Chemical Potential and Solubility of Oxygen in Ni(s, l) Equilibrated with both NiO(s) and NiX₂O₄(s) [X=Al, Ga]*

By Nobumasa Kemori**, Iwao Katayama**, and Zensaku Kozuka**

The oxygen potentials for Ni(s, l)+NiO(s)+NiAl₂O₄(s) and Ni(s, l)+NiO(s)+NiGa₂O₄(s) have been measured using solid oxide galvanic cells of the type:

The results are expressed as follows:

(i) for Ni(s, l)+NiO(s)+NiAl₂O₄(s),

$$\Delta\mu(\text{O}_2)/\text{J mol}^{-1} \pm 300 = -(467500 \pm 2200) + (168.6 \pm 0.7)(T/\text{K}) \text{ at } 1285 \text{ to } 1558 \text{ K,}$$

$$\Delta\mu(\text{O}_2)/\text{J mol}^{-1} \pm 400 = -(456800 \pm 4900) + (161.9 \pm 2.7)(T/\text{K}) \text{ at } 1726 \text{ to } 1835 \text{ K,}$$

(ii) for Ni(s, l)+NiO(s)+NiGa₂O₄(s),

$$\Delta\mu(\text{O}_2)/\text{J mol}^{-1} \pm 200 = -(469200 \pm 700) + (170.0 \pm 0.5)(T/\text{K}) \text{ at } 1271 \text{ to } 1528 \text{ K,}$$

$$\Delta\mu(\text{O}_2)/\text{J mol}^{-1} \pm 500 = -(460300 \pm 5500) + (163.8 \pm 3.1)(T/\text{K}) \text{ at } 1717 \text{ to } 1853 \text{ K,}$$

where the errors are given as standard deviations.

The solubilities of oxygen in liquid nickel equilibrated with NiO(s) and NiAl₂O₄(s), and with NiO(s) and NiGa₂O₄(s) have been measured by a phase equilibration technique. They are given by

(i) for liquid nickel in equilibrium with NiO(s) and NiAl₂O₄(s),

$$\ln N_{\text{O}} \pm 0.012 = -(24070 \pm 300)/(T/\text{K}) + (9.346 \pm 0.167) \text{ at } 1720 \text{ to } 1850 \text{ K,}$$

(ii) for liquid nickel in equilibrium with NiO(s) and NiGa₂O₄(s),

$$\ln N_{\text{O}} \pm 0.016 = -(23870 \pm 470)/(T/\text{K}) + (9.215 \pm 0.262) \text{ at } 1725 \text{ to } 1845 \text{ K.}$$

From this work, it was found that

(1) the solubilities of Al₂O₃ and Ga₂O₃ in NiO were negligible up to about 1573 and 1553 K, respectively,

(2) the oxygen activity and the oxygen concentration in liquid nickel coexisting with NiO(s) and NiAl₂O₄(s), and with NiO(s) and NiGa₂O₄(s) satisfied the relation between those in the Ni–O system.

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I. Introduction

The solubility limits and thermodynamic properties of oxygen in liquid nickel have been studied by many researchers^{(1)~(7)}. Moreover the influence of additive elements (W, Mo, Mn, Cr, V, Ti, Al, Si, C) on the oxygen activity in liquid nickel has been investigated by Janke and Fischer⁽⁸⁾. However the activity and the solubility of oxygen in liquid nickel equilibrated with spinel type oxides containing NiO have not been reported hitherto.

The phase diagrams of the NiO–Al₂O₃

and NiO–Ga₂O₃ systems are characterized by the existence of only one intermediate compound with spinel type structure, i.e. NiAl₂O₄ or NiGa₂O₄, which has a relatively large homogeneous range in the vicinity of the middle composition. These phase diagrams have been studied by von Wartenberg and Reusch⁽⁹⁾, Iida⁽¹⁰⁾, Phillips *et al.*⁽¹¹⁾, Lejus⁽¹²⁾, Colin⁽¹³⁾ (the NiO–Al₂O₃ system), and by Laqua and Reuter⁽¹⁴⁾ (the NiO–Ga₂O₃ system), while the activity of each component in these systems has not been investigated.

