Thermodynamic Properties of NiCr$_2$O$_4$-NiFe$_2$O$_4$ Spinel Solid Solution

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The tie lines delineating ion-exchange equilibria between NiFe$_2$O$_4$-NiCr$_2$O$_4$ spinel solid solution and Fe$_2$O$_3$-Cr$_2$O$_3$ corundum solid solution were determined at 900, 1000, and 1200 °C by electron microprobe and energy dispersive X-ray analysis of oxide phases, using the flux growth technique. Activities of the spinel components were calculated from the tie lines, assuming Temkin's ideal mixing in the corundum solid solution. The spinel phase could be expressed by a regular solution with negative deviations from ideality. The Gibbs free energies of mixing for spinel solid solution were discussed in terms of the cation distribution model, based on site preference energies and assuming random mixing on both tetrahedral and octahedral sites.

Experimental Section

α-Fe$_2$O$_3$ (>99.99 wt.%) was purchased from Rare Metallic Co. and Na$_2$B$_2$O$_7$, Cr$_2$O$_3$, and NiO were all reagent grade (Aldrich Co.). An excess amount of these powders, about 1.5 times greater than the solubility predicted from the phase diagram, was mixed with the Na$_2$O · 2B$_2$O$_3$ flux. The experiments were conducted in a vertical resistance furnace having SiC heating elements. The mixtures (15 g) in a Pt crucible were conditioned at the desired temperatures and stirred with a Pt stirrer (10 rad/sec) under dry air environment to make the homogeneous mixture. After standing for 2-8 hrs, the sample was quenched into water. No solid solution phases were precipitated on quenching. Contents of the spinel and corundum component in the crystal grains were determined using electron microprobe and energy dispersive X-rays (Hidachi, X650S) rather than wet chemical analysis, since it was difficult to separate the two phases. The strong point of this experimental method compared with conventional quenching method can be found in the fact that the elemental concentrations in the crystal grown in the solution are constant depending on time and they are in equilibrium resulting from homogeneous state. More detailed descriptions are given in the previous report.$^5$

Results and Discussion

Tie line between corundum and spinel phases. The Fe$_2$O$_3$, NiO, and Cr$_2$O$_3$ crystals, with initial average sizes of 0.1-1.0 μm in saturated solution of Na$_2$O · 2B$_2$O$_3$ flux, were found to grow to the size of 10-20 μm in a period of 2-8 hrs. The observed coarsening of crystals was considered to be due to the Ostwald ripening mechanism in which the driving force is the reduction of total interfacial energy of the larger crystals. More details of this mechanism are discussed elsewhere.$^5$ The corundum and spinel crystals were formed under equilibrium conditions during Ostwald ripening due to the low degree of supersaturation with respect to crystal growth. The experimental results for the equilibrium compositions are summarized in Table 1 and the tie lines delineating the spinel and corundum solid solution at 900, 1000, 1200 °C are shown in Figure 1.

As can be seen in Figure 1, the deviation from the stoichiometric spinel composition increases with an increase in temperature and tends to decrease with increasing nickel content. Tie lines in the region of Fe$_2$O$_3$-poor compositions could not be determined since the Na$_2$O-Fe$_2$O$_3$-Cr$_2$O$_3$ solid solution was observed to be formed. The contents of Na and B in both phases were analyzed to be less than 30 wt.ppm, respectively.

Stoichiometry of spinel solid solution. In the present experimental conditions, ferrous ions are produced as predicted from the previous works$^6$-9 concerning the phase equilibria in the ferrite region of Fe-Ni-O system as a function of temperature and oxygen partial pressure. Therefore, the experimental data should be plotted in the Fe$_2$O$_3$-FeO-Cr$_2$O$_3$-NiO quartenary system, not in the ternary system as shown in Figure 1. However, since the content of ferrous ion in the spinel solid solutions could not be determined by the present analytical method, the experimental data are plotted in the ternary system of Fe$_2$O$_3$-Cr$_2$O$_3$-NiO, assuming that the
analyzed Fe content is equal to that of ferric ion. It should be noted, therefore, that the standard state for NiFe\textsubscript{2}O\textsubscript{4} is not the oxygen-saturated phase in equilibrium with Fe\textsubscript{2}O\textsubscript{3}. The data points at 900 and 1000 °C, having comparatively small deviation from stoichiometric spinel composition, were used for the calculation of activities in spinel phase.

