Distribution Equilibria of Fe, Co and Ni between MgO-saturated FeO$_x$–MgO–SiO$_2$ Slag and Ni Alloy

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As a fundamental study related to the recycle of Ni–Fe–Co alloy, the distribution equilibrium of Fe, Co and Ni between MgO saturated FeO$_x$–MgO–SiO$_2$ slag and nickel alloy was investigated at 1 773, 1 823 and 1 873 K with controlled oxygen partial pressure between $10^{-4}$ to $10^2$ Pa. The distribution ratios of Fe, Co and Ni at 1 773 K vary from 0.61 to 26, 0.040 to 4.2 and 0.0030 to 0.34 respectively with increasing oxygen partial pressure.

The distribution ratios of Fe, Co and Ni between MgO saturated FeO$_x$–MgO–SiO$_2$ slag and nickel alloy suggest that most of nickel and cobalt can remain in the alloy phase with lower oxygen partial pressure, and iron can be eliminated adequately from nickel alloys with higher oxygen partial pressure. However, the solubility of nickel and cobalt oxide in the slag also increases with increasing the oxygen partial pressure. Lower oxygen partial pressure and higher temperature are favorable for decreasing the loss of nickel and cobalt into slag. An oxygen partial pressure at which the separation coefficients show minimum was observed.

The MgO solubility in the FeO$_x$–MgO–SiO$_2$ slag decreases when the NiO content exceeds about 25% at higher oxygen partial pressure.

The activity coefficients of NiO and CoO in slags were calculated and found that their values increased with increasing of the NiO and CoO contents in slag respectively.

KEY WORDS: thermodynamics; distribution ratio; radioactive waste; recycle; cobalt; nickel; iron.

1. Introduction

Structural materials in a shutdown nuclear power plant contain some long-lived radionuclides such as $^{60}$Co, $^{59}$Ni and $^{63}$Ni formed in iron alloy especially in stainless steel irradiated in fusion reactors. Now from year to year the problem of induced radioactivity in the structural materials has received more and more attention. As for nuclear power plants, this problem is associated mainly with the waste management of great amounts (up to several hundred tons per power unit) of radioactive materials after reactors are shut down. The separation of nickel and cobalt from the materials with induced radioactivity is required to reduce the volume of the activated components and recycle the iron.

On the other hand, the alloy recycled from Nickel–Hydrogen battery parts by wet chemical process contains about 80% Nickel and 19% Cobalt. Cobalt in Fe–Ni scrap as the raw materials of stainless steel is considered as impurity in smelting. The cobalt behaves quite similarly with nickel in chemical and physical properties. Therefore, it is very difficult to separate between them. Although cobalt could be separated from nickel with hydrometallurgical process, the disadvantage of secondary contamination limited its application. The separation of nickel from cobalt with alloy liquation was also studied by using tin and silicon or calcium and cerium, the drawback of this method is the high cost of the metal solvents. Thus the fundamental information such as the distribution equilibria of nickel and cobalt between the nickel alloys and some slag or solvent is necessary for the separation of nickel and cobalt from iron by pyrometallurgy process.

Lian et al. studied the separation of cobalt in stainless steels with Fe$_2$O$_3$–SiO$_2$–TiO$_2$–CaF$_2$ slag at 1 823 and 2 023 K in a magnesia lined induction furnace. Their experimental conditions were not well defined.

Pagador et al. studied the distribution behavior of minor elements between the nickel based alloy and MgO saturated FeO$_x$–MgO–SiO$_2$ or FeO$_x$–CaO–MgO–SiO$_2$ slag at 1 773 and 1 873 K with controlled oxygen partial pressure ranging from $10^{-5}$ to $10^{-1}$ Pa to obtain fundamental information related to nickel smelting. It was found that the values of cobalt distribution ratio between the MgO saturated FeO$_x$–MgO–SiO$_2$ slag and Ni–Fe alloy at 1 773 K are lower than unity and shift downwards with increasing temperature.

Henao et al. reported the effect of slag additives of CaO and Al$_2$O$_3$ on the distribution behavior of Fe, Cr, Ni and Cu in the same temperature and oxygen partial pressure ranging from $10^{-5}$ to $10^{-1}$ Pa. It was shown that the addition of
lime in the plain slag and the increase of temperature reduce the dissolution of chromium into the slag and the addition of alumina reduces the dissolution of copper and nickel while it does not change appreciably the dissolution of iron.

