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Abstract

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THERMODYNAMIC ANALYSIS OF THE SOLID SOLUTION

$MgAl_2O_4$—Fe_3O_4

On the basis of the results of a study of the process of reduction of magnesium ferroaluminate by hydrogen under equilibrium conditions ([3]), we shall carry out a thermodynamic analysis of the $MgAl_2O_4$—Fe_3O_4 solution formed in the reduction process and in equilibrium with the solid solution MgO—FeO of variable composition.

In calculating the thermodynamic characteristics, the statistical method was used for determining the activities of the components of a spinel-type solid solution for the case of its equilibrium with a wüstite phase of variable concentration ([2]). This method makes it possible to represent the concentration dependence of the activities of the components of a binary spinel solution in the form

$$a_i = C_i \left[\frac{1 - C_1\lambda_1^0 - C_2\lambda_2^0}{1 - \lambda_i^0} \right]^{1-\lambda_i^0} \left[\frac{1 + C_1\lambda_1^0 + C_2\lambda_2^0}{1 + \lambda_i^0} \right]^{1+\lambda_i^0} e^{\alpha(1-C_i)^2}, \qquad (1)$$

where a_i and C_i are, respectively, the activity and concentration of the i-th component (Fe_3O_4 or $MgAl_2O_4$); λ_1^0 and λ_2^0 are the degrees of inversion of the crystal lattice of the pure components (formula (1) was derived under the assumption of a linear dependence of the degree of inversion on concentration, but this formula was used because of the absence of experimental data on $\lambda = \lambda(C)$ for the given solid solution); α is an energy parameter determined experimentally.

Since the experimentally obtained crystal-lattice parameter of hypothetical wüstite (4.320 + 0.003 Å ([1])) in solution with MgO corresponds to the composition $FeO_{1.02}$, the equilibrium constant of the reaction for the reduction of magnetite from the $MgAl_2O_4$—Fe_3O_4 solution, proceeding according to the equation

$$(Fe_3O_4)_p \rightleftharpoons 3(FeO_{1.02})_p + 0.47O_2, \qquad (2)$$

is expressed as

$$k = \frac{a^{3}_{FeO_{1.02}} P^{0.47}_{O2}}{a_{M}}, \tag{3}$$

where $a_{FeO_{1.02}}$ and a_M are the activities of wüstite and magnetite.

Substituting into (1) the degrees of inversion of magnetite ($\lambda_1^0 = 0$) and magnesium aluminate ($\lambda_2^0 = 1$), if λ is taken as the fraction of divalent cations in tetrahedral sites, we obtain

$$a_{M} = C_{M}\left[1 - (1 - C_{M})^{2}\right] e^{\alpha(1-C_{M})^{2}}, \tag{4}$$

$$a_{MgAl2O_4} = \frac{1}{4} C_{MgAl2O_4} (1 + C_{MgAl2O_4})^{2} e^{\alpha(1-C_{MgAl2O_4})^{2}}. \tag{5}$$

For the activity of $FeO_{1.02}$ in a binary wüstite solution, the formula given in (3) is