As Al₂O₃ and Ga₂O₃ are much more stable than NiO, solid and liquid nickel can coexist with the NiO–X₂O₃ (X=Al, Ga) system over the whole composition range. Using this coexisting state, Schmalzried⁽¹⁵⁾, Levitskij and Rezhikhina⁽¹⁶⁾, Katayama *et al.*⁽¹⁷⁾ have measured the oxygen potential of the Ni(s)+NiAl₂O₄(s)+Al₂O₃(s) or the Ni(s)+NiGa₂O₄

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** Department of Metallurgical engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan.

(s) + Ga₂O₃(s) system by an e.m.f. method and determined the standard free energies of formation of NiAl₂O₄(s) and NiGa₂O₄(s). However the oxygen potentials of the Ni(s) + NiO(s) + NiAl₂O₄(s), and Ni(s) + NiO(s) + NiGa₂O₄(s) systems have not been measured so far.

Therefore the present work was carried out to determine the chemical potentials and the solubilities of oxygen in Ni(s, l) in equilibrium with NiO(s) and NiX₂O₄(s) [X = Al, Ga]. Furthermore, based on the present results, the thermodynamic behavior of oxygen in liquid nickel coexisting with NiO(s) and NiX₂O₄(s) [X = Al, Ga] and the activities of NiO along the solvus on the NiO rich side of the NiO–Al₂O₃ and NiO–Ga₂O₃ systems were discussed and evaluated.

II. Experimental Principle

Galvanic cells used in the present work can be expressed as follows:

Based on the e.m.f. and the temperature of cell(I), the equilibrium oxygen pressure of Ni(s, l) + NiO(s) + NiX₂O₄(s), i.e. the square of the oxygen activity in Ni(s, l) coexisting with NiO(s) and NiX₂O₄(s), is calculated from eq. (1):

$$E = \frac{RT}{4F} \ln \frac{P^a(\text{O}_2)}{P^e(\text{O}_2)}, \quad (1)$$

where E is the e.m.f. of cell(I), $P^a(\text{O}_2)$ the oxygen partial pressure in air (0.2095×101.325 kPa), $P^e(\text{O}_2)$ the equilibrium oxygen pressure over Ni(s, l) + NiO(s) + NiX₂O₄(s), R the gas constant ($8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$), T the thermodynamic temperature, and F the Faraday constant ($9.6485 \times 10^4 \text{ C mol}^{-1}$). Consequently the chemical potential of oxygen in the Ni(s, l) + NiO(s) + NiX₂O₄(s) system, which is denoted by $\Delta\mu(\text{O}_2)$, can be expressed as

$$\begin{aligned} \Delta\mu(\text{O}_2) &= RT \ln \{P^e(\text{O}_2)/P^\circ\}, \\ &= RT \ln \{P^a(\text{O}_2)/P^\circ\} - 4FE. \end{aligned} \quad (2)$$

Here P° is a standard pressure, 101.325 kPa.

Table 1 Chemical composition of nickel (mass %).

Ni	Co	Zn	C	Fe	S
	0.01	0.0038	0.002	0.0016	0.0011
99.98	Cu	Pb	Si	As	Mn
	0.0006	0.0005	0.0002	0.0002	0.0001

