The Thermodynamic Behaviour of Nickel in a Molten LiF-KF-O^{2-} System

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The thermodynamic behaviour of nickel in a molten LiF-KF-O^{2-} system was investigated by using Pt(O_2)/stabilized zirconia electrode as an oxide-ion-concentration indicator. The potentials of the Pt(O_2)/stabilized zirconia/LiF-KF-O^{2-} electrode and the Ni/NiO/LiF-KF-O^{2-} electrode at 550 °C were measured as :

$$E = 2.25 - \frac{RT}{2F} \ln X_{O^{2-}} \text{ (V. } vs. \text{ Li-K/Li}^+, \text{ K}^+)$$

and:

$$E = 1.42 - \frac{RT}{2F} \ln X_{O^{2-}} \text{ (V. } vs. \text{ Li-K/Li}^+, \text{ K}^+)$$

respectively. The solubility product of NiO in the melt was thus determined to be $K_{sp}=1.3\times10^{-6}$ at 550 °C. With these results, a potential-pO^{2-} diagram of the nickel in the system was presented.

Molten fluoride is a useful material for use in many energy processes, such as the Molten Salt Breeder Reactor and heat-storage systems.[1] To use this melt for such purposes, however, it is necessary to protect the metal container from the corrosion caused by any oxidizing agents as contaminated water and oxygen. The corrosion behaviour of metals in a fluoride melt is strongly dependent on the oxide film formed on the metal surface, the stability of which is influenced by the redox potential and the oxide-ion concentration in a melt system.

In this paper, an LiF-KF eutectic melt containing oxide ions has been selected as an example of a fluoride melt, and the oxide concentration and solubility product of NiO in this melt have been determined by the use of a stabilized zirconia electrode. Finally, a potential-pO^{2-} diagram of nickel has been constructed on the basis of a thermochemical analysis of this system. Recently it has been shown that a stabilized zirconia solid electrolyte can be used as an oxide-ion-concentration indicator in melt systems, especially molten chloride systems. Also, the solubility product of metal oxide,[2-4] and the chemical equilibrium associated with oxide ion[5] have been investigated by using this electrode. However, in molten fluoride systems, the solubility products of oxide were mainly determined by a chemical analysis method[6,7] that may derive higher solubility product values caused by colloidal metal oxide; this type of electrode has not been used as an oxide-ion indicator. By the use of a stabilized zirconia oxide indicator, not only a rigorous value of the solubility product, but also direct thermodynamic information about the oxide ion in the melt can be obtained.

Thermodynamic Description

By means of a constant-current electrolysis of a molten LiF-KF-O^{2-} system, the Li-K alloy is formed on the cathode; its composition is almost constant (Li:K=2:1) independent of the current densities.[8] That is, the single-electrode potential of the Li-K/Li^+, K^+ couple can be chosen as a common reference electrode in this system. In this paper, as will be described later, the potentials were measured with respect to a quasi-reference electrode, such as the Ni/NiO or Ni/NiF_2 electrode, but the data obtained were converted to the potential against the Li-K/Li^+, K^+ couple.

The emf of the electrochemical cell:

$$\text{Li-K/LiF-KF-O}^{2-}\text{/stabilized ZrO}_2\text{/O}_2\text{(Pt)} \tag{1}$$

will obey the following Eq. 2 if the stabilized zirconia acts as an oxide-ion-concentration indicator:

$$E = E^\circ_{O_2/O^{2-}} - \frac{RT}{2F} \ln X_{O^{2-}} \tag{2}$$

$X_{O^{2-}}$ represents the anionic mole fraction of the oxide ion in the melt. By the use of Eq. 2, the thermodynamic behaviour of nickel in this system can be described as below. To simplify the situation, only three chemical species are considered in this paper: Ni(s), the Ni(II) ion, and NiO(s). Among these three species, there exist the following three electrochemical or chemical equilibria:

$$\text{Ni(II)} + 2e^- = \text{Ni(s)} \tag{3}$$

$$\text{NiO(s)} + 2e^- = \text{Ni(s)} + O^{2-} \tag{4}$$

$$\text{NiO(s)} = \text{Ni(II)} + O^{2-} \tag{5}$$

The equilibria involving the trivalent nickel ion, *e.g.* Ni(III) and Ni_2O_3(s), are not considered in this paper, since their existence has not been reported in the literature.[9)]