$$a_j = C_j e^{\alpha'(1-C_j)^2}. \tag{6}$$

Table 1

Thermodynamic characteristics of the solid solution $MgAl_2O_4$–Fe_3O_4

$C_{Fe_3O_4}$	$C_{FeO_{1.02}}$	$a_{Fe_3O_4}$, 900°C	$a_{Fe_3O_4}$, 1000°C	$a_{Fe_3O_4}$, 1100°C	$a_{MgAl_2O_4}$, 900°C	$a_{MgAl_2O_4}$, 1000°C	$a_{MgAl_2O_4}$, 1100°C	$\Delta H^{\Pi}_{Fe_3O_4}$, kcal/mol	$\Delta H^{\Pi}_{MgAl_2O_4}$, kcal/mol	ΔH^{Π}, kcal/mol	$\Delta F^{\Pi}_{Fe_3O_4}$, kcal/mol 1000°C	$\Delta F^{\Pi}_{MgAl_2O_4}$, kcal/mol 1000°C	ΔH^{Π}, cal/mol	$\Delta S^{\Pi}_{Fe_3O_4}$, cal/(mol·deg)	$\Delta S^{\Pi}_{MgAl_2O_4}$, cal/(mol·deg)	ΔS^{Π}, cal/(mol·deg)	$\Delta \bar{S}_{Fe_3O_4}$, cal/(mol·deg)	$\Delta \bar{S}_{MgAl_2O_4}$, cal/(mol·deg)	$\Delta \bar{S}$, cal/(mol·deg)
0	—	0	0	0	1.0	1.0	1.0	0	0	0	0	0	0	0	0	0	0	0	0
0.05	0.664	0.00017	0.00020	0.00023	0.9012	0.9014	0.9016	−779	−9.3	−48	−2491	−2.8	−124	−13.1	+0.23	+0.85	+13.1	+0.23	+0.85
0.1	0.664	0.00071	0.00083	0.00094	0.803	0.805	0.806	−4435	−48.7	−487	−12115	−750	−1205	−3.07	+0.45	+0.98	+3.07	+0.45	+0.98
0.2	0.647	0.0033	0.0037	0.00046	0.638	0.636	0.632	−4996	−499	−1365	−8315	−1205	−2627	−3.79	+0.59	+1.39	+3.79	+0.59	+1.39
0.3	0.64	0.0085	0.0093	0.0100	0.452	0.463	0.467	−2682	−1086	−1110	−6013	−1812	−3478	−2.69	+0.33	+1.61	+2.69	+0.33	+1.61
0.4	0.63	0.0465	0.0477	0.0488	0.307	0.326	0.334	−1998	−845	−1306	−4379	−2836	−3453	−1.87	+0.25	+1.69	+1.87	+0.25	+1.69
0.5	0.595	0.277	0.29	0.313	0.202	0.218	0.227	−1411	−1596	−1437	−3342	−5055	−3306	−1.34	+0.04	+1.64	+1.34	+0.04	+1.64
0.6	0.555	0.414	0.43	0.444	0.127	0.136	0.144	−1071	−1973	−1432	−2137	−6452	−2987	−0.80	+0.18	+1.36	+0.80	+0.18	+1.36
0.7	0.49	0.514	0.541	0.584	0.071	0.078	0.085	−485	−2910	−1213	−1374	−8285	−2822	−0.70	+0.41	+1.33	+0.70	+0.41	+1.33
0.8	—	0.731	0.736	0.74	0.033	0.037	0.041	−266	−3968	−668	−774	−9452	−2298	−0.45	+0.70	+0.71	+0.45	+0.70	+0.71
0.9	—	0.888	0.881	0.883	0.011	0.014	0.015	−51.3	−3455	−1491	−319	−10894	−1377	−0.21	+0.59	+0.70	+0.21	+0.59	+0.70
0.95	—	0.9458	0.9462	0.9466	0.0046	0.0055	0.0063	−41.6	−4484	−130	−140	−13178	−119	−0.10	+0.48	+0.42	+0.10	+0.48	+0.42

$C_{Fe_3O_4}$	$C_{FeO_{1.02}}$	$a_{Fe_3O_4}$, 900°C	$a_{Fe_3O_4}$, 1000°C	$a_{Fe_3O_4}$, 1100°C	$a_{MgAl_2O_4}$, 900°C	$a_{MgAl_2O_4}$, 1000°C	$a_{MgAl_2O_4}$, 1100°C	$\Delta H^{\Pi}_{Fe_3O_4}$, kcal/mol	$\Delta H^{\Pi}_{MgAl_2O_4}$, kcal/mol	ΔH^{Π}, kcal/mol	$\Delta F^{\Pi}_{Fe_3O_4}$, kcal/mol 1000°C	$\Delta F^{\Pi}_{MgAl_2O_4}$, kcal/mol 1000°C	ΔH^{Π}, kcal/mol 1000°C	$\Delta S^{\Pi}_{Fe_3O_4}$, cal/(mol·deg)	$\Delta S^{\Pi}_{MgAl_2O_4}$, cal/(mol·deg)	ΔS^{Π}, cal/(mol·deg)	$\Delta \bar{S}_{Fe_3O_4}$, cal/(mol·deg)	$\Delta \bar{S}_{MgAl_2O_4}$, cal/(mol·deg)	$\Delta \bar{S}$, cal/(mol·deg)
1.0	–	1.0	1.0	1.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Substituting into (3) the explicit form of the concentration dependence of the activities (4) and (6), we find that

