Measurement on Interaction Parameter between Co and Al in Molten High Al Steel

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Nowadays Al is commonly used as deoxidizer and sometimes alloying element. On the other hand, due to the increase in scrap addition, suppress in the concentration of tramp element in molten steel during refining process becomes more important than ever. Co is one of the tramp elements in steel scrap and its content is increasing due to the increase in the production of Co materials world widely. As fundamentals to understand the thermodynamic behaviors of Co in the molten steel containing high Al, the interaction parameter between Co and Al has been measured in this study through a chemical equilibrium method. From the equilibrium composition of the Fe–Co–Al alloy and Ag, the interaction parameter between Co and Al in molten Fe–Co–Al alloy was determined as follows,

ε_{CoAl} = 7.3 ± 0.9 at 1823 K, 0 < \chi_{Al}^{Fe} < 0.14

By converting the temperature and the reference state, the following values were also obtained,

ε_{CoAl} = 6.9 ± 0.8 at 1823 K
\epsilon_{Co} = 0.060 ± 0.007 at 1873 K
\epsilon_{Al} = 0.030 ± 0.004 at 1873 K

KEY WORDS: high Al steel; aluminum; cobalt; interaction parameter; activity coefficient.

1. Introduction

In steelmaking process, Al is often used as a deoxidation agent and in some cases alloying element such as Twinning-induced plasticity steel, and thus the equilibrium relationships relating to Al has drawn many attentions. On the other hand, due to the increase in the application of scrap, the increase in the contents of tramp elements must be paid attention because they may affect the refining process and the quality of steel product. In steel scrap, the existence of Co makes it become one of the tramp elements, and due to the increase in the world production of Co materials, the enrichment of Co in scrap can be predicted. In addition to the negative effects, Co is also an important alloying element especially for high Cr ferrite steel to improve mechanical properties. Therefore, in terms of the quality control for steel scrap and the control of alloying element during refining process, the thermodynamic properties of Co in molten Fe should be understood. Previously, studies on measuring the activity coefficient of Co have been conducted for either Fe or Co based alloys. However, the knowledge on the relation between Al and Co in molten steel remains poor. Therefore, in present study, the interaction parameter between Co and Al in molten Fe with various Al contents at 1823 K has been measured by a chemical equilibrium technique.

2. Experimental Method

The chemical equilibrium was achieved by equilibrating a prepared Fe–Al–Co alloy with Ag at 1823 K which was similar to previous report. To prepare the Fe–Al–Co alloy, electrolytic iron, reagent grade of metallic Al and Co were melted and quenched using an arc furnace. In order to suppress Al oxidation during melting, reagent grade of metallic Ti was placed in the chamber of the arc furnace to remove oxygen inside the chamber. After quenching, the surface of the prepared alloy was polished to remove oxide film and then crashed into small lumps. The composition of the Fe–Al–Co alloy is shown in Table 1.

The set-up for the equilibrium experiment is shown in Fig. 1. For each experiment, approximately 7 g of Ag and 8 g of the Fe–Al–Co alloy were loaded in a high purity Al2O3 crucible, and a graphite lid was put on top of the crucible.
Table 1. Compositions of Fe–Al–Co alloy before experiment, mass%.

| Sample No. | Fe   | Al   | Co   |
|------------|------|------|------|
| 1          | 98   | 1    | 1    |
| 2          | 96   | 3    | 1    |
| 3          | 94   | 5    | 1    |
| 4          | 92   | 7    | 1    |
| 5          | 90   | 9    | 1    |
| 6          | 88   | 11   | 1    |

crucible to suppress oxygen contamination during experiment. The Al$_2$O$_3$ crucible was chosen because the Fe–Al–Co alloy contains high content of Al, and the crucible is of a slender shape to minimize the entrapment of alloy and Ag into each phase. Three Al$_2$O$_3$ crucibles loaded with samples were set in a protection crucible and then placed in the hot zone of a vertical electric resistance furnace before heating up. Before and during heating, the atmosphere of the furnace was controlled by continuously flowing high purity Ar gas (99.9999%) with a rate of 200 ml/min. The temperature of the hot zone was controlled at 1 823 K (±3 K). After keeping the samples at 1 823 K for 4 h, the crucibles were carefully withdrawn from the furnace and quenched by a helium gas stream. The time required to achieve equilibrium between the molten alloy and Ag was predetermined as 4 h. After quenching, the Fe–Al–Co alloy and Ag was easily separated and about 2 g of each were cut out for composition analysis. The cut part was away from the interface between alloy and Ag.