**Activities of components in the spinel solid solution.**

When tie lines between two phases in equilibrium are known and activity data for one phase are available, the activities of the components in the second phase can be derived using the following modified Gibbs-Duhem integration method suggested by Wagner\textsuperscript{10} and applied to oxide systems by Muan.\textsuperscript{11} In the present calculation, Ni\textsubscript{0.5}FeO\textsubscript{2}, Ni\textsubscript{0.5}CrO\textsubscript{2}, FeO\textsubscript{1.5}, and CrO\textsubscript{1.5} are used as the composition variables. Intracrystalline ion-exchange equilibrium is written as,

$$\text{FeO}_{1.5} \cdot \text{Ni}_{0.5} \text{CrO}_2 \leftrightarrow \text{Ni}_{0.5} \text{FeO}_2 \cdot \text{CrO}_{1.5} \quad (1)$$

and the modified Gibbs-Duhem integration is given by

$$\log \gamma_{\text{Ni}_{0.5} \text{FeO}_2} = \frac{1}{x_{\text{Ni}_{0.5} \text{FeO}_2}} \frac{d}{x_{\text{Ni}_{0.5} \text{CrO}_2} \frac{d}{x_{\text{Ni}_{0.5} \text{FeO}_2}}}$$

Mixing of the corundum solid solution is ideal according to the Temkin model; that is, activities of Cr\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3} will be equivalent to the square of their mole fractions.\textsuperscript{11-17} This is further supported by the fact that Fe\textsubscript{2}O\textsubscript{3} and Cr\textsubscript{2}O\textsubscript{3} have the same crystal structure and the cations are nearly the same size - Cr\textsuperscript{3+} (0.615 Å) and Fe\textsuperscript{3+} (0.645 Å) - according to the Shannon and Prewitt scale\textsuperscript{18} for six fold coordination.

The modified Gibbs-Duhem integration plot for Ni\textsubscript{0.5}CrO\textsubscript{2} and Ni\textsubscript{0.5}FeO\textsubscript{2} is shown in Figures 2 and 3. In these plots, mole fractions of Ni\textsubscript{0.5}CrO\textsubscript{2} and Ni\textsubscript{0.5}FeO\textsubscript{2} can be recalculated as $X_{\text{Ni}_{0.5} \text{CrO}_2} + X_{\text{Ni}_{0.5} \text{FeO}_2}$. The value of log $\gamma_{\text{Ni}_{0.5} \text{FeO}_2}$ is obtained by the area below integration in Figures 2 and 3, while log $\gamma_{\text{Ni}_{0.5} \text{CrO}_2}$ can be evaluated from the area above the curve. However, there is a considerable uncertainty in extrapolating the logarithmic terms $v.s.$ $X_{\text{Ni}_{0.5} \text{CrO}_2}$ line to $X_{\text{Ni}_{0.5} \text{CrO}_2}$ due to the lack of data at the Fe\textsubscript{2}O\textsubscript{3}-poor compositions. For this reason, the activities of Ni\textsubscript{0.5}CrO\textsubscript{2} were deter-
mined by Gibbs-Duhem integration plot. The results are shown in Figure 4. It should be noted that the straight line indicated in Figures 2 and 3 suggests that the spinel solid solution is regular. The regular solution parameter, \( \alpha \), was determined either by the slope which is equal to \( (RT/2\alpha) \) or the area which is equal to \( \log \gamma = -\alpha \phi/\theta \). These values should be constant regardless of temperature, but those for obtained at 900 and 1000 °C are found to be -13.1 and -10.4 (kJ/mol), respectively.