The Nernst equation corresponding to the electrochemical equilibria 3 and 4 are expressed as Eqs. 6 and 7 respectively, while the equilibrium constant of Eq. 5 is expressed as Eq. 8 with the use of the solubility product of NiO, K_{sp}:

$$E_{Ni/Ni(II)} = E^\circ_{Ni/Ni(II)} + \frac{RT}{2F} \ln X_{Ni(II)} \tag{6}$$

$$E_{Ni/NiO} = E^\circ_{Ni/NiO} - \frac{RT}{2F} \ln X_{O^{2-}} \tag{7}$$

$$K_{sp} = X_{Ni(II)} \cdot X_{O^{2-}} \tag{8}$$

(when the melt is saturated with NiO(s))

When the melt is saturated with NiO, $E_{Ni/Ni(II)}$ is equal to $E_{Ni/NiO}$; hence, from Eqs. 6, 7, and 8, Eq. 9 can be derived:

$$E^\circ_{Ni/NiO} = E^\circ_{Ni/Ni(II)} + \frac{RT}{2F} \ln K_{sp} \tag{9}$$

For the drawing of the Potential-pO^{2-} diagram, the determination of the values of $E^\circ_{Ni/Ni(II)}$, $E^\circ_{Ni/NiO}$, and K_{sp} would seem to be necessary, but, as Eq. 9 is valid, it is sufficient to measure the values of K_{sp} and $E^\circ_{Ni/NiO}$. The K_{sp} value can be obtained from the emf response of the cell (1) to the amount of metal oxide (NiO in this case) added to the melt. That is, when the amount of NiO added to the melt is small, free oxide ions are produced corresponding to the amount of NiO added, and the potential shifts to the negative side according to the Nernst Eq. 2. However, once the melt is saturated with NiO, the added NiO does not dissociate any more and the emf remains constant. Hence, the intersection of the two lines gives the solubility of NiO, from which the solubility product, K_{sp} can be calculated by means of Eq. 10:

$$\begin{aligned} K_{sp} &= [X^\circ_{NiO}(\text{added})]^2 \\ &= [X^\circ_{Ni(II)(\text{added})}][X^\circ_{O^{2-}(\text{added})}] \end{aligned} \tag{10}$$

where X°_{NiO} is the solubility of NiO.

Concerning the value of $E^\circ_{Ni/NiO}$, it can be calculated from the standard electrode potential, $E^\circ_{O_2/O^{2-}}$, of the reaction:

$$1/2\, O_2 + 2e^- = O^{2-} \tag{11}$$

and the difference ($E^\circ_{O_2/O^{2-}} - E^\circ_{Ni/NiO}$) which can be calculated from the standard free-energy change of the reaction:

$$NiO(s) = Ni(s) + 1/2O_2$$

Experimental Method and Apparatus

The experimental cell is shown in Fig. 1.

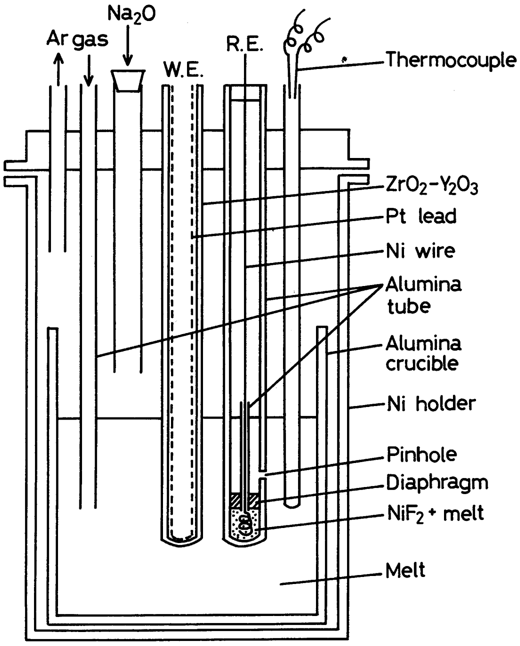

Fig. 1. Experimental cell.

Commercial LiF and KF (Reagent Grade, Wako Chemicals Co., Ltd.) were mixed, and the eutectic mixture was dried under a vacuum for a week at 200 °C, after which it was placed in a high-purity alumina crucible (Nippon Kagaku Togyo Co., Ltd., SSA-S) and melted under an argon (water content<10 ppm) atmosphere at 550 °C. By this procedure, the oxide-ion-concentration level could be reduced to the order of 10^{-4} mole fraction.[10)] For an oxide ion indicating electrode, an yttria- or magnesia-stabilized zirconia tube (Nippon Kagaku Togyo Co., Ltd.) was used. The inside of the tube was coated with a platinum powder layer which acted as an air electrode. The measured emf was converted to the potential of the oxygen (Pt)/stabilized zirconia electrode, taking into account the partial pressure of oxygen in air. Several types of electrodes, for example, NiF_2/Ni and NiO/Ni electrodes, were used as quasi-reference electrodes, according to the experimental conditions. The potential of the quasi-reference electrode was calibrated *versus* the Li-K/Li^+, K^+ electrode potential before use. By means of a constant-current electrolysis between the graphite anode and the stainless-steel cathode, Li-K alloy of a finite composition (Li:K=2:1)[8)] was deposited on the cathode. The cathode potential measured against the quasi-reference electrode was kept constant for several tens of minutes after the current interruption. From this constant potential value, the potential of the quasi-reference electrode against the Li-K/Li^+, K^+ electrode was determined. The oxide-ion concentration in the melt was controlled by adding the appropriate amount of dry Na_2O (Aldrich Co., Ltd.). For the solubility-product measurement of NiO(s), commercial NiO(s) (Wako