The equilibrium composition of the Fe–Co–Al alloy and Ag were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) with an internal standard method using Gallium. The use of internal standard method aimed to give an accurate analysis of Co by canceling the interference from Ag or Fe, and the interference by the differences in liquid viscosity. Gallium was selected after several preliminary tests because it showed a steady emission intensity which was not affected by Ag or Fe in the solution under current analysis conditions. Because the contents of Co in both alloy and Ag were low at equilibrium, 2 g of each phase was dissolved by 100 ml of nitric acid so that the content of Co in a solution could reach to a concentration of the order of some mg/L to ensure the precision of analysis. In addition, some of the alloy samples were imbedded in resin and polished to observe the cross-sectional via electron probe microanalysis (EPMA). In addition, the reproducibility of the above chemical equilibrium experiments and the analysis methods have been confirmed through preliminary experiments.

3. Results and Discussion

The cross sections of sample No. 1 after equilibration are shown in Fig. 2. Figure 2(A) shows the interface between the Fe–Co–Al alloy and Ag, while Figs. 2(B) and 2(C) show the cross sections of the alloy and Ag away from the interface respectively. Near the interface, large suspended particles of the Fe–Co–Al alloy was observed in Ag. About several centimeters away from the interface, significant suspensions were observed neither in the alloy nor Ag, though some fine particles alloy existed in Ag. Towards these fine particles, because their shape was not sphere but irregular, it was considered that these particles were formed by precipitation during quenching because the solubility of Fe in Ag decreases with temperature. Therefore, we considered that the effect of suspensions on the compositions analysis for each phase was small when the parts away from the interface were used.

The equilibrium composition of both Fe–Co–Al alloy and Ag analyzed by ICP-AES are given in Table 2. The amounts of Fe and Ag that transited into the opponent phases are small, and the maximum molar ratios of Ag and Fe in alloy and Ag were 0.032 and 0.007 respectively. In addition, Al concentration of Ag phase increased with an increase in the initial Al concentration of the Fe–Co–Al alloy, and the molar ratio of Al in the Ag reached at most 0.108 mole.

In order to determine the interaction parameter between Al and Co in the Fe–Co–Al alloy, the activity of Co in the Ag phase ($a_{Co}^{Ag}$) needs to be calculated firstly. The activity coefficient of Co in Ag ($\gamma_{Co}^{Ag}$) was defined by the partially differential of the excess Gibbs energy of mixing Ag and Co at molten state by the molar ratio of Co ($G_{Co}(L)$, J/mol), as shown in Eq. (1).\(^{15}\) The $G_{Co}(L)$ was expressed as Eq. (2).\(^{15}\) Here, $H_{Co}^{ex}(J/(mol K))$ and $S_{Co}^{ex}(L)/(mol)$ are the partially differentials of the excess enthalpy and entropy of mixing Ag and Co by the molar ratio of Co, respectively. Their values in a Ag rich liquid phase of Ag–Co binary system was calculated using Eqs. (3) and (4).\(^{16}\) Here, the $H^{mix}(L)$ means the partially differential of the mixing enthalpy of Ag and Co, and which equals to $H_{Co}^{ex}$.\(^{15}\) In addition, $\gamma_{Co}^{Ag}$ is the molar ratio of element i in phase M; $R$ is the gas constant (J/K·mol); and $T$ is temperature (K). In addition, the above calculation of the activity coefficient of Co in Ag has to be conducted without considering the effects of Al and Fe in Ag, because the interaction parameter between Al and Co, Fe and Co in Ag have not been reported.

