Activity Measurements of Na$_2$O in Na$_2$O–Fe$_2$O$_3$ System
by EMF Method Using Sodium Beta Alumina
as a Solid Electrolyte

By Shu Yamaguchi*, Yasuo Kaneko* and Yoshiaki Iguchi*

Activity measurements of Na$_2$O in the system Na$_2$O–Fe$_2$O$_3$ have been made by EMF method using sodium beta-alumina as a solid electrolyte between 850 and 1500 K. The cell employed in this study was written as:

\[
\text{Na}_2\text{O} + \text{Fe}_2\text{O}_3 (\Delta_{\text{Na}_2\text{O}}) \quad \text{Reference} \\
\text{Pt}, \text{O}_2(g) \quad \text{beta-alumina} \quad 5\text{Na}_2\text{O} + 21\text{Fe}_2\text{O}_3 \text{ or Na}_3\text{CO}_3 \text{ or O}_2 + \text{CO}_2(g), \text{ Pt}
\]

From the determined values of Na$_2$O activity, the values of the standard free energy change for the formation of Na$_3$Fe$_5$O$_9$ and Na$_2$Fe$_2$O$_4$ from pure solid Na$_2$O and Fe$_2$O$_3$ were also calculated as:

\[
\Delta G^\circ(\text{Na}_3\text{Fe}_5\text{O}_9)/\text{kJ mol}^{-1} = -(248.6 \pm 1.1) - (2.447 \pm 1.188) \times 10^{-3} \ T/K \quad (<1405 \ K),
\]

\[
\Delta G^\circ(\text{Na}_2\text{Fe}_2\text{O}_4)/\text{kJ mol}^{-1} = -(160.2 \pm 2.5) - (3.909 \pm 1.245) \times 10^{-3} \ T/K \quad (<1047 \ K),
\]

\[
= -(152.7 \pm 2.4) - (1.332 \pm 1.227) \times 10^{-3} \ T/K \quad (1047 < T < 1278 \ K),
\]

\[
= -(147.3 \pm 2.9) - (13.37 \pm 1.268) \times 10^{-3} \ T/K \quad (1278 < T < 1405 \ K).
\]

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**Keywords:** beta-alumina, electromotive force method, solid electrolyte, Na$_2$O–Fe$_2$O$_3$, activity, thermochemical properties

I. Introduction

Sodium ferrite compounds are attracting increasing attention from their significant effects on the damage to the nuclear reactor, their important roles in a blast furnace operation, and their applications for a magnetic material. It is of interest to determine the thermodynamic properties of the sodium ferrite system in order to clarify the chemical reactions taking place in these problems and the processing of the materials. However, only few studies have been done on the thermodynamic properties of Na$_2$O–Fe$_2$O$_3$ system. The determination of the activities of component in the present system have been reported by Dai, Seetharaman and Staffansson(1) and by Shaiu et al.(2) using the EMF method. However, these results should be revised, since the phase equilibria adopted in these studies are inconsistent with the phase diagram for the present system.

The phase diagram for the Na–Fe–O system has been reported by Dai et al.(3) Thery(4), and Knick and Kohlmeyer(5). However, the phase diagram for a Na$_2$O–Fe$_2$O$_3$ quasibinary system has not been well established for the phase stability range of Na$_3$Fe$_5$O$_9$ and the eutectic reaction between Fe$_2$O$_3$ and Na$_2$Fe$_2$O$_4$ reported by Knick and Kohlmeyer(5).