Chemicals Co., Ltd.) was added to the melt. The Ni/NiO electrode could be prepared by baking nickel wire for several tens of minutes in air at around 900 °C.

Results and Discussion

The relation between emf of the cell(1) and the oxide-ion concentration is shown in Fig. 2. A clear Nernst relation can be observed in the figure. From this straight line, obtained experimentally, the potential of the $Pt(O_2)$/stabilized zirconia/LiF-KF-O^{2-} electrode can be written as:

$$E = 2.25 - \frac{RT}{2F} \ln X_{O^{2-}} \quad (\text{V. } \mathit{vs.} \text{ Li-K/Li}^+, \text{ K}^+) \qquad (2')$$

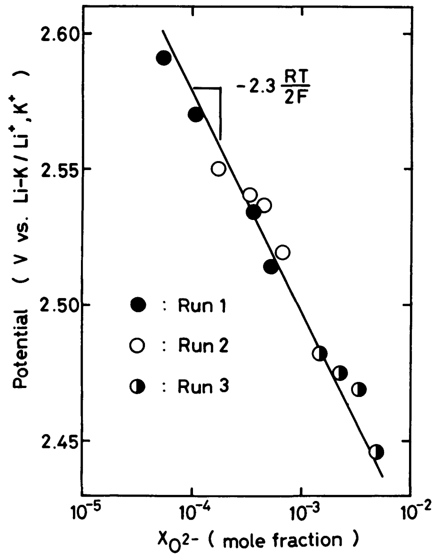

Fig. 2. Relation between emf of the cell: Li-K/LiF-KF-O^{2-}/stabilized zirconia/$Pt(O_2)$ and oxide-ion concentration.

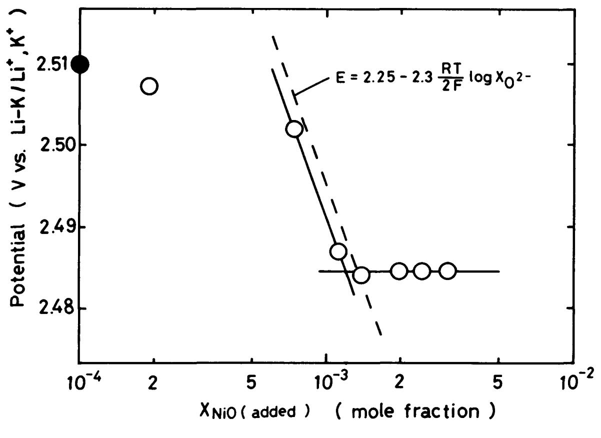

Fig. 3. Relation between $Pt(O_2)$/stabilized zirconia/LiF-KF-O^{2-} electrode potential and the added cmount of NiO (mole fraction).

Figure 3 shows the relation between the $Pt(O_2)$/stabilized zirconia/LiF-KF-O^{2-} electrode potential and the added NiO (expressed as a mole fraction). In the figure, the closed circle represents the potential before the addition of the NiO. This potential is determined by the concentration of the oxide ion contaminating the melt. In an early stage of the increase in the amount of NiO added, the potential response is not so quantitative because of the contaminating oxide ion, but when the amount of added NiO exceeds the contamination level, the potential shifts towards the negative side, obeying the Nernst equation. When the NiO in the melt is saturated, the potential remains constant at any amount of added NiO. From the intersection of the two lines, the K_{sp} values can be calculated by the use of Eq. 10.

In a practical calculation, however, the oxide-ion concentration, $X^\circ_{O^{2-}}$, due to the contamination before the experiment should also be taken into account. That is, the Ni(II)-ion concentration in the NiO-saturated melt is the difference between the measured oxide-ion concentrations, $X_{O^{2-}}$, and $X^\circ_{O^{2-}}$, thus, Eq. 10 is rewritten as:

$$\begin{aligned} K_{sp} &= X_{Ni(II)} \cdot X_{O^{2-}} \\ &= [X_{O^{2-}} - X^\circ_{O^{2-}}] \cdot X_{O^{2-}} \qquad (10') \end{aligned}$$

From Eq. 10′ and Fig. 3, and several other similar experimental results like Fig. 3 which are not given in this paper, the averaged K_{sp} value was determined to be 1.3×10^{-6} at 550 °C.

