Distribution of Cobalt between MgO-Saturated FeO$_x$-MgO-CaO-SiO$_2$ Slag and Fe-Cu-Co Molten Alloy

Shin-ya Kitamura$^1$, Hideki Kuriyama$^{1,*}$, Nobuhiro Maruoka$^1$, Katsunori Yamaguchi$^2$ and Akira Hasegawa$^3$

$^1$Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
$^2$Department of Materials Science and Technology, Faculty of Engineering, Iwate University, Morioka 020-8551, Japan
$^3$Department of Quantum Science and Energy Engineering, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

During the decommissioning phase of a nuclear reactor, most of the steel-reinforced concrete shielding around a pressure vessel is considered as low-level radioactive waste. It is highly desirable to reduce the radioactivity level of this waste to below the clearance level. Normally, the radioactivity of steel after irradiation is found to be proportional to the cobalt content. In this study, for the production of low-activation steel in steelmaking process, cobalt distribution between MgO-saturated FeO$_x$-MgO-CaO-SiO$_2$ slag and Fe-Cu-Co molten alloy was investigated. The results are summarized as follows: (1) the distribution ratio increases with decreasing temperature and (2) the activity coefficient of CoO decreases with increasing temperature and decreasing slag basicity. Although low temperature and low basicity are suitable conditions for refining, it is extremely difficult to decrease the Co content by an oxidation reaction, because of a very small distribution ratio of cobalt. [doi:10.2320/matertrans.MAW200831]

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1. Introduction

During the decommissioning phase of a nuclear reactor, most of the steel-reinforced concrete shielding around a pressure vessel is considered as low-level radioactive waste. In terms of life-cycle cost reduction, it is highly desirable to reduce the radioactivity level of this waste to below the clearance level. With support from the Ministry of Economy, Trade and Industry, a project termed “Low-activation Reinforced Concrete Design Methodology (LARC-DM)” has been undertaken in Japan.$^1$ One of the objectives of this project is to develop low-activation steel for use in structural components.

Generally, steel contains small amounts of Co, Ni, Nb, Zn, and Sn, which is transformed into $^{60}$Co, $^{59}$Ni or $^{63}$Ni, $^{94}$Nb, $^{65}$Zn, and $^{125}$Sb, respectively, by thermal-neutron irradiation. The radioactivity of steel after irradiation is found to be proportional to the cobalt content.$^1$ According to a study on the cobalt content in commercial steel bars, the content was found to widely vary from 10 to 140 ppm and the average value was 66 ppm.$^{1-3}$ From these studies, it could be inferred that the main sources of cobalt are Ni-containing scrap, serpentine as a flux material for blast furnaces, and some kind of ferro-alloys. Despite the precise selection of the raw materials in the ironmaking and steelmaking processes,$^{2,3}$ the minimum cobalt content was reported to be 10 ppm. In order to decrease the cobalt content in steel, it is important to understand the optimum refining condition which shows the highest distribution ratio between slag and metal.

Since cobalt is a by-product of the copper or nickel smelting process, the activity coefficient of CoO and the distribution of cobalt between slag and metal were measured for SiO$_2$- or Al$_2$O$_3$-saturated slag systems.$^{4-8}$ The activity coefficient of CoO was approximately 0.4 for the Al$_2$O$_3$-saturated slag and around 2 for the SiO$_2$-saturated slag and other slag systems. Compare with the smelting conditions of non ferrous metal, temperature, oxygen potential and slag basicity are relatively high in steelmaking process. In this study, the distribution ratio of cobalt in steelmaking condition include hot metal pretreatment has been investigated.

2. Experimental Conditions

In the steelmaking process, refining conditions such as temperature, oxygen potential, and slag basicity vary widely. Experiments have been performed to measure the distribution ratio under these wide conditions.

2.1 Slag composition

As an MgO crucible was used, an MgO-saturated FeO$_x$-CaO-SiO$_2$ system containing 0.2 mass% of CoO was selected. The oxygen potential in gas atmosphere was controlled by CO-CO$_2$ gas. The equilibrium oxygen potential can be calculated using eqs. (1) and (2), where $P$ is the partial pressure, $K_1$ is the equilibrium constant of reaction (1), and $R$ is the gas constant. To calculate the partial pressure, atmospheric pressure ($10^5$ Pa) is used as the total pressure.

$$2\text{CO(g)} + \text{O}_2\text{(g)} = 2\text{CO}_2\text{(g)}$$  \hspace{1cm} (1)

$$P_{O_2} = \left( \frac{P_{CO_2}}{P_{CO}} \right)^2 \times \frac{1}{K_1}$$ \hspace{1cm} (2)

The mass percentage ratio of CaO to SiO$_2$, referred to as basicity ($B$) and defined by eq. (3) in this study, was changed to 0.8, 1.0, and 1.2.

$$B = (\%\text{CaO})/(\%\text{SiO}_2)$$ \hspace{1cm} (3)

When the experimental temperature was lower than 1723 K

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$^*$Graduate Student, Tohoku University, Present address: NOK Corporation, Tokyo 105-8585, Japan
and the basicity was 1.2. CaF\(_2\) was added. In this case, the mass percentage ratio of CaF\(_2\) to CaO was set to 0.2, and the Ca in CaF\(_2\) was converted into CaO to calculate the basicity.