In the present work the distribution equilibria of Fe, Co, and Ni between nickel alloy and MgO saturated FeO–MgO–SiO$_2$ slag at 1773, 1823 and 1873 K were investigated with controlled oxygen partial pressure ranging from $10^{-4}$ to $10^{-6}$ Pa. The purpose of the present study is focused on the distribution behavior of Fe, Co and Ni between slag and alloy phases over wide oxygen partial pressure range.

2. Experimental

A chemical equilibration technique was employed in the present study to measure the distribution ratio of Fe, Co and Ni. Six grams of Ni–Fe–Co alloy and six grams of FeO–MgO–SiO$_2$–NiO–CoO slags were equilibrated in a MgO crucible (625×20×120 mm) set in an electric furnace. Nickel granule (99.9%), electrolytic iron (99.99%) and electrolytic cobalt (99.9%) were preliminary melted at 1773 K to produce Ni–Fe–Co alloy. Reagent grade of FeO, SiO$_2$, MgO, NiO and CoO were preliminary melted at 1723 K to form slags. The dense MgO crucible containing sample was put into a porous MgO protection crucible that located in the constant temperature zone of the mullite tube. CO–CO$_2$ atmosphere was kept during experiment to control the oxygen partial pressure. The flow rate was 200 to 400 ml/min. The moisture in CO$_2$ gas was removed by bubbling it through sulphuric acid and then passing through an anhydrous magnesium perchlorate column. CO gas was purified by bubbling it through sulphuric acid and then passing through the columns of soda lime and anhydrous magnesium perchlorate respectively. The CO$_2$/CO ratio was changed from 0.1 to 100, and the oxygen partial pressure was calculated according to the reaction

$$\text{CO}(g) + 1/2 \text{O}_2(g) \rightleftharpoons \text{CO}_2(g)$$

$$\Delta G^\circ = -280,000 + 85,237 \frac{1}{T} \text{ J/mol}$$

The time needed to reach equilibrium was determined as 48 hr in preliminary experiments. After keeping for 48 hr at the experiment temperature, the sample was taken out of the furnace and then quenched with argon stream. The slag sample was taken out after cracking the magnesia crucible and the surface layer contacted with crucible was removed by grinding. Then the slag sample was ground to powder and the small alloy particles were removed carefully by magnetic separation. The alloy sample was sliced and ground, cut to small pieces and washed by acetone. The silica content in slag was analyzed by the gravimetric method. The total iron and acid-soluble ferrous oxide(II) contents were analyzed by titrating the dissolved samples with K$_2$Cr$_2$O$_7$. The other elements were analyzed by Inductively Coupled Argon Plasma-(ICP) Atomic Emission Spectroscopy method.

3. Results and Discussion

The experimental conditions and the analyzed compositions of slags and alloys are listed in Table 1.

### Table 1. Experimental conditions and the compositions of slag and alloy.

| Exp. No. | Time (h) | Temperature (K) | CO$_2$/CO | FeO/Fe$_2$O$_3$ | Co/CoO | Ni/NiO | MgO | SiO$_2$ |
|----------|----------|----------------|------------|----------------|--------|--------|------|--------|
| A1       | 48       | 1773           | 0.2        | 0.83           | 0.25   | 0.30   | 30.61| 47.22  |
| A2       | 48       | 1773           | 0.5        | 0.28           | 0.73   | 31.64  | 46.62|        |
| A3       | 48       | 1773           | 1          | 0.23           | 0.85   | 23.9  | 24.62| 39.18  |
| A4       | 48       | 1773           | 1          | 0.76           | 0.96   | 32.9  | 29.84| 40.29  |
| A5       | 48       | 1773           | 2          | 0.70           | 1.06   | 39.2  | 26.66| 37.10  |
| A6       | 48       | 1773           | 4          | 0.44           | 1.56   | 8.42  | 29.86| 33.72  |
| A7       | 48       | 1773           | 6          | 0.35           | 1.65   | 10.46 | 27.03| 32.97  |
| A8       | 48       | 1773           | 10         | 0.52           | 2.07   | 11.71 | 24.55| 27.35  |
| A9       | 48       | 1773           | 5          | 0.63           | 2.07   | 11.71 | 24.55| 27.35  |
| A10      | 48       | 1773           | 20         | 0.45           | 2.16   | 15.15 | 24.50| 28.06  |
| A11      | 48       | 1773           | 29         | 0.70           | 2.62   | 13.46 | 27.80|        |
| A12      | 48       | 1773           | 40         | 0.44           | 2.93   | 18.59 | 22.85|        |
| A13      | 48       | 1773           | 60         | 0.40           | 2.52   | 21.76 | 26.51|        |
| A14      | 48       | 1773           | 100        | 0.36           | 2.63   | 30.88 | 17.95| 23.33  |
| A15      | 48       | 1773           | 130        | 0.23           | 2.20   | 40.99 | 9.98 | 30.00  |
| A16      | 48       | 1773           | 160        | 0.08           | 2.16   | 32.68 | 17.06| 25.45  |
| B1       | 48       | 1823           | 0.1         | 0.91           | 0.25   | 0.25  | 32.83| 52.18  |
| B2       | 48       | 1823           | 0.4         | 0.97           | 0.21   | 0.38  | 30.58| 50.50  |
| B3       | 48       | 1823           | 1          | 0.71           | 0.61   | 1.96  | 30.15| 42.60  |
| B4       | 48       | 1823           | 4          | 0.69           | 1.42   | 8.78  | 30.45| 38.77  |
| B5       | 48       | 1823           | 10         | 0.57           | 2.16   | 16.85 | 26.86| 33.12  |
| B6       | 48       | 1823           | 20         | 0.39           | 1.97   | 37.08 | 19.06| 22.68  |
| B7       | 48       | 1823           | 40         | 0.39           | 2.17   | 46.48 | 14.55| 23.45  |
| C1       | 48       | 1873           | 0.70        | 0.26           | 1.45   | 37.86 | 44.33|        |
| C2       | 48       | 1873           | 23.50       | 0.40           | 1.34   | 53.48 | 16.27| 20.27  |
| C3       | 48       | 1873           | 74.00       | 0.30           | 1.50   | 64.76 | 11.29| 13.58  |