By the method described above, $E^\circ_{Ni/NiO}$ can be calculated from the standard free-energy change of reaction (12) and the $E^\circ_{O_2/O^{2-}}$ value of 2.25 V appearing in Eq. 2′ to be 1.42 V. That is, Eq. 7 is rewritten as:

$$E_{Ni/NiO} = 1.42 - \frac{RT}{2F} \ln X_{O^{2-}} \qquad (7')$$

The validity of Eq. 7′ was confirmed experimentally by using a cell similar to that in Fig. 1 and measuring the emf of the cell:

$$\text{Ni/NiO/LiF-KF-O}^{2-}\text{/stabilized zirconia/O}_2\text{(Pt)} \qquad (13)$$

The emf change of this cell with the time is shown in Fig. 4. About 2 h after the immersion of the Ni/NiO electrode in the melt, the emf remains almost constant at around 830 mV. This value exactly coincides with the value calculated from the difference between Eqs. 2′ and 7′.

From the data obtained above, the potential-pO^{2-} diagram of Ni-LiF-KF-O^{2-} system can be drawn as in Fig. 5.

After the experiment, the stabilized zirconia tube was examined carefully by visual observation; no mechanical damage nor chemical corrosion could be

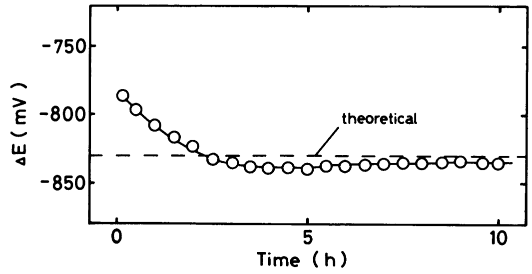

Fig. 4. Emf change of the cell: Ni/NiO/LiF-KF-O^{2-}/stabilized zirconia/Pt(O$_2$) with immersion time.

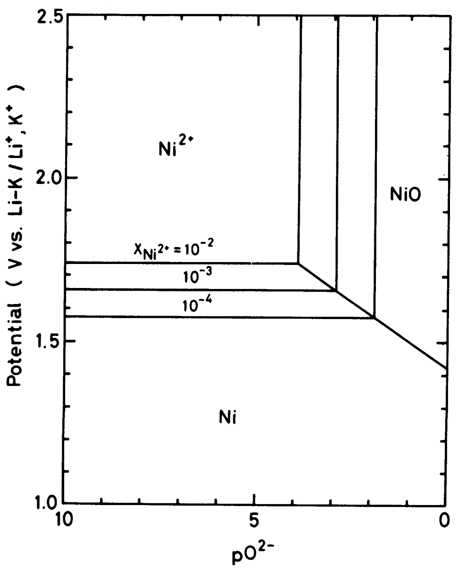

Fig. 5. Potential-pO^{2-} diagram of Ni-LiF-KF-O^{2-} system at 550 °C.

observed. During the whole experiment, reproducible measurements were possible. From these facts, it seems that stabilized zirconia can be used for an oxide-ion-concentration measurement in a fluoride melt at 550 °C.

Conclusion

The thermodynamic behaviour of nickel in a molten LiF-KF-O^{2-} system was investigated, and a potential-pO^{2-} diagram of the nickel in the system was presented, in which stabilized zirconia played an important role in measuring the oxide-ion concentration in the melt. The potential of the Pt(O$_2$)/stabilized zirconia/LiF-KF-O^{2-} electrode and the potential of the Ni/NiO/LiF-KF-O^{2-} electrode can be written as:

$$E = 2.25 - \frac{RT}{2F} \ln X_{O^{2-}} \quad (\text{V. } vs. \text{ Li-K/Li}^+, \text{K}^+\text{: } 550\,°\text{C})$$

and:

$$E = 1.42 - \frac{RT}{2F} \ln X_{O^{2-}} \quad (\text{V. } vs. \text{ Li-K/Li}^+, \text{K}^+\text{: } 550\,°\text{C})$$

respectively.

The solubility product of NiO in the melt was determined to be $K_{sp}=1.3\times10^{-6}$ at 550 °C.

Further refinement of the experimental technique might be necessary to get more rigorous and wider information. Especially, the improvement of the melt-purification technique and improvement of zirconia solid electrolyte might help us to get more reliable data. At least, though, this paper has shown that our method of using stabilized zirconia can offer useful information about the behaviour of metals in an oxide-ion-containing fluoride melt.

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