III. Experimental Procedure

Materials: Nickel powder used for e.m.f. measurements was 99.9 mass % pure. Nickel used for oxygen solubility measurements, which was obtained from Sumitomo Metal Mining Co., Ltd., was 99.98 mass % pure. Impurities in this nickel are summarized in Table 1. NiO powder was the most pure reagent grade, Al₂O₃ powder the reagent grade, and Ga₂O₃ powder 99.99 mass % pure. In order to form NiAl₂O₄ and NiGa₂O₄, equal molar proportions of NiO and Al₂O₃, or of NiO and Ga₂O₃ were sufficiently mixed in an agate mortar and heated in air at 1623 K for 24 h. After the heat treatment, the desired spinel phase was confirmed by X-ray analysis. Ar gas used as the atmosphere during e.m.f. and oxygen solubility measurements had been purified by passing through silica gel, activated alumina, molecular sieves, sponge titanium (1123 to 1223 K), and phosphorus pentoxide. Round-bottomed solid electrolyte tubes (0.89 ZrO₂ + 0.11CaO, OD 8 mm, ID 5 mm, length 300 mm) and lanthanum-chromium oxide rods (LaCrO₃, diameter 2 mm, length 10 mm) were supplied by Nippon Kagaku Togyo Co., Ltd.

Apparatus and Procedure:

(1) E.m.f. measurements; The apparatus and cell arrangements were similar to those described in detail in the previous paper⁽¹⁸⁾. A three-phase mixture (about 1 g) of Ni, NiO, and NiX₂O₄ powders in the mass ratio 6: 1: 1 was loaded in the zirconia tube. Air used as the reference electrode was supplied at about $8.3 \times 10^{-7} \text{ m}^3/\text{s}$ through an alumina tube.

The e.m.f.'s of cell(I) were measured at desired temperatures with a digital voltmeter (Yokogawa Electric Co., Ltd.; Type 2502). The temperatures of cell(I) were increased stepwise from 1273 to 1873 K and measured with

a calibrated Pt-Pt·13Rh thermocouple. When nickel in the mixture was solid, the equilibrium e.m.f. was obtained in 14.4~21.6 ks at the first temperature (about 1273 K) and in about 1.8 ks at the following temperatures. However, when nickel in the mixture was liquid, the equilibrium e.m.f. was gained soon after the temperature of cell (I) reached the desired level. After each experimental run, it was confirmed by an X-ray diffractometer that three phases, i.e. Ni, NiO, and NiX₂O₄, coexisted with one another.

(2) Oxygen solubility measurements; The apparatus for oxygen solubility measurements was similar to that drawn in Reference (7). To eliminate the influence of alumina crucibles on the true equilibrium among NiO, NiX₂O₄, and liquid nickel, the alumina crucibles were lined up with NiO to a thickness of about 0.8 mm and heated in air at 1473 K for 36 ks. This process was repeated again, and then a mixture of NiO (about 9 g) and NiX₂O₄ (about 4 g) powders with distilled water was coated to a thickness of about 1.5 mm on the second layer of NiO and dried at 400 K. It has been previously reported⁽⁷⁾ that the first and second layers of NiO are effective in preventing the contamination of liquid nickel by the alumina crucibles. Nickel (about 140 g) was melted in this crucible under purified Ar gas atmosphere and equilibrated with both NiO and NiX₂O₄. The experimental operations and oxygen analysis were similar to those described in detail elsewhere⁽⁷⁾.

IV. Results

1. E.m.f. measurements

(i) For the Ni(s, l) + NiO(s) + NiAl₂O₄(s) system: The variation in the e.m.f. of cell(I) for X=Al with temperature is shown in Figs. 1 and 2. One kind of symbol in these figures expresses the results obtained from one experimental run. Solid lines in Figs. 1 to 4 are drawn on the basis of the results of e.m.f. measurements for cell(II) in the previous work⁽¹⁸⁾, and they are given by eqs. (3) and (4):
(II) Pt·LaCrO₃/Ni(s, l), NiO(s)/ZrO₂ + CaO/air/Pt,

Fig. 1 The variation of E with T of cell (I) for X=Al and Ni(s).

Fig. 2 The variation of E with T of cell (I) for X=Al and Ni(l).

Fig. 3 The variation of E with T of cell (I) for X=Ga and Ni(s).