The distribution ratio of an element X between the slag and alloy phases is defined as Eq. (2).
According to reaction (3), the distribution ratio of an element X between the slag and alloy phases can be expressed as following.

\[
X(l) + \frac{\nu}{4}O_2(g) = XO_{\nu/2}(s) \quad \text{....................}(3)
\]

\[
\log L_X = \log \left( \frac{n_T}{n_T'} \right) + \log \left( \frac{\gamma_{XO_{\nu/2}}}{\gamma_X} \right) + \log K_3 + \frac{\nu}{4} \log P_{O_2} \quad \text{.........................}(4)
\]

Where the ( ) and [ ] denote those values in the slag and alloy phases, respectively. \(n_T\) is the total number of moles in 100 grams of each phase. \(\gamma\) is the activity coefficient relative to pure substance. \(K_3\) is the equilibrium constant of reaction (3) and \(P_{O_2}\) is the oxygen partial pressure.

As observed by Pagador et al.,\(^7\) the value of \(\frac{n_T}{n_T'}\) exhibited constant for the equilibrium between the MgO saturated FeO\(_x\)-MgO-SiO\(_2\) slag phase and the Ni-Cu-Fe alloy in their experimental conditions. If the activity coefficient \(\gamma\) of a metal element in the alloy phase is known then the activity coefficient of its oxide in the slag phase can be calculated.

### 3.2. Distribution of Fe, Co, and Ni between Slag and Ni Alloy

The distribution ratios of Fe, Co and Ni between MgO saturated MgO-SiO\(_2\)-FeO\(_x\) slag and Ni alloy at 1 773, 1 823 and 1 873 K with various oxygen partial pressures are plotted against the oxygen partial pressure in Fig. 1. The results obtained by Pagador et al.\(^4\) are also shown in this figure. It can be seen that the present results agree with Pagador’s results very well in the same range of oxygen partial pressure. The relationship between \(\log L_X\) and \(\log P_{O_2}\) shows a good linearity and the slope is close to 1/2. However this linear relationship changed when the oxygen partial pressure exceeded about \(3 \times 10^{-2}\) Pa. The distribution ratios of Fe, Co and Ni increase with increasing oxygen partial pressure. The distribution ratio for Co is about 4 at \(P_{O_2} = 24\) Pa and over 9 at \(P_{O_2} = 2.1 \times 10^4\) Pa when the slag and the alloy was brought to equilibrium with air. It should be noted that the value of \(\nu\) does not increase with increasing oxygen partial pressure. It means that the valence of Ni and Co is 2, meanwhile the ratio of ferric oxide increased with the increase of oxygen partial pressure, as described later. The composition of slag varied in a wide range when the oxygen partial pressure was changed. As shown in Table 1, the CoO content varied from 0.21 mass% to 2.32 mass%, while that of NiO varied from 0.25 mass% to 64.36 mass%. The change of slag composition resulted in the variation of the activity coefficients of CoO and NiO and caused the deviation of the linear relationship between \(\log L_X\) and \(\log P_{O_2}\). As described in Sec. 3.7, for example, the activity coefficient of CoO increased from 0.88 to 4.25 when the CoO content varied from 0.25 to 2.16 mass% (the oxygen partial pressure was in the range of \(9.5 \times 10^{-5}\) to \(9.5 \times 10^{-1}\) Pa) at 1 773 K while the activity coefficient of Co in alloy varied from 0.86 to 0.96. Thus the \(\frac{\gamma_{CoO}}{\gamma_{Co}}\) ratio decreased due to the increase of \(\gamma_{CoO}\) and the linear relationship between \(\log L_Co\) and \(\log P_{O_2}\) changed. The values of \(L_Ni\) at 1 873 and 1 823 K is lower than those of 1 773 K in the lower oxygen partial pressure range but the influence of temperature is not obvious when the \(P_{O_2}\) increases. The temperature dependence of distribution ratios at a constant oxygen partial pressure is shown in Fig. 2.

