m.f. of the cell $(-)\text{Ni}, \text{NiO}/\text{ZrO}_2 + \text{CaO}/(\text{Fe}_3\text{O}_4)_x (\text{ZnFe}_2\text{O}_4)_{1-x}, \text{ZnO}(+)$.

$X_{\text{Fe}_3\text{O}_4}$	E.M.F. (mV)	Temperature (°C)
0.1	$-311.0 + 0.3172T(\text{K}) \pm 3.7$	841-1101
0.2	$-309.0 + 0.2916T \pm 1.8$	845-1091
0.3	$-318.9 + 0.2670T \pm 2.5$	905-1101
0.4	$-327.0 + 0.2486T \pm 2.5$	843-1101
0.5	$-281.7 + 0.1988T \pm 2.5$	842-1080
0.6	$-289.0 + 0.1856T \pm 3.2$	842-1014
0.7	$-311.6 + 0.1920T \pm 3.2$	838-1025
0.8	$-258.1 + 0.1243T \pm 3.7$	833-1032

$$E = \frac{RT}{4F} \ln \frac{P_{\text{O}_2}(\text{spinel S.S.} + \text{ZnO})}{P_{\text{O}_2}(\text{Ni} + \text{NiO})} \quad (14)$$

$$\Delta G_{\text{Ni} + 1/2\text{O}_2 = \text{NiO}}^0 = -55840 + 20.3T(^{\circ}\text{K}) \text{ cal}^{(10)} \quad (15)$$

In order to calculate the value of $a_{\text{Fe}_3\text{O}_4}$, a least-squares method was applied to the relationship between $-X_{\text{ZnFe}_2\text{O}_4}/(4X_{\text{ZnFe}_2\text{O}_4} + 6X_{\text{Fe}_3\text{O}_4})$ and $\log P_{\text{O}_2}$. The relationship between them at 900°C is shown in Fig. 5. The derived values of $a_{\text{Fe}_3\text{O}_4}$ at 850°C and 1050°C are plotted against $X_{\text{Fe}_3\text{O}_4}$ in Fig. 6 with data by Tretyakov and those by Benner and Kenworthy. The results in this investigation are in good agreement with those by Tretyakov in the Fe_3O_4 -rich range. It is found that $a_{\text{Fe}_3\text{O}_4}$ has a non-zero value at the composition of ZnFe_2O_4 ($X_{\text{Fe}_3\text{O}_4} = 0$).

Fig. 5 The relationship between $-X_{\text{ZnFe}_2\text{O}_4}/(4X_{\text{ZnFe}_2\text{O}_4} + 6X_{\text{Fe}_3\text{O}_4})$ and $\log P_{\text{O}_2}$ in Fe_3O_4 - ZnFe_2O_4 solid solutions coexisting with ZnO at 900°C.

Fig. 6 Activity-composition curves for magnetite in Fe_3O_4 - ZnFe_2O_4 solid solutions coexisting with ZnO .

V. Discussion

1. Experimental conditions for derivation of activity of Fe_3O_4

For calculation of equilibrium oxygen pressures using cell [I] or [II], no other assumptions than the unity of the transference number of ions in the electrolyte are needed. Consider the solid solutions coexisting with Fe_2O_3 . When one calculates $a_{\text{Fe}_3\text{O}_4}$ according to the experimental principle 1, it is necessary to assume that the chemical potential of Fe_2O_3 at the right hand electrode equals that at the left hand one in cell [I]. It requires that the solubility of spinel solid solution in Fe_2O_3 should be very small. According to the phase diagram of the Fe-O system⁽¹¹⁾ the solubility of Fe_3O_4 in Fe_2O_3 is small. According to the studies on the phase diagram of the Zn-Fe-O system by Kushima and Amanuma⁽¹²⁾ or Yamaguchi and Takei⁽¹³⁾, mutual solubility of Fe_2O_3 and ZnFe_2O_4 (or ZnO and ZnFe_2O_4) increases with temperature above 1050°C, but it is small below 1050°C. The e.m.f. measurements in this investigation were undertaken in the lower temperature range.