\[
RT\ln\gamma_{Co}^{Ag} = G_{Co}^{ex}(L) \quad \ldots \quad (1)
\]
\[
G_{Co}^{ex}(L) = H_{Co}^{ex}(L) - TS_{Co}^{ex}(L) \quad \ldots \quad (2)
\]
Eq. (7) was used to determine the Raoultian activity of Co in Ag is not a constant but equals to an equilibrium constant \(K_2\) as shown in Eq. (8). To determine this equilibrium constant, the experimental results of sample No. 1 which has low Al molar ratio in both alloy and Ag were used. The value for the activity of Co in Ag is shown in Table 3. To calculate the activity of Co in the alloy \(a_{Co}^Ag\), Eq. (7) was used to determine the activity coefficient of Co in Fe–Co–Al alloy \(\gamma_{Co(Fe-Co)}\) at 1 873 K, and the value was converted to 1 823 K using Eq. (8) because Fe–Co melt behaved regular solution. In this calculation, the interaction between Ag and Co in Fe–Co–Al alloy was ignored because lacking available data. Finally, the equilibrium constant for reaction (5) was determined as 8.7 at 1 823 K. Using this value, both the activity and the activity coefficient of Co in the Fe–Co–Al alloy for sample 2 to 6 were determined and the results are shown in Table 3.

\[
\frac{[Co]_{Ag}}{[Co]_{Fe}} = \gamma_{Co(Fe-Co)} \tag{5}
\]

\[
a_{Co}^Ag / a_{Co}^Fe = \frac{\gamma_{Co(Fe-Co)}}{K_2} \tag{6}
\]

\[
\log \gamma_{Co(Fe-Co)} = -0.257X_{Co}^Ag \tag{7}
\]

Next, we assumed the activity coefficient of Co in the Fe–Co–Al could be expressed as Eq. (9) and ignored the secondary interactions. Here, \(\gamma_{Co}^{Fe}\) is the Raoultian activity coefficient of Co at infinite dilution in the molten alloy, which is 0.55 at 1 873 K and 0.54 at 1 823 K using regular solution conversion.\(^{12}\) \(K_3\) is the interaction parameter of solvent \(j\) on Co in the Fe–Co–Al alloy. In this study, the effect of dissolved oxygen on the activity coefficient of Co in Fe–Co–Al alloy was ignored, because the amount of the dissolved oxygen was low due to the equilibrium between dissolved Al and Al\(_2\)O\(_3\). In addition, the effect of dissolved Ag was also ignored for the same reason. For the self-interaction of Co, the \(\gamma_{Co}^{Ag}\) of 1.2 was used.\(^{13}\)

\[
RT \ln \gamma = \text{constant} \tag{8}
\]

The calculated activity coefficient of Co in Ag using the molar ratios of Co and Ag in Ag that measured by current study are shown in Table 3. By using these values and the equilibrium molar ratio of Co in Ag, the activities of Co in Ag has been derived and are also shown in Table 3.

Table 3. Activity coefficient and activity of Co in Ag and Fe–Co–Al alloy.

| Sample No. | Ag       | Fe–Co–Al alloy | \(\gamma_{Co}^{Ag}\) | \(a_{Co}^{Ag}\) | \(a_{Co}^{Fe}\) | \(\gamma_{Co}^{Fe}\) |
|------------|----------|----------------|----------------------|----------------|----------------|----------------|
| 1          | 24.6     | 5.6×10^{-4}    | 4.9×10^{-3}          | 0.6            |
| 2          | 24.6     | 9.3×10^{-4}    | 8.2×10^{-3}          | 0.9            |
| 3          | 24.6     | 6.4×10^{-4}    | 5.6×10^{-3}          | 0.7            |
| 4          | 24.6     | 9.8×10^{-4}    | 8.6×10^{-3}          | 1.0            |
| 5          | 24.6     | 1.1×10^{-3}    | 9.9×10^{-3}          | 1.2            |
| 6          | 24.6     | 2.0×10^{-3}    | 1.7×10^{-3}          | 2.0            |

\[
H_{Co}^{Ag}(L) = H_{Co}^{Molten}(L) = 59 000X_{Co}^{Ag} + 66 000X_{Co}^{Ag}X_{Ag} \tag{3}
\]