In this study, the EMF method was employed using sodium beta-alumina as a solid electrolyte, which has been successfully used by the present authors to determine the activity of Na$_2$O in Na$_2$O–bearing slag systems(6)(7).
II. Experimental

1. Concentration cell

A sodium concentration cell using sodium beta-alumina (Na$_2$O·11Al$_2$O$_3$) has been constructed in this study to determine the activity of the Na$_2$O in Na$_2$O–Fe$_2$O$_3$ system, which are written as

$$E = \frac{2FE}{RT} \ln \left( \frac{a_{Na_2O}^{cell}}{a_{Na_2O}^{ref}} \right) - \frac{1}{2} \frac{2FE}{RT} \ln \left( \frac{p_{O_2}}{p_{O_2}^*} \right),$$

(1)

where $E$ is the electromotive force of the cell, $T$, the absolute temperature, and $R$ and $F$ denote the gas constant ($=8.313/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and Faraday constant ($=96487/\text{coul}\cdot\text{equiv.}^{-1}$), respectively. Under the same partial pressure of oxygen gas, eq. (1) is simplified as

$$2FE = RT \ln \left( \frac{a_{Na_2O}^{cell}}{a_{Na_2O}^{ref}} \right).$$

(2)

Therefore, Na$_2$O activity in the sample electrode will be determined by measuring reversible EMF and the cell temperature, if the activity value in the reference electrode is known.

In this study, the Na$_2$O activity in the reference electrode was also determined by the EMF method by using sodium carbonate (Na$_2$CO$_3$) as a standard. The cell construction is written as;

$$E = -\frac{\Delta G^\circ(A)}{RT} + RT \ln \left( \frac{a_{Na_2O}^*}{a_{Na_2O}^{ref}} \right) - \frac{1}{2} \frac{2RT}{2RT} \ln \left( \frac{p_{O_2}^*}{p_{O_2}} \right) + RT \ln p_{CO_2},$$

(3)

where $p_{O_2}^*$ and $p_{CO_2}$ are the partial pressure of oxygen and CO$_2$ gas over Na$_2$CO$_3$ electrode, respectively. $\Delta G^\circ(A)$ is the standard free energy change of the reaction shown below.

$$\text{Na}_2\text{O} (\text{sol./liq.}) + \text{CO}_2 (\text{gas}) = \text{Na}_2\text{CO}_3 (\text{sol./liq.}) \quad (A)$$

The values of $G^\circ(A)$ were calculated by using the standard free energy change for the formation of Na$_2$O (sol./liq.), CO$_2$ gas, and Na$_2$CO$_3$ (sol./liq.) from the stable elements tabulated in JANAF thermochemical tables. The standard state of Na$_2$O activity was taken as pure solid Na$_2$O below the melting point of Na$_2$O (1405 K) and pure liquid Na$_2$O above the melting point.

2. Materials

Materials used in this study were all reagent-grade chemicals, supplied in a powdery form. Na$_2$CO$_3$ was used instead of Na$_2$O because of handling easiness. Na$_2$CO$_3$ was dried at 443 K in a drying oven for more than 86.4 ks (24 h). Fe$_2$O$_3$ was dried at 1273 K for 43.2 to 86.4 ks (12 to 24 h).

These raw materials were weighed after the drying process, and then mixed in an alumina bowl. The mixture was charged into a plat-
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inum crucible, and was heated up and kept at 1473 K for 7.2 ks (2 h) in SiC furnace. Subsequent annealing was made at 1273 K for 7.2 to 86.4 ks. The samples were ground in alumina bowl after the heat treatment, and were examined by the X-ray powder diffraction on the existing phases. Heat treatment was repeated until the equilibrium phases were obtained.

The examined cells and the compositions of the reference and the sample electrode of the cell were summarized in Table 1. Attempt was made to prepare the samples of higher Na₂O contents than 0.5 mole fraction of Na₂O (X_{Na₂O}). A complete decomposition of Na₂CO₃ used as a source of Na₂O could not be obtained, and the cell EMF was not stable for the measurement using the sample of X_{Na₂O}=0.65. Therefore, successful measurements were done on the samples with the composition of X_{Na₂O} < 0.5.

The X-ray powder diffraction was made by using Co irradiation to identify the existing phases in the samples.

In the present study, the phase existing in the composition range between Fe₂O₃ and Na₂Fe₂O₄ was identified as Na₃Fe₅O₉ from the agreement of the diffraction pattern with that of JCPDS CARD No. 18-1213.