2. Activity in the solid solutions of Fe_3O_4 - ZnFe_2O_4

Activity curves are shown in Fig. 2 and Fig. 6. Data by Benner and Kenworthy were derived from gas equilibrium measurements

performed in the single phase field of spinel type solid solutions of Fe_3O_4 - ZnFe_2O_4 at higher temperatures. Data by Tretyakov and those in this study were derived from e.m.f. measurements performed in the spinel solid solutions coexisting with Fe_2O_3 or ZnO . As shown in Fig. 2, the activities derived by Tretyakov and by the present authors show a large discrepancy in spite of a similar condition that Fe_2O_3 coexists with Fe_3O_4 - ZnFe_2O_4 solid solutions. The cause of the discrepancy does not come from the analytical method of the experimental results, because one can get the same activity as shown by Tretyakov applying the analytical method used in this study to his data.

In the solid solutions coexisting with ZnO , it is found, as shown in Fig. 6, that the activity in this study is in good agreement with that of Tretyakov in spite of the different analytical method. The activities of Fe_3O_4 in pure ZnFe_2O_4 are found to have finite values in both experimental results.

3. Equilibrium oxygen pressure for the spinel solid solutions coexisting with Fe_2O_3 or ZnO

It was shown that the equilibrium oxygen pressure for the solid solutions coexisting with ZnO could be calculated from eqs. (14) and (15) and the results shown in Table 2. In a similar way, one can calculate the oxygen pressure for the solid solutions coexisting with Fe_2O_3 using eqs. (16) and (17) and the results shown in Table 1.

$$E = \frac{RT}{4F} \ln \frac{P_{\text{O}_2(\text{Solid solution} + \text{Fe}_2\text{O}_3)}}{P_{\text{O}_2(\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4)}} \quad (16)$$

$$\begin{aligned} \Delta G_{2\text{Fe}_3\text{O}_4 + 1/2\text{O}_2 = 3\text{Fe}_2\text{O}_3}^0 \\ = -59000 + 33.9T(\text{K}) \text{ cal}^{(10)} \end{aligned} \quad (17)$$

They are shown in Fig. 7 and Fig. 8. In Fig. 7, data by Popov *et al.*⁽¹⁴⁾ using a gas equilibrium method at 900°C are also shown. The result in this study is in agreement with that by Tretyakov, but is higher than the result by Popov *et al.* in the solid solutions coexisting with ZnO . In the solid solutions coexisting with Fe_2O_3 , discrepancy between the result by Tretyakov and that in this study

Fig. 7 Equilibrium oxygen pressures for the coexistence of zinc oxide and Fe_3O_4 - ZnFe_2O_4 solid solutions.

Fig. 8 Equilibrium oxygen pressures for the coexistence of hematite and Fe_3O_4 - ZnFe_2O_4 solid solutions at 900°C.

is large. Unfortunately the reason is not clear.

VI. Conclusion

The e.m.f. of the galvanic cells with the solid electrolyte has been measured in the temperature range of 850–1050°C in the whole composition range of spinel type solid

solutions Fe_3O_4 - ZnFe_2O_4 . The activities of Fe_3O_4 were derived from the e.m.f. according to a new calculating method. The following results were obtained: (1) In the solid solutions coexisting with Fe_2O_3 , $a_{\text{Fe}_3\text{O}_4}$ curve shows a small positive deviation from Raoult's law in the ZnFe_2O_4 -rich range, and obeys Raoult's law in the Fe_3O_4 -rich range. (2) In the solid solutions coexisting with ZnO , the $a_{\text{Fe}_3\text{O}_4}$ curve shows a large positive deviation from Raoult's law in the whole composition range and $a_{\text{Fe}_3\text{O}_4}$ has a finite non-zero value in pure ZnFe_2O_4 . The equilibrium oxygen partial pressure for the solid solutions coexisting with Fe_2O_3 or ZnO was calculated from the results. These results were compared with published data.

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