### 2.2 Metal composition

When the experimental temperature was higher than 1823 K, Fe-1\%Co molten alloy was used as a metal phase. To measure the distribution ratio in hot metal pretreatment temperature range, Fe-1\%Co alloy can not be melted. So, when the experimental temperature was lower than 1773 K, Fe-Cu-1\%Co molten alloy was used.

### 2.3 Experimental procedure

In this experiment, the FeO\(_x\)-MgO-CaO-SiO\(_2\) slag and the Fe-Cu-Co molten alloy were equilibrated under CO/CO\(_2\) atmosphere. As the system consisted of 8 elements (Fe, Mg, Ca, Si, Cu, Co, C, and O) and 4 phases (gas, molten slag, molten alloy, and crucible), a degree of freedom was calculated to be 6 by using the phase rule. Therefore, when the temperature, total pressure, CO/CO\(_2\), Fe/Co, Fe/Cu, and CaO/SiO\(_2\) are set, an equilibrium relationship could be achieved.

The furnace consisted of a “Kanthal Super” heating element and an alumina reaction tube. The temperature of the sample was controlled within ±5 K by using a Pt/Pt-Rh thermocouple. A reagent mixture of approximately 4 g was pressed to form a tablet. Approximately 13 g of electrolytic iron, refined copper, and metallic cobalt were melted with the tablet in a fused magnesia crucible. For each experimental condition, the sample was heated in a suitable CO/CO\(_2\) atmosphere in a furnace and the flow rate of CO-CO\(_2\) gas was 1.7 \times 10^{-5} \text{ m}^3\cdot\text{s}^{-1}. The preliminary experiment confirmed that the reaction achieved equilibrium after 9 ks. Therefore, the sample was removed from the furnace after 9 ks and then quenched in a water pool.

The contents of Cu, Fe, and Co in metal and Fe, Cu, Co, Mg, and Ca in slag were analyzed by either inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or inductively coupled plasma-mass spectroscopy (ICP-MS). The Si content in slag was analyzed by X-ray fluorescence Analysis (XRF).

### 3. Results

#### 3.1 Equilibrium partition ratio

The results of the experiments are summarized in Table 1. Each series corresponds to the experimental temperature. The oxygen potential is calculated using eq. (2). The distribution ratio of cobalt (\(L_{\text{Co}}\)) is expressed in eq. (4), where [\%Co] and [\%Co] are the Co contents in slag and metal phases, respectively (mass%).

\[
L_{\text{Co}} = \frac{[\%\text{Co}]}{[\%\text{Cu}]} \quad (4)
\]

Figure 1 shows the effect of the oxygen potential on the distribution ratio at a temperature of 1623 K. Even though the observed distribution ratio was very small, its value increased in proportion to \(1/2\) the power of the oxygen potential. From the oxidation reaction of cobalt and the distribution ratio that are expressed in eqs. (5) and (6), it can be considered that the result shown in Fig. 1 is reasonable.

\[
\text{Co (in Cu-Fe)} + 1/2\text{O}_2(g) = \text{CoO (in slag)} \quad (5)
\]

\[
L_{\text{Co}} = K_{\text{Co}} \times \frac{[\%\text{Co}]}{[\%\text{Cu}]} \times \frac{\rho_T}{\rho_T} \times P_{\text{O}_2}^{1/2} \quad (6)
\]

where, \(K_{\text{Co}}\) is the equilibrium constant for (5), \(\gamma_{\text{Co}}\) and \(\gamma_{\text{CoO}}\) are the thermodynamic factors of Co and CoO.
are the activity coefficients of cobalt in the metal phase and that of CoO in the slag phase, respectively, and \( [\eta_T] \) and \( [\eta_T] \) are the total number of moles in 100 g of slag and metal phases, respectively. To calculate \( K_{Co} \), the following equilibrium equation was considered.

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

\[
\Delta G^0 = 229412 + 69.355 \times T
\]

To compare distribution ratios measured under various oxygen potentials, the normalized value to \( 10^{-11} \) is defined in eq. (9).

\[
L_{Co} = L_{Co} \times \left( \frac{10^{-11}}{P_o_2} \right)^{1/2}
\]

Figure 2 shows the effect of temperature and slag composition on the normalized distribution ratio for Fe and Cu-Fe molten alloy.

The distribution ratio obtained using Fe melt at a high temperature is considerably smaller than that obtained using Cu-Fe molten alloy at a low temperature. However, the dependence of the distribution ratio on slag basicity is uncertain.