$$\lg k = 3 \lg C_{FeO_{1.02}} + 1.302(1-$$

$$-C_{FeO_{1.02}})^2 \alpha' + 0.47 \lg P_{O_2} -$$

$$-\lg C_M - \lg[1-(1-C_M)^2] -$$

$$-0.434(1-C_M)^2 \alpha. \tag{7}$$

By processing the data of study (1), analytical dependences were established for the equilibrium oxygen pressure on the concentration of magnetite (C_M) in the solution at 900, 1000, and 1100°C:

$$\lg P_{O_2}^{900} = -19.30 + 5.50 C_M, \tag{8}$$

$$\lg P_{O_2}^{1000} = -16.52 + 5.24 C_M, \tag{9}$$

$$\lg P_{O_2}^{1100} = -14.23 + 4.92 C_M, \tag{10}$$

as well as relations for the equilibrium concentrations of magnetite in the spinel and wüstite in the solid solutions.

From equation (7), taking (8), (9), and (10) into account, for three fixed concentrations of magnetite the values of $\lg k$, α, and α' were obtained for each temperature: $\lg k_{900} = -7.720$, $\alpha_{900} = -1.228$, $\alpha' = +0.795$, $\lg k_{1000} = -6.767$, $\alpha_{1000} = -1.011$, $\alpha'_{1000} = +0.977$, $\lg k_{1100} = -5.788$, $\alpha_{1100} = -0.859$, $\alpha'_{1100} = +1.135$.

By substituting the corresponding values of α into (4) and (5), the activities of magnetite and magnesium aluminate in the spinel solution were determined

Fig. 1. Concentration dependence of the activities of the components of the solid solution $MgAl_2O_4$—Fe_3O_4 at 1000°.

Figure 1: Fig. 1. Concentration dependence of the activities of the components of the solid solution $MgAl_2O_4$—Fe_3O_4 at 1000°.

(Table 1). As follows from Fig. 1, in the solid solution $MgAl_2O_4$—Fe_3O_4 a significant negative deviation from ideality is manifested. The activities of $FeO_{1.02}$ and MgO in the MeO solution, which is in equilibrium with the spinel solution and were calculated from (6) using α', proved to be in good agreement with (4), where the MgO—FeO solution was investigated.

The values of the activities of the components of the spinel solid solution were used to calculate the concentration dependence of the partial molar ($\Delta\bar{X}_i$) and integral (ΔX_p) thermodynamic functions (X) of mixing:

enthalpy ΔH, free energy ΔF, entropy ΔS, as well as the excess partial molar $\Delta\bar{S}_\mathrm{ex}$ and integral ΔS_ex entropy (Table 1).

The temperature dependence of the equilibrium constant of reaction (2) can be represented in the form

$$\lg k_2 = -15510\frac{1}{T} + 5.44. \tag{11}$$

In accordance with the Fe–O phase diagram (5), the dependence known in the literature (6) of the oxygen pressure on temperature for the equilibrium of pure magnetite with wüstite should, taking into account the real composition of wüstite, be referred to the reaction

$$Fe_3O_4 \rightleftarrows 3FeO_{1.13} + 0.305O_2, \tag{12}$$

whose equilibrium constant is

$$k_{12} = P_{O_2}^{0.305}. \tag{13}$$

Combination of (13) with

$$\lg P_{O_2} = -\frac{32623}{T} + 13.07\,^{(6)} \tag{14}$$

gives

$$\lg k_{12} = -9950\frac{1}{T} + 3.986. \tag{15}$$

Fig. 1. Concentration dependence of the activities of the components of the solid solution $MgAl_2O_4$—Fe_3O_4 at 1000°.

The difference between the equilibrium constants (11) and (15) is due to the different composition of the equilibrium wüstite phase in reactions (2) and (12). Their values agree if, along with (12), one considers the reaction of dissociation of magnetite and dissolution of iron in wüstite:

$$\frac{1}{4}Fe_3O_4 \rightleftarrows \frac{3}{4}Fe + \frac{1}{2}O_2, \tag{16}$$

$$Fe_{tv} \rightleftarrows (Fe)_{\text{dissolved in wüstite}}. \tag{17}$$

By Hess' s law, from (12), (16), and (17), (11) is obtained if the solution of iron in wüstite is regarded as ideal within the limits of the homogeneity region, and the equilibrium constant of reaction (16) is determined by extrapolation to the interval 900—1100°C.

The considerations presented may be used for calculating the equilibrium constants of reactions involving wüstite of another nonstoichiometry.

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