3. EMF measurements

The schematics of the cell are shown in Fig. 1. The closed one-end beta-alumina tubes (10 mm OD x 8 mm ID x 100 mm long) manufactured by Toshiba Ceramics Co., Ltd. were used as a solid electrolyte. The electrode materials mixed with thick platinum paste were charged into both inside and outside of the beta-alumina tube. Platinum lead wires were immersed into the electrode materials. The electrode material set outside was contained in a alumina crucible (99.5% Al₂O₃). The electrolyte tube and the inner electrode were spring-loaded to keep good electrical contact between the electrolyte and electrodes. The temperature of the cell was monitored by a Pt/Pt-13%Rh thermocouple. All the components used to construct the cell around the electrolyte were made of alumina ceramics and alumina cement.

The assembled cell was placed in a SiC furnace controlled by the Chino E-500 or DD type controller. The accuracy of the temperature control was within 3 K. Purified air was passed over the cell for the measurements with cell Nos. 6, 9, 10, and 11.

In the measurements with the cell No. 0, the inner and outer compartments were separated to keep them under different atmospheres. A

Table 1  The composition of the electrode material examined (F=Fe₂O₃, N₃F₅=Na₃Fe₅O₉ and NF=Na₂Fe₂O₄).

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>Composition</th>
<th>Sample</th>
<th>Phases</th>
<th>Composition</th>
<th>Reference</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5Na₂O+21Fe₂O₃</td>
<td>(F+N₃F₅)</td>
<td>Na₂CO₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>10Na₂O+13Fe₂O₃</td>
<td>(N₃F₅+NF)</td>
<td>5Na₂O+21Fe₂O₃</td>
<td>(F+N₃F₅)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>10Na₂O+13Fe₂O₃</td>
<td>(N₃F₅+NF)</td>
<td>5Na₂O+21Fe₂O₃</td>
<td>(F+N₃F₅)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>3Na₂O+7Fe₂O₃</td>
<td>(F+N₃F₅)</td>
<td>5Na₂O+21Fe₂O₃</td>
<td>(F+N₃F₅)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>32Na₂O+68Fe₂O₃</td>
<td>(F+N₃F₅)</td>
<td>5Na₂O+21Fe₂O₃</td>
<td>(F+N₃F₅)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1 Schematics of the cell employed in the present study.
mixture of the purified CO₂ and O₂ gas was flown over the pure Na₂CO₃ (solid/liquid) reference electrode, and the purified air was passed over the other electrode. The partial pressures of CO₂ and O₂ gas were kept at 80 and 20 kPa (0.8 and 0.2 atm), respectively. The composition of the gas mixture was determined by measuring the EMF values from the oxygen gas sensor using stabilized zirconia electrolyte with air as a reference gas during the experiment. The measured values of the EMF was 5.3 ± 3 mV at 1150 K.

The values of the cell EMF and the EMF from Pt/Pt-13%Rh thermocouple were measured by Takeda Riken digital multimeter model TR-4646 (input impedance of 10⁸ Ω).

The stable EMF values were recorded as equilibrium ones, when the value stayed within 1 mV for 3.6 ks (1 h). Then a new temperature was set for the next measurement. The equilibrium EMFs were measured with increasing and decreasing temperatures of the cell until cell performance showed the irreversible feature. The time required to attain a new stable value was 7.2 to 108 ks (2 to 30 h) depending on its temperature, and the life time of the cell was more than 2.6 Ms (30 d).

III. Results and Discussion

1. EMF measurement

Measured EMF values obtained with the cell No. 0 were plotted against temperature in Fig. 2. Reversibility of the cell EMFs on changing temperature was confirmed by the good reproducibility of the EMFs obtained by the measurements on both heating and cooling the cell. The cell EMFs were expressed by straight lines, and the changes in the slope of the line were obtained in accordance with the transformations of the electrode materials, which are expressed as

(1) Na₂CO₃(sol.) ⇌ Na₂CO₃(liq.) at 1123 K

(2) Fe₂O₃(sol.) + Na₃Fe₅O₉ ⇌ Fe₂O₃(sol.) + Liq. at 1405 K.