Fig. 4 The variation of E with T of cell (I) for $X=\text{Ga}$ and Ni(l) .

$$E/\text{mV} \pm 0.5 = (1204.4 \pm 1.3) - (0.4667 \pm 0.0009) \times (T/\text{K}) \text{ at } 1191 \sim 1699 \text{ K}, \quad (3)$$

$$E/\text{mV} \pm 0.6 = (1298.1 \pm 9.9) - (0.5205 \pm 0.0056) \times (T/\text{K}) \text{ at } 1722 \sim 1823 \text{ K}. \quad (4)$$

where the errors are given as standard deviations. Figures 1 and 2 show that the e.m.f.'s of cell(I) for $X=\text{Al}$ agree very well with those of cell(II) at temperatures below 1573 K, while at temperatures above 1573 K the difference between them becomes larger as temperature is elevated. As will be detailed in Discussion 2, the difference between the e.m.f.'s of cells(I) and (II) corresponds to the activity of NiO in the $\text{NiO}-\text{Al}_2\text{O}_3$ pseudobinary system. Therefore, it may be concluded that the solubility of Al_2O_3 in NiO is negligibly small below 1573 K and increases gradually above this temperature.

The present results were treated by the method of least squares and expressed as eqs. (5) and (6):

$$E/\text{mV} \pm 0.9 = (1211.4 \pm 5.7) - (0.4705 \pm 0.0019) \times (T/\text{K}) \text{ at } 1285 \sim 1558 \text{ K}, \quad (5)$$

$$E/\text{mV} \pm 1.1 = (1183.6 \pm 12.4) - (0.4531 \pm 0.0070) \times (T/\text{K}) \text{ at } 1726 \sim 1835 \text{ K}. \quad (6)$$

According to eq. (2), the chemical potential of oxygen in the $\text{Ni(s, l)} + \text{NiO(s)} + \text{NiAl}_2\text{O}_4(\text{s})$

system can be represented by the following equations:

$$\begin{aligned} \Delta\mu(\text{O}_2)/\text{J mol}^{-1} \pm 300 \\ = -(467500 \pm 2200) + (168.6 \pm 0.7)(T/\text{K}) \\ \text{at } 1285 \sim 1558 \text{ K}, \end{aligned} \quad (7)$$

$$\begin{aligned} \Delta\mu(\text{O}_2)/\text{J mol}^{-1} \pm 400 \\ = -(456800 \pm 4900) + (161.9 \pm 2.7)(T/\text{K}) \\ \text{at } 1726 \sim 1835 \text{ K}. \end{aligned} \quad (8)$$

(ii) For the $\text{Ni(s, l)} + \text{NiO(s)} + \text{NiGa}_2\text{O}_4(\text{s})$ system: The relation between the e.m.f. and the temperature of cell(I) for $X=\text{Ga}$ is depicted in Figs. 3 and 4. One kind of symbol in Figs. 3 and 4 expresses the results obtained from one experimental run. It is found from these figures that the solubility of Ga_2O_3 in NiO is negligibly small in the temperature range from 1273 to 1553 K and becomes gradually large at temperatures above 1711 K, which is the eutectic temperature of the $\text{Ni}-\text{NiO}$ system, as temperature is increased. In the temperature range from 1553 to 1711 K, the difference of the e.m.f.'s between cells(I) and (II) becomes larger at first and then smaller with temperature. The reason why the e.m.f. of cell (I) in this temperature range varies with temperature is difficult to understand. However, in the light of the reproducibility of experimental runs and the internal consistency of the data at temperatures around 1711 K, the data obtained in this temperature range are also considered to be reliable.

The e.m.f.'s of cell(I) for $X=\text{Ga}$ can be represented by

$$E/\text{mV} \pm 0.6 = (1215.8 \pm 1.9) - (0.4741 \pm 0.0014) \times (T/\text{K}) \text{ at } 1271 \sim 1528 \text{ K}, \quad (9)$$

$$\begin{aligned} E/\text{mV} \pm 1.3 = (1192.6 \pm 14.2) - (0.4580 \\ \pm 0.0080)(T/\text{K}) \text{ at } 1717 \\ \sim 1853 \text{ K}. \end{aligned} \quad (10)$$