Figure 3 shows the difference in the distribution ratios with the metal phase composition. An apparent difference is not found.

### 3.2 Activity coefficient of Co and CoO

From eq. (6), it is necessary to obtain the activity coefficient of cobalt in metal phase to calculate the activity coefficient of CoO in slag phase. No data of activity in the Fe-Cu-Co alloy system are available by an experimental measurement. Using cubic Margules equations, Derin and Yücel have calculated the activity coefficient of cobalt in Fe-Cu-Co molten alloy.

\[
RT \ln \gamma_{Co} = A_{Cu-Co} X_{Cu}^2 + A_{Co-Fe} X_{Fe}^2 + (A_{Cu-Co} + A_{Co-Fe} - A_{Cu-Fe}) X_{Cu} X_{Fe}
\]

where, \( X \) is the molar fraction and \( A \) is the interaction
The activity coefficient of each binary alloy. The following values of $A$ are used at a temperature of 1673 K; $A_{\text{Co-Fe}} = -10647$, $A_{\text{Cu-Co}} = 33252$, $A_{\text{Cu-Fe}} = 32446$.

The activity coefficients of cobalt with respect to pure liquid cobalt as a standard state in Fe-Co alloy and Cu-Co alloy have already been reported.\(^9,10\)

$$\ln \gamma_{\text{Co}} = 0.592 \times X_{\text{Fe}}^2$$  \hspace{1cm} (11)

$$\ln \gamma_{\text{Co}} = 0.0116 + \frac{1.85 \times 10^3}{T}$$  \hspace{1cm} (12)

Comparing these values with those calculated by eq. (10), $A_{\text{Co-Fe}}$ and $A_{\text{Cu-Co}}$ are revised to $-8500$ and $36525$, respectively, so that the calculated values are in accordance with the observed results. Figure 4 shows the comparison of these values.

The activity coefficient of CoO in slag can be calculated using the activity coefficient of cobalt and the observed partition ratio and the results are shown in Table 2. Pagador et al. have measured the distribution of cobalt between MgO-saturated FeO$_x$-MgO-CaO-SiO$_2$ slag and Ni-Cu-Fe alloy at 1773 K.\(^7\) Figure 5 shows the comparison of the activity coefficients of CoO obtained by this research with those obtained by their results. Even though the experimental temperature and the oxygen potential are different, both the results show similar values.

Figure 6 shows the effect of temperature and slag composition on the activity coefficients of CoO. An inverse relationship between the temperature and the activity coefficients is observed; therefore, an increase in the temperature causes a decrease in the activity coefficients of CoO.

<table>
<thead>
<tr>
<th>Series</th>
<th>Run</th>
<th>Temp. (K)</th>
<th>$P_{\text{O}_2}$</th>
<th>$B$</th>
<th>$L_{\text{Co}}$</th>
<th>$L_{\text{CoO}}$</th>
<th>$\gamma_{\text{Co}}$</th>
<th>$\gamma_{\text{CoO}}$</th>
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<td>0.0255</td>
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<td>0.56</td>
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</table>
Low-basicity slag has a smaller activity coefficient of CoO as compared to that of high-basicity slag. On the basis of this result, eq. (13) is obtained for the activity coefficient of CoO in slag.

\[
\ln \gamma_{\text{CoO}} = 8.3283 + \frac{14.9763 \times 10^3}{T} + 0.9552 \times B
\]

4. Discussion

The behavior of cobalt in the steelmaking process can be estimated from these results. The activity coefficient of CoO in slag phase was estimated from eq. (13), and the Fe-C-Co alloy was considered as the metal phase. In this case, the effect of carbon on the activity coefficient of cobalt was not taken into account. The cobalt content and the slag volume before the oxidation treatment were assumed to be 50 ppm and 300 kg/t, respectively. Figure 7 shows the calculation results. The distribution ratio increases with the increase in temperature as the strong temperature dependence of equilibrium constant, although the activity coefficient of CoO increases. Therefore, the treatment with acid slag under low temperature is considered to be favorable for increasing the distribution ratio. Nevertheless, as the maximum oxygen potential in the steelmaking process is about $10^{-10}$, the distribution ratio would be less than 0.1, and the decrease in the cobalt content would be negligibly small.

5. Conclusions

For the production of low-activation steel by the steelmaking process, the cobalt distribution between MgO-saturated FeO-MgO-CaO-SiO$_2$ slag and Fe-Cu-Co molten alloy has been investigated. The results are summarized as follows: (1) the distribution ratio increases with decreasing temperature and (2) the activity coefficient of CoO decreases with increasing temperature and decreasing slag basicity. Even though low temperature and low basicity are suitable conditions for refining, it would be very difficult to reduce the cobalt content by the oxidation reaction, owing to the small distribution ratio of cobalt.
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REFERENCES