The measured EMF values of the cell Nos. 6, 9, 10, and 11 are shown in Fig. 3. A good reproducibility of the EMF-temperature relationship was obtained between the cells composed of the same of reference and sample electrode.
(cell Nos. 6 and 9, cell Nos. 10 and 11), as shown in Fig. 3. For the cell Nos. 6 and 9, the breaks in the slope are observed at the transition temperature of the Na$_2$Fe$_2$O$_4$ phase:

\[
\alpha \leftrightarrow \beta \quad \text{at 1033 K, and}
\]

\[
\beta \leftrightarrow \gamma \quad \text{at 1278 K.}
\]

These temperatures are in good agreement with the reported values\(^4\).

The abrupt change in the slope was obtained at 1430 K. A possible reaction taking place is estimated as the incongruent decomposition of Na$_3$Fe$_5$O$_9$ phase as

\[
\text{Na}_3\text{Fe}_5\text{O}_9 \leftrightarrow \text{Liquid} + \gamma - \text{Na}_2\text{Fe}_2\text{O}_4
\]

at 1430 K.

Comparing Figs. 2 and 3, the temperatures of the break in the slope of the lines above 1400 K differs from each other. This fact indicates that the reaction of the liquid formation occurs at different temperatures in Na$_3$Fe$_5$O$_9$ + Fe$_2$O$_3$ and Na$_3$Fe$_5$O$_9$ + Na$_2$Fe$_2$O$_4$ coexisting region. One of the possible explanations is to assume the incongruent decomposition of Na$_3$Fe$_5$O$_9$ phase associated with eutectic reaction in the composition range between Na$_3$Fe$_5$O$_9$ and Fe$_2$O$_3$. DTA experiments similar to those described below were performed to determine the temperature and composition of these invariant reactions. However, uncertainty still remains on the definite composition and the temperature of the reactions.

According to Thery\(^6\), the Na$_3$Fe$_5$O$_9$ phase was reported to decompose to Fe$_2$O$_3$ and Na$_2$Fe$_2$O$_4$ at 1033 K. The present results, however, indicate that Na$_3$Fe$_5$O$_9$ phase is stable below 1033 K as shown in Fig. 3. In order to examine the phase transition, DTA was employed to detect the heat exchange due to the decomposition. The measurements were done at constant heating and cooling rates from 0.33 K/s (20 K/min) to 0.033 K/s (2 K/min) using fresh samples for each experimental run. In addition, the samples of the same composition for DTA were examined by an X-ray diffractometer after annealing at 973 K in air for more than 4.32 Ms (120 h). No evidence for the decomposition were detected by DTA or X-ray analysis. Therefore, the Na$_3$Fe$_5$O$_9$ phase is concluded to be stable over the temperature range of the present study. The possible interpretation of the results of Thery will be that the transformation between $\alpha$- and $\beta$-Na$_2$Fe$_2$O$_4$ have been detected as a decomposition of the Na$_3$Fe$_5$O$_9$ phase due to the inhomogeneity of the sample, prepared with insufficient annealing duration.

For the cell No. 10 and 11, the EMF values should remain null throughout the measured temperature, since the phases in the sample electrode is identical with those in the reference electrode. The observed values would be considered as a thermal EMF of the cells.

The Na$_2$O activity in the Fe$_2$O$_3$ + Na$_3$Fe$_5$O$_9$ co-existing region ($a_{\text{Na}_2\text{O}(\text{F}/\text{N}_3\text{F}_5)}$, where F and N$_3$F$_5$ denote Fe$_2$O$_3$ and Na$_3$Fe$_5$O$_9$, respectively) is determined by using eq. (2), and the estimated activity values were plotted as a function of reciprocal absolute temperature in Fig. 4. The coefficients of the best fit were calculated by the least squares analysis for log $a_{\text{Na}_2\text{O}(\text{F}/\text{N}_3\text{F}_5)}$ against $1/T$ in this region, and are listed in Table 3.