### 3.3. The Separation Coefficient

The separation coefficient of cobalt to nickel is defined as Eq. (5)

\[
\alpha_{CoNi} = \frac{L_{Co}}{L_{Ni}} = \frac{[\text{mass}\% Co]}{[\text{mass}\% Ni]} \quad \text{..................}(5)
\]

In the same way, the separation coefficient of Fe to (Ni+Co) can be expressed as

\[
\alpha_{Fe(Ni+Co)} = \frac{(\text{mass}\% Fe)}{[\text{mass}\% Ni] + [\text{mass}\% Co]} \quad \text{.................}(6)
\]
Figure 3 shows the variation of the separation coefficient with the change of oxygen partial pressure. Both the values of $\alpha_{Co/Ni}$ and $\alpha_{Fe/(Co+Ni)}$ in the oxygen partial pressure range of present study are larger than unity. The value of $\alpha_{Fe/(Co+Ni)}$ is larger than that of $\alpha_{Co/Ni}$ at the same oxygen partial pressure and it sharply changes with the oxygen partial pressure. It means that the separation of Fe from nickel alloys by the increase of oxygen partial pressure is easier than that of Co from Ni. There are minimum values appeared at $P_{O_2} = 0.1$ Pa in the curves of $\alpha$ versus $\log P_{O_2}$. It is not favorable for the separation processing in this oxygen partial pressure range. In fact, the ratio of metal content in alloy is the absolute measure of reduction in a metal content. As shown in Fig. 4, the ratio of Fe/(Ni+Co) in nickel alloys will decrease two orders when the oxygen partial pressure increases from $10^{-4}$ to 100 Pa.

3.4. Fe, Co, Ni Contents in Slag

In Fig. 5, nickel and cobalt contents (mass%) in slag equilibrated with liquid nickel alloys are plotted against the oxygen partial pressure. The contents of nickel and cobalt increases rapidly with increasing oxygen partial pressure. The contents of nickel and cobalt in slag are very low comparing with that of total iron at the lower oxygen partial pressure according to the result listed in Table 1. Therefore, most of nickel and cobalt can exist in alloy phase when the oxygen partial pressure is low enough even the Fe/(Ni+Co) ratio in alloys is higher. From the tendency of the data points at 1 823 and 1 873 K the small loss of nickel and cobalt in slag is expected at higher temperature especially when the oxygen partial pressure is lower than 10 Pa.

3.5. Solubility of MgO in the Slag

The slag is saturated with MgO because magnesia crucible is used in the present study. The MgO content in slag is shown in the MgO–SiO$_2$–(FeO$_x$–CoO+NiO) ternary system in Fig. 6. The result obtained by Pagador et al.8 at 1 773 K is also indicated by a broken line. The present result is in good agreement with those one in the range of FeO$_x$+CoO+NiO contents less than about 52%. The MgO

![Fig. 3. Change of the separation coefficients of Fe/(Co+Ni) and Co/Ni with oxygen partial pressure.](image1)

![Fig. 4. Change of the Fe/(Co+Ni) ratio in alloy with oxygen partial pressure.](image2)

![Fig. 5. Change of the Co and Ni contents of slags with oxygen partial pressure.](image3)

![Fig. 6. MgO solubility of MgO–SiO$_2$–FeO$_x$–CoO–NiO slag at 1 773, 1 823 and 1 873 K.](image4)
solubility decreases when the NiO content increases with high oxygen partial pressure. The MgO solubility increases slightly at higher temperature.