Comparison with cation distribution model. Distribution of cations between the tetrahedral and octahedral sites of pure spinels can be estimated from octahedral site preference energies, assuming ideal Temkin mixing of cations on each cation sublattice.1,4 Jacob and Alcock19 have shown that the cation distribution estimated from the site preference energies for a number of aluminate spinels is in good agreement with X-ray and neutron diffraction measurements. The approach used by Jacob and Alcock2 is used to estimate the activity-composition relationship in the present intracrystalline ion-exchange equilibria between tetrahedral and octahedral sites. The values for the octahedral site preference energies for Ni\(_{2+}\) (~86.2 kJ/mol), Fe\(_{3+}\) (0 kJ/mol), and Cr\(_{3+}\) (~157.7 kJ/mol) obtained by Dunitz and Orgel20 from crystal-field theory are used.

The intracrystalline ion-exchange equilibria can be written and the enthalpy change for the exchange equilibria, \( \Delta H^{EX} \), can be deduced from the site preference energies for Ni\(_{0.5}\)Cr\(_{2}\)O\(_{4}\).

\[
\text{Ni}^{2+} + [\text{Cr}^{3+}] = [\text{Ni}^{2+}] + \text{Cr}^{3+} ; \Delta H^{EX} = 71.5 \text{ (kJ/mol)} \quad (3)
\]

and for Ni\(_{0.5}\)Fe\(_{2}\)O\(_{4}\),

\[
\text{Ni}^{2+} + [\text{Fe}^{3+}] = [\text{Ni}^{2+}] + \text{Fe}^{3+} ; \Delta H^{EX} = 86.2 \text{ (kJ/mol)} \quad (4)
\]

where \( ( ) \) and \( [ ] \) denote tetrahedral and octahedral sites, respectively. The cation distribution on octahedral sites is calculated from the solution to the following pair of equations:2,21~23

\[
71.5 = –RT \ln (2[x_{\text{Ni}^{2+}}] – [x_{\text{Cr}^{3+}}]/[1–2[x_{\text{Ni}^{2+}}] [x_{\text{Cr}^{3+}}]) \quad (5)
\]

\[
86.2 = –RT \ln (2[x_{\text{Ni}^{2+}}] – [x_{\text{Fe}^{3+}}]/[1–2[x_{\text{Ni}^{2+}}] [x_{\text{Fe}^{3+}}]) \quad (6)
\]

where \( x_i \) represent the ion fraction on the octahedral site and mole fraction of each spinel component. The calculated results for the cation distributions are listed in Table 2.

The activities can be evaluated from the cation distribution values relative to a normal spinel for Ni\(_{0.5}\)Cr\(_{2}\)O\(_{4}\), and an inverse spinel for Ni\(_{0.5}\)Fe\(_{2}\)O\(_{4}\), as the standard state using the following equations:12

\[
a_{\text{Ni}^{0.5}\text{Fe}^{0.5}\text{O}_2} \left[ \left(x_{\text{Fe}^{3+}} [x_{\text{Fe}^{3+}}] [x_{\text{Ni}^{2+}}] \right)^{1/2} \right] \quad (7)
\]

\[
a_{\text{Ni}^{0.5}\text{Cr}^{0.5}\text{O}_2} \left[ \left(x_{\text{Cr}^{3+}} [x_{\text{Cr}^{3+}}] [x_{\text{Ni}^{2+}}] \right)^{1/2} \right] \quad (8)
\]

where \( x_{\text{Ni}^{2+}} \) and \( x_{\text{Ni}^{2+}} \) denote ion fractions in pure components.

The calculated results for activities of spinel components and Gibbs energy of mixing, \( \Delta G^M \), are given in Figures 4 and 5, indicating that the experimental values for \( \Delta G^M \) are less negative than those of the model. The values for Gibbs energy of mixing in other spinel solid solutions with common cation, obtained by Jacob and co-workers,13,21~23 are also included in Figure 5 for comparison along with those obtained at 1000 °C according to Temkin’s law. It is of interest to note that the values for \( \Delta G^M \) in the group of normal-inverse spinel solid solution are approximately half the values in the group of normal-inverse spinel solid solution, except for the Fe\(_{0.5}\)Al\(_{0.5}\)O\(_{2}\)-Fe\(_{1.5}\)O\(_{2}\) system.