Consequently eqs. (11) and (12) are obtained as the chemical potential of oxygen in the $\text{Ni(s, l)} + \text{NiO(s)} + \text{NiGa}_2\text{O}_4(\text{s})$ system:

$$\begin{aligned} \Delta\mu(\text{O}_2)/\text{J mol}^{-1} \pm 200 \\ = -(469200 \pm 700) + (170.0 \pm 0.5)(T/\text{K}) \\ \text{at } 1271 \sim 1528 \text{ K}, \end{aligned} \quad (11)$$

Table 2 The solubilities of oxygen in liquid nickel equilibrated with NiO(s) + NiX₂O₄(s) [X = Al, Ga].

Ni(l) + NiO(s) + NiAl ₂ O ₄ (s)		Ni(l) + NiO(s) + NiGa ₂ O ₄ (s)	
T/K	mass % O	T/K	mass % O
1720	0.2682	1725	0.2684
1727	0.2742	1742	0.3045
1740	0.3091	1758	0.3571
1754	0.3435	1779	0.4059
1785	0.4454	1801	0.4948
1806	0.5173	1820	0.5544
1830	0.6199	1845	0.6657
1850	0.7074		

$$\Delta\mu(\text{O}_2)/\text{J mol}^{-1} \pm 500$$

$$= -(460300 \pm 5500) + (163.8 \pm 3.1)(T/\text{K})$$

at 1717 ~ 1853 K. (12)

As the oxygen potential calculated from eq. (8) is higher than that from eq. (12), at constant temperatures the oxygen activity in liquid nickel coexisting with NiO(s) and NiGa₂O₄(s) is found to be lower than that in liquid nickel equilibrated with NiO(s) and NiAl₂O₄(s).

2. Oxygen solubility measurements

The results for oxygen analysis and the corresponding temperatures are listed in Table 2. They are expressed as eqs. (13) and (15), or as eqs. (14) and (16):

(i) for liquid nickel in equilibrium with NiO(s) and NiAl₂O₄(s),

$$\ln N_{\text{O}} \pm 0.012$$

$$= -(24070 \pm 300)/(T/\text{K}) + (9.346 \pm 0.167)$$

at 1720 ~ 1850 K, (13)

$$\log (\text{mass \% O}) \pm 0.005$$

$$= -(10570 \pm 130)/(T/\text{K}) + (5.567 \pm 0.073)$$

at 1720 ~ 1850 K, (14)

(ii) for liquid nickel in equilibrium with NiO(s) and NiGa₂O₄(s),

$$\ln N_{\text{O}} \pm 0.016$$

$$= -(23870 \pm 470)/(T/\text{K}) + (9.215 \pm 0.262)$$

at 1725 ~ 1845 K, (15)

$$\log (\text{mass \% O}) \pm 0.007$$

$$= -(10490 \pm 200)/(T/\text{K}) + (5.510 \pm 0.114)$$

at 1725 ~ 1845 K. (16)

Fig. 5 The solubilities of oxygen in liquid nickel in equilibrium with oxides containing NiO.

Solubilities of oxygen in liquid nickel equilibrated with various oxides containing NiO are plotted as a function of the reciprocal temperature in Fig. 5. Bowers⁽²⁾ has reported that alumina crucibles give rise to lower solubilities than the true solubility limits of oxygen in liquid nickel coexisting with NiO, NiO reacting with Al₂O₃ to form NiAl₂O₄. As shown in Fig. 5, the present work proved quantitatively that Bowers' result is valid. But Bowers cannot conclude the above statement from his experimental results because (i) it should be judged that his data for alumina crucibles are in agreement with those for nickel oxide crucibles within experimental error, and (ii) his results for alumina crucibles differ substantially from those of the Ni(l) + NiO(s) + NiAl₂O₄(s) system obtained in the present work.