3.6. The Redox Equilibrium of Iron

Redox equilibria in iron-containing slags have been the subject of numerous investigations in which the slag was brought into equilibrium with gas mixtures of known composition and oxygen partial pressure at a given temperature. The redox reaction of iron oxides in slag can be written as

\[
\text{(FeO)} + \frac{1}{4} \text{O}_2 = \text{(FeO}_{1.5})
\]

According to which the ratio of Fe\(^{3+}\)/Fe\(^{2+}\) may be expressed as

\[
\log(\%\text{Fe}^{3+}/\%\text{Fe}^{2+}) = 1/4 \log P_{O_2} + \log(\gamma_{\text{FeO}}/\gamma_{\text{FeO}_{1.5}}) + \log K_7 \quad \ldots \ldots \ldots (8)
\]

Where \(K_7\) is the equilibrium constant of reaction (7), \(\gamma_{\text{FeO}}\) and \(\gamma_{\text{FeO}_{1.5}}\) are the activity coefficients for the ferrous and the ferric oxide relative to pure substance, respectively. The dependence of oxygen partial pressure in this work at 1 773, 1 823 and 1 873 K is shown in Fig. 7. A linear relationship between \log(\%\text{Fe}^{3+}/\%\text{Fe}^{2+}) and \log P_{O_2} was obtained. The slopes of lines in Fig. 7 obtained by the least square method are 0.20 at 1 773 and 0.24 at 1 823 K, respectively. It can be seen that the effect of temperature on the Fe\(^{3+}/\text{Fe}^{2+}\) ratio is not significant.

3.7. Activity Coefficients of NiO and CoO in the Slag

Activity coefficient is an important thermodynamic parameter for estimating the elimination of impurities into slag and recovery of valuable metals in the alloy. The activity coefficient of oxide can be calculated from Eq. (9).

\[
\gamma_{\text{NiO}_{1.5}} = \frac{K_3(n_4)[\gamma_X]}{[n_1]^{L_X}} P_{O_2}^{1/4} \quad \ldots \ldots \ldots (9)
\]

The equilibrium constant \(K_3\) of reaction (3) is calculated using the standard Gibbs free energy of reactions (10) and (11).

\[
\text{Ni (l)} + \frac{1}{2} \text{O}_2 (g) = \text{NiO (s)}
\]

\[
\Delta G^\circ = -253 100 + 96.197T \quad \text{J/mol} \quad \ldots \ldots \ldots (10)
\]

\[
\text{Co (l)} + \frac{1}{2} \text{O}_2 (g) = \text{CoO (s)}
\]

\[
\Delta G^\circ = -261 800 + 87.827T \quad \text{J/mol} \quad \ldots \ldots \ldots (11)
\]

The activity coefficient of Ni and Co were calculated according to the report of Gokcen and Baren,\(^{9}\) where the activities of Fe, Co and Ni at 1 825 K were calculated based on the published data of Fe–Co, Fe–Ni and Co–Ni binary systems and the results were expressed as a function of alloy composition. Those data for 1 773 and 1 873 K were extrapolated from those of 1 825 K by assuming the regular behavior of the components in Fe–Co–Ni alloy. It should be noted that the oxygen dissolution in the Fe–Co–Ni alloy affects the activity coefficients of Fe, Co and Ni especially at high oxygen potential, for \(\gamma_{\text{NiO}}\) only the data of \(\gamma_{\text{Ni}}\) in the range of oxygen potential lower than 1 Pa is applicable in the present work.

4. Conclusions

As a fundamental study related to the recycle of nickel alloy, the distribution equilibria of Fe, Co and Ni between nickel alloy and MgO saturated FeO\(_x\)–MgO–SiO\(_2\) slag at 1 773, 1 823 and 1 873 K were investigated with controlled oxygen partial pressure ranging from \(10^{-4}\) to \(10^2\) Pa. The following results were obtained.

The distribution ratios of Fe, Co and Ni between MgO
saturated FeO–MgO–SiO₂ slag and nickel alloy suggest that most of nickel and cobalt can remain in the alloy phase in the condition of lower oxygen partial pressure, and iron can be eliminated adequately from nickel alloys at the condition of high oxygen partial pressure, but the solubility of nickel and cobalt oxide in the slag also increase with the increase of oxygen partial pressure.

The relationship between the separation coefficients and oxygen partial pressure suggests that the separation of iron from nickel alloy is easier than that of cobalt. An oxygen partial pressure range at which the separation coefficients show minimum should be avoided in the practical process. Lower oxygen partial pressure and higher temperature are favorable for decreasing the loss of nickel and cobalt into slag.

The MgO solubility in the SiO₂–MgO–FeOₓ–CoO–NiO slag decreases when the NiO content exceed 25% at higher oxygen partial pressure.

The activity coefficients of NiO and CoO in slags were calculated and found that their values increased with increasing CoO and NiO contents respectively.

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