The activity values in the region of Na$_3$Fe$_5$O$_9$ + Na$_2$Fe$_2$O$_4$ ($a_{\text{Na}_2\text{O}(\text{N}_3\text{F}_5/\text{NF})}$, where NF denotes Na$_2$Fe$_2$O$_4$) are calculated from the results of the cell Nos. 6 and 9, using eq. (2).
2. Estimation of the thermochemical properties

The standard free energy change for the formation of Na$_3$Fe$_5$O$_9$ and Na$_2$Fe$_2$O$_4$ ($\alpha$, $\beta$, and $\gamma$) was estimated from the determined values of $a_{Na_2O}(N_3F_5/NF)$ and $a_{Na_2O}(F/N_3F_5)$. The calculation was made below 1405 K, since the values of Na$_2$O activity were not known over the liquid phase.

The standard free energy change for the reaction:

$$3Na_2O(s) + 5Fe_2O_3(s) = 2Na_3Fe_5O_9,$$

(B)
is calculated by the equation shown below, assuming $a_{Fe_2O_3}$ (solid hematite as a standard state) and $a_{Na_3Fe_5O_9}$ to be unity in this region.

$$\Delta G^\circ(B) = 2\Delta G^\circ(\text{Na}_3\text{Fe}_5\text{O}_9)$$

$$= 3RT \ln a_{Na_2O}(F/N_3F_5), \quad (4)$$

where $\Delta G^\circ(B)$ is the standard free energy change for the reaction (B). The coefficients were estimated from those for $\ln a_{Na_2O}(F/N_3F_5)$ tabulated in Table 3, and the estimated coefficients for $\Delta G^\circ(B)$ ($= 2\Delta G^\circ(\text{Na}_3\text{Fe}_5\text{O}_9)$) are summarized in Table 4.

The standard free energy change for the formation of Na$_2$Fe$_2$O$_4$ ($\Delta G^\circ(\text{Na}_2\text{Fe}_2\text{O}_4)$) is calculated from the following reaction:

$$2Na_3FeO_9 + 2Na_2O (s, l) = 5Na_2Fe_2O_4,$$

(C)

Assuming Na$_3$Fe$_2$O$_9$ to be stoichiometric, the standard free energy change for the reaction (C), $\Delta G^\circ(C)$, is written by following equation.

$$\Delta G^\circ(C) = 2RT \ln a_{Na_2O}(\text{N}_3\text{F}_5/NF). \quad (5)$$

Combining (B) and (C), the standard free energy of the following reaction ($\Delta G^\circ$ (Na$_2$Fe$_2$O$_4$));

$$\text{Na}_2O (s, l) + Fe_2O_3 = \text{Na}_2Fe_2O_4,$$

(D)
could be calculated by using eqs. (4) and (6) as

$$\Delta G^\circ(\text{Na}_2\text{Fe}_2\text{O}_4) = 1/5[\Delta G^\circ(B) + \Delta G^\circ(C)]$$

$$= 1/5\Delta G^\circ(B) + 2RT \ln a_{Na_2O}(\text{NF}/N_3F_5). \quad (6)$$

The coefficients for $\Delta G^\circ(\text{Na}_2\text{Fe}_2\text{O}_4)$ were calculated from those for $a_{Na_2O}(\text{NF}/N_3F_5)$ and $\Delta G^\circ(C)$, and the results are summarized in Tables 3 and 4.

The values of $\Delta G_{mix}$, the integral free energy change of mixing in Na$_3$Fe$_5$O$_9$ ($\Delta G^\circ(\text{Na}_3\text{Fe}_5\text{O}_9)/4$) and Na$_2$Fe$_2$O$_4$ ($\Delta G^\circ(\text{Na}_2\text{Fe}_2\text{O}_4)/2$) phases, are calculated respectively, and are shown in Fig. 5, showing a slight dependency on temperature.