It is seen from Fig. 5 that the solubilities of oxygen in liquid nickel become larger in the order of NiGa₂O₄ + NiO, NiAl₂O₄ + NiO, and NiO alone, which are the oxide phases coexisting with liquid nickel. For the Ni(l) + NiO(s) + NiAl₂O₄(s) and Ni(l) + NiO(s) + NiGa₂O₄(s) systems investigated in this work, therefore, the order of the magnitude of oxygen activities in liquid nickel agrees with that of the magnitude of oxygen solubilities. Considering that the content of Al or Ga in liquid nickel equilibrated with NiO(s) and NiAl₂O₄(s), or with NiO(s) and NiGa₂O₄(s) is negligibly small⁽¹⁹⁾, this agreement shows that there is

no contradiction between the results of e.m.f. and oxygen solubility measurements.

V. Discussion

1. Thermodynamic behavior of oxygen in liquid nickel in equilibrium with NiO(s) and NiX₂O₄(s) [X=Al, Ga]

As Al₂O₃ and Ga₂O₃ are more stable than NiO, and the melting points of these three oxides are approximate to one another and are considerably higher than the maximum temperature in this work, the content of Al or Ga in liquid nickel equilibrated with NiO(s) and NiX₂O₄(s) [X=Al, Ga] is considered to be negligibly small compared with the oxygen content. According to Kulikov⁽¹⁹⁾, in fact, the contents of Al in liquid nickel coexisting with NiO(s) and NiAl₂O₄(s) are 2.8×10^{-8} mass % at 1726 K and 1.5×10^{-7} mass % at 1873 K, and the influence of Al on the oxygen activity in liquid nickel is negligible. Therefore, by a comparison of the relation between the activity and the concentration of oxygen in liquid nickel equilibrated with NiO(s) and NiX₂O₄(s) [X=Al, Ga] with that for oxygen in the Ni–O system, we can confirm whether the present data are reliable.

For the Ni–O system, the relation between the activity coefficient of oxygen and the oxygen concentration at 1733, 1783, and 1833 K has been investigated⁽⁷⁾ up to the oxygen solubility limits. Consequently the present data are compared with the results for the Ni–O system in Fig. 6. E° constituting the ordinate in this figure is the e.m.f. of cell(III):

Hence the ordinate values of the present data depicted in Fig. 6 were calculated by subtracting the e.m.f. of cell(II) given as eq. (4) from that of cell(I) obtained in this work. Three lines shown in Fig. 6 are drawn from the results of the previous work⁽⁷⁾ and their inclination corresponds to the first order self-interaction coefficient of oxygen in liquid nickel. It is found from this figure that the present results agree fairly well with those for the Ni–O system within experimental errors. This agreement

Fig. 6 The relation between $[E^\circ + (RT/2F) \ln N_O]$ and N_O .

demonstrates that both results in e.m.f. of cell(I) and in the solubility of oxygen in liquid nickel equilibrated with NiO(s) and NiX₂O₄(s) [X=Al, Ga], which were obtained in this work, are reliable. In the previous work⁽⁷⁾, the oxygen activity in liquid nickel has been measured using alumina crucibles. Figure 6 shows that the previous work has been carried out in the oxygen concentration range where the oxygen activity in liquid nickel could be measured using alumina crucibles.

2. Activities of NiO along the solvus on the NiO rich side of the NiO–Al₂O₃ and NiO–Ga₂O₃ systems

Combining cell(I) and cell(II) results in the following cell(IV):

The e.m.f. E^* of cell(IV) is given by

$$E^* = \frac{RT}{2F} \ln \left\{ \frac{P^*(\text{O}_2)}{P^e(\text{O}_2)} \right\}^{1/2}, \quad (17)$$

where E^* is equal to the difference between the e.m.f.'s of cells(I) and (II), and $P^*(\text{O}_2)$ is the

equilibrium oxygen pressure over Ni(s, l) + NiO(s). In the electrodes of cell(IV) are established the following equilibrium reactions respectively:

(i) in the right-hand side electrode,

(ii) in the left-hand side electrode,

The equilibrium constants of reactions (18) and (19) are respectively expressed as

$$K(18) = \frac{a_{\text{NiO}}^*}{a_{\text{Ni}}^* \{P^*(\text{O}_2)/P^\circ\}^{1/2}}, \quad (20)$$

$$K(19) = \frac{a_{\text{NiO}}}{a_{\text{Ni}} \{P^e(\text{O}_2)/P^\circ\}^{1/2}}. \quad (21)$$

Here (a_{Ni}^* and a_{NiO}^*) and (a_{Ni} and a_{NiO}) are activities of Ni and NiO in the binary system (Ni + NiO) and in the ternary system (Ni + NiO + NiX₂O₄), respectively. As $K(18) = K(19)$ and $a_{\text{NiO}}^* = 1$,

$$\left\{ \frac{P^*(\text{O}_2)}{P^e(\text{O}_2)} \right\}^{1/2} = \frac{a_{\text{Ni}}}{a_{\text{Ni}}^* a_{\text{NiO}}}. \quad (22)$$

Substituting eq. (22) into eq. (17) and rearranging, one obtains:

$$\ln a_{\text{NiO}} = -\frac{2FE^*}{RT} + \ln \frac{a_{\text{Ni}}}{a_{\text{Ni}}^*}. \quad (23)$$

When nickel is solid, $\ln(a_{\text{Ni}}/a_{\text{Ni}}^*) = 0$. Since the content of Al or Ga in liquid nickel in equilibrium with NiO and NiAl₂O₄, or with NiO and NiGa₂O₄ is negligible, $\ln(a_{\text{Ni}}/a_{\text{Ni}}^*)$ for liquid nickel can be expressed by using the oxygen content and the first order self-interaction coefficient of oxygen in liquid nickel as follows:

$$\ln \frac{a_{\text{Ni}}}{a_{\text{Ni}}^*} = (1 + \varepsilon_0^0) \ln \frac{1 - N_{\text{O}}}{1 - N_{\text{O}}^*} + \varepsilon_0^0(N_{\text{O}} - N_{\text{O}}^*), \quad (24)$$

where N_{O}^* is the solubility limit of oxygen in liquid nickel [$\ln N_{\text{O}}^* \pm 0.020 = -(25080 \pm 480)/(T/\text{K}) + (9.960 \pm 0.269)$]⁽⁷⁾, ε_0^0 is the first order self-interaction coefficient of oxygen in liquid nickel [$\varepsilon_0^0 \pm 1.0 = -(158900 \pm 46700)/(T/\text{K}) + (75.8 \pm 26.2)$]⁽⁷⁾, and N_{O} is given by eq. (13) or (15). Therefore, $\ln a_{\text{NiO}}$ can be expressed as

(i) for solid nickel,

$$\ln a_{\text{NiO}} = -\frac{2FE^*}{RT}, \quad (25)$$

(ii) for liquid nickel

$$\begin{aligned} \ln a_{\text{NiO}} = & -\frac{2FE^*}{RT} + (1 + \varepsilon_0^0) \ln \frac{1 - N_{\text{O}}}{1 - N_{\text{O}}^*} \\ & + \varepsilon_0^0(N_{\text{O}} - N_{\text{O}}^*). \end{aligned} \quad (26)$$

Fig. 7 The activity of NiO along the solvus on NiO rich side of the NiO-Al₂O₃ system.

Fig. 8 The activity of NiO along the solvus on the NiO rich side of the NiO-Ga₂O₃ system.

The relationship between temperature and the activity of NiO calculated from eqs. (25) and (26) is depicted in Figs. 7 and 8. The symbols in Fig. 7 and in Fig. 8 correspond to those in Figs. 1 and 2 and in Figs. 3 and 4, respectively. As the intermediate compounds NiAl_2O_4 and NiGa_2O_4 exist respectively in the $\text{NiO}-\text{Al}_2\text{O}_3$ and $\text{NiO}-\text{Ga}_2\text{O}_3$ systems, the activity coefficient of NiO is smaller than unity. Hence the solvus on NiO rich side of these systems is considered to lie between the ordinate and the data points shown in Figs. 7 and 8.

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