\[
S_{Co}^{Ag}(L) = 5.737X_{Co}^{Ag} \tag{4}
\]
\[ \ln \gamma_{Fe}^{Al} - \ln \gamma_{Co}^{Al} - \varepsilon_{Co}^{Al} \cdot \chi_{Al}^{Fe} \] and the equilibrium \( \chi_{Al}^{Fe} \) can be regressed using least squares method with a fixed interception of 0. The regression result is shown in Fig. 3. A linear relationship has been obtained which proves the assumption for not considering the secondary interactions is reasonable. However, there is a deviation between some experimental data and the regression line. The reason was considered as that the evaluation on the activity coefficient of Co in Ag was probably less precise, because the effect of dissolved Al and Fe in Ag was not considered due to lack of available thermodynamic data.

\[ \ln \gamma_{Co}^{Fe} = \ln \gamma_{Co}^{0,Fe} + \varepsilon_{Co}^{Al} \cdot \chi_{Al}^{Fe} + \varepsilon_{Co}^{Fe} \cdot \chi_{Ag}^{Fe} + \varepsilon_{Fe}^{Co} \cdot \chi_{Co}^{Fe} + \varepsilon_{O}^{Co} \cdot \chi_{O}^{Fe} \]  

\[ \ln \gamma_{Co}^{Fe} = \ln \gamma_{Co}^{0,Fe} - \varepsilon_{Co}^{Al} \cdot \chi_{Al}^{Fe} = \varepsilon_{Co}^{Al} \cdot \chi_{Co}^{Fe} \]  

(10)

Basing on the slope of the linear fitting as show in Fig. 3, the interaction parameter between Al and Co in molten Fe–Co–Al alloy (\( \varepsilon_{Co}^{Al} \)) at 1 823 K has been determined as follows (11). Therefore, the activity coefficient of Co in Fe–Co–Al alloy basing on Eq. (9) can be written as Eq. (12).

\[ \varepsilon_{Co}^{Al} = 7.3 \pm 0.9 \text{ at } 1823 \text{ K, } 0 < X_{Al}^{Fe} < 0.14 \]  

\[ \ln \gamma_{Co}^{Fe} = 7.3 \cdot X_{Al}^{Fe} + 1.2 X_{Co}^{Fe} - 0.6 \text{ at } 1823 \text{ K, } 0 < X_{Al}^{Fe} < 0.14 \]  

(12)

The above activity coefficient has been derived to 1 873 K assuming a regular solution. In addition, the interaction parameter has also been converted to Henrian standard state. The results are shown as follows. Here, \( \varepsilon_{i}^{j} \) is the interaction parameter of element \( i \) on \( j \).

\[ \varepsilon_{Co}^{Al} = 6.9 \pm 0.8 \text{ at } 1873 \text{ K, } 0 < X_{Al}^{Fe} < 0.14 \]

\[ \varepsilon_{Co}^{Al} = 0.060 \pm 0.007 \text{ at } 1873 \text{ K, } 0 < X_{Al}^{Fe} < 0.14 \]

\[ \varepsilon_{Co}^{Al} = 0.030 \pm 0.004 \text{ at } 1873 \text{ K, } 0 < X_{Al}^{Fe} < 0.14 \]

4. Conclusions

By equilibrating a Fe–Co–Al alloy of various Al contents with Ag at 1 823 K using an Al₂O₃ crucible, the interaction parameter between Co and Al in molten Fe–Co–Al alloy was determined as follows with an effective composition range of 0 < \( X_{Al}^{Fe} < 0.14 \) (0 < Al mass% < 6):

\[ \varepsilon_{Co}^{Al} = 7.3 \pm 0.9 \text{ at } 1823 \text{ K} \]

Using an assumption of the regular solution, the interaction parameters at 1 873 K was derived as follows,

\[ \varepsilon_{Co}^{Al} = 6.9 \pm 0.8 \text{ at } 1873 \text{ K} \]

\[ \varepsilon_{Co}^{Al} = 0.060 \pm 0.007 \text{ at } 1873 \text{ K} \]

\[ \varepsilon_{Co}^{Al} = 0.030 \pm 0.004 \text{ at } 1873 \text{ K} \]

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