In the present study, the error estimation
have been made only on the statistical terms, which can be estimated directly from the experimental results. As described in the previous study(6), the statistical errors were calculated as a standard deviation of the coefficients summarized in the Table 3 for the results obtained by the cell No. 0. On the other hand, as shown in Tables 3 and 4, the errors for \( \ln a_{\text{Na}_2\text{O}}(\text{F/N}_3\text{F}_5) \) and for \( \Delta G^{\circ}(\text{Na}_2\text{Fe}_2\text{O}_4) \) were estimated by taking into account of the statistical errors for the \( \ln a_{\text{Na}_2\text{O}}(\text{F/N}_3\text{F}_5) \) and for \( \Delta G^{\circ}(\text{Na}_2\text{Fe}_2\text{O}_4) \).

3. Comparison of the present data with the previous reports

Thermochemical properties of \( \text{Na}_2\text{O}-\text{Fe}_2\text{O}_3 \) system at elevated temperatures have been investigated by Dai, Seetharaman and Staffansson(1), by Shaiu et al.(2), by employing EMF method. The former utilized beta-alumina solid electrolyte, while the latter used stabilized zirconia as a solid electrolyte. However, the phase equilibria assumed in both studies were inaccurate on the phase relationship.

Dai et al. determined \( \text{Na}_2\text{O} \) activity in the sample of equimolar mixture of \( \text{Fe}_2\text{O}_3 \) and \( \text{Na}_2\text{Fe}_2\text{O}_4 \), and calculated \( \Delta G^{\circ}(C) \) by assuming \( \text{Fe}_2\text{O}_3 \) coexist with \( \text{Na}_2\text{Fe}_2\text{O}_4 \) at 700–1000 K. Their assumption for the phase equilibria is inconsistent with the present result and that by Thery(4), since both suggest that \( \text{Na}_3\text{Fe}_5\text{O}_9 \) phase is stable within the temperature range of their experiment. Therefore, the phases coexist in their experiment are estimated as \( \text{Fe}_2\text{O}_3 \) and \( \text{Na}_2\text{Fe}_2\text{O}_4 \), if the equilibrium is attained.

By assuming that the sample is in \( \text{Fe}_2\text{O}_3 + \text{Na}_2\text{Fe}_2\text{O}_4 \) two phase equilibrium, the values of \( \text{Na}_2\text{O} \) activity and \( \Delta G^{\circ}(\text{Na}_2\text{Fe}_2\text{O}_4)/8 \) were calculated from their EMF data, and are shown in Figs. 4 and 5 by dotted broken line. The results are higher than those in the present value, and the values of \( \Delta G^{\circ}(\text{Na}_2\text{Fe}_2\text{O}_4)/4 \) shown in Fig. 5 exhibit higher values than the present data. One of the possible reason for the discrepancy between the results is caused from the thermochemical properties of the sodium tungstate reference melt used by Dai et al. The activity data for \( \text{Na}_2\text{O} \) in the reference were quoted from the results by Lin and Elliott(9), who determined the activity in the \( \text{Na}_2\text{O–WO}_3 \) system by EMF method using sodium beta alumina with W/WS\(_2\)/Na\(_2\)S as a reference. The \( \text{Na}_2\text{O} \) activity and thermo-dynamic properties in the \( \text{Na}_2\text{O–SiO}_2 \) system determined by Neudorf and Elliott(10) using the tungstate reference showed the smaller dependency on reciprocal absolute temperature compared with those by the present authors(6)(7). The major difference would arise from the smaller partial molar enthalpy for \( \text{Na}_2\text{O} \) in the sodium tungstate melts determined by Neudorf and Elliott.

In Fig. 5, the results after Shaiu et al.(2) were plotted. The results are in poor agreement with the present data. It is because of the indefinite phase equilibria as pointed by Dai et al.(3)

IV. Summary

The values of \( \text{Na}_2\text{O} \) activity in the system \( \text{Na}_2\text{O–Fe}_2\text{O}_3 \) have been determined by EMF method using sodium beta-alumina as a solid electrolyte, and the standard free energy change for the formation of \( \text{Na}_3\text{Fe}_5\text{O}_9 \) and \( \text{Na}_2\text{Fe}_2\text{O}_4 \) has been estimated.

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