It has been shown that the correlation between experimentally derived and calculated Gibbs energy of mixing is very poor in most spinel solid solutions. Therefore, Jacob and co-workers13,23 discussed the difference between theoretical and experimental values, \( \Delta G^M_{\text{Ni}^{0.5}\text{Fe}^{0.5}\text{O}_2} \), in terms of the lattice distortion effect due to cation size difference. The present results are shown in Figure 6, together with those obtained in other spinel solid solutions13,21~23 with common cation. It can be seen that these values in the normal-inverse spinel solid solution increase in the order of Ni\(_{0.5}\)Cr\(_{2}\)O\(_{4}\)-Ni\(_{0.5}\)Fe\(_{2}\)O\(_{4}\) > Fe\(_{0.5}\)Al\(_{0.5}\)O\(_{2}\)-Fe\(_{1.5}\)O\(_{2}\) > Fe\(_{0.5}\)Cr\(_{2}\)O\(_{4}\)-Fe\(_{1.5}\)O\(_{2}\) which cannot be

**Table 2. Calculated cation distributions based on cation distribution model**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tetrahedral site, Number of ions</th>
<th>Octahedral site, Number of ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>X(_{\text{Ni}^{0.5}\text{Cr}^{0.5}\text{O}_2})</td>
<td>(\text{Fe}^{3+})</td>
<td>(\text{Cr}^{3+})</td>
</tr>
<tr>
<td>0.0</td>
<td>0.000</td>
<td>4.655×10⁻²</td>
</tr>
<tr>
<td>0.1</td>
<td>0.200</td>
<td>7.943×10⁻³</td>
</tr>
<tr>
<td>0.2</td>
<td>0.400</td>
<td>2.757×10⁻¹</td>
</tr>
<tr>
<td>0.3</td>
<td>0.600</td>
<td>1.081×10⁻¹</td>
</tr>
<tr>
<td>0.4</td>
<td>0.799</td>
<td>3.502×10⁻²</td>
</tr>
<tr>
<td>0.5</td>
<td>0.983</td>
<td>1.979×10⁻¹</td>
</tr>
<tr>
<td>0.6</td>
<td>0.999</td>
<td>1.311×10⁻⁴</td>
</tr>
<tr>
<td>0.7</td>
<td>0.999</td>
<td>4.172×10⁻⁰</td>
</tr>
<tr>
<td>0.8</td>
<td>0.999</td>
<td>2.086×10⁰</td>
</tr>
<tr>
<td>0.9</td>
<td>1.000</td>
<td>8.941×10⁰</td>
</tr>
<tr>
<td>1.0</td>
<td>1.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

**Figure 4. Activities for Ni\(_{0.5}\)Fe\(_{2}\)O\(_{4}\) and Ni\(_{0.5}\)Cr\(_{2}\)O\(_{4}\) in spinel solid solution at 900 and 1000 °C.**
explained by the cation size difference, whereas those in the normal-normal spinel solid solutions are approximately the same. It must be noted, however, that the cation distribution model proposed by O’Neill and Navrotsky, in which the enthalpy of cation disordering, $\Delta H^{\text{dis}}$, is not independent of the cation distribution in the spinel seems to be more reasonable for the explanation of thermodynamic properties of spinel solid solutions. This model was not applied to the present results, because the present spinel solid solution has a significant width in the spinel field, and the parameters for this model were not accurately determined.

**Conclusions**

The activities for Ni$_{0.5}$FeO$_2$ and Ni$_{0.5}$CrO$_2$ spinel solid solution were determined from the experimental tie-line data at 900 and 1000 °C, thus, resulting in a regular solution with a negative deviation from ideality. The Gibbs energy of mixing in this system was found to be considerably less negative, compared with that derived from the cation distribution model based on site preference energies. The observed values for $\Delta G^M$ was found to be approximately twice as much as those observed in the normal-normal spinel solid solutions. The difference between experimental and theoretical Gibbs energy of mixing in the present system was greater than those observed in the previous spinel solid solutions.

**References**