Removal of P and Cr by Oxidation Refining of Fe–36%Ni Melt

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Removal of P and Cr, which are impurities in a Fe–36%Ni alloy, was investigated by conducting experiments 30 kg scale on oxidation refining of a 36% Ni melt containing 0.1 mass% P and 0.4–1.5 mass% Cr with a CaO–SiO₂–CaF₂–Fe₂O slag. FeCr₂O₄ was identified of X-ray diffraction analysis of water-cooled slag sample just after the experiments. Therefore, the oxygen potential of the dephosphorization reaction was taken to be controlled by the formation reaction of FeCr₂O₄. The removal reaction of P and Cr occurred along the P–Cr equilibrium (Eq. (A)), and consequently high temperature treatment was effective in lowering the P content in the range of the present Cr contents.

The phosphorus distribution ratio (L_P) decreased with increasing Cr content in the metal. This was considered because the oxygen partial pressure was lowered by increasing the content of Cr. In addition, L_P increased with increasing in Ni content in the metal. It was concluded that this was because the oxygen partial pressure was increased with increasing Ni content mainly.

KEY WORDS: Fe–36%Ni alloy; removal of phosphorus and chromium; oxygen potential; activity coefficient.

1. Introduction

P and Cr impair the characteristics of Fe–36%Ni alloy which has come into use as a shadowmask material for use in color cathode-ray tubes. Therefore, in the manufacturing of Fe–36%Ni industrially, it is necessary to remove both P and Cr, which originate from impurities in the raw materials and the furnaces, used for oxidation refining. There have no report on the removal of both P and Cr by oxidation refining of a high Ni melt. Therefore, an attempt has been made to clarify the behavior of removal of both P and Cr in a high Ni melt.

2. Experimental Method

A schematic diagram of furnace and the experimental conditions are shown in Fig. 1 and in Table 1, respectively. Thirty kg of Fe–36%Ni alloy was melted in a MgO

crucible by means of a high frequency induction furnace. Temperature of the metal bath was continuously measured by immersing thermocouple and was controlled within the range of ± 7 K. Around the outside of a crucible, at the flux line, a carbon ring was placed to prevent the falling of flux temperature. After reaching the target temperature, CaO–SiO₂–CaF₂ flux was added on the molten bath. Thereafter, specific amounts of ferro-phosphorus (6.3 g/kg-metal) and electrolytic Cr (10 g/kg-metal) were added to the melt, and O₂ gas was blown into the bath. Metal samples were taken at regular intervals after the flux addition. Slag samples were taken just after the experiment, and were water-cooled to avoid phase transformation.

3. Results and Discussions

3.1. Oxidation Behavior of Both P and Cr in Cr-containing Fe–36%Ni Melt

Table 2 shows the chemical composition range of metal and slag samples which were taken just after the

Fig. 1. Schematic diagram of furnace.

Table 1. Experimental conditions.

Initial flux composition (mass%)	CaO 55		SiO ₂ 25		CaF ₂ 20	
Amount of flux (g/kg-metal)	40					
Initial metal composition (mass%)	C	Si	Mn	P	Cr	Ni
Cr-containing Fe-36%Ni melt	0.001	<0.1	<0.1	0.15	0.8	36.0
Fe-Ni melt	0.001	<0.1	<0.1	0.15	0	5.0-36.0
Amount of metal (kg)	30					
Treating time (min)	20					
Temperature of metal (K)	1823-1973					

Table 2. Chemical composition range of metal and slag samples taken just after the experiments following removal of both P and Cr in Cr-containing, Fe-36%Ni melt.

Heat No.	[Cr]	[P]	CaO	SiO ₂	CaF ₂	FeO	MgO	Cr ₂ O ₃	P ₂ O ₅	N _{FeCr₂O₄}	Temperature
	(mass%)		(mass%)							(-)	
CRP-1	0.21	0.025	45.3	14.3	17.1	13.4	4.3	3.1	4.0	0.013	1873K
CRP-2	0.23	0.018	44.1	15.2	16.5	12.3	4.8	2.7	4.1	0.012	
CRP-3	0.44	0.040	42.3	14.0	17.0	12.7	4.1	4.8	2.3	0.022	
CRP-4	0.63	0.053	45.5	15.1	17.4	9.2	4.0	5.8	2.2	0.026	
CRP-5	0.82	0.062	40.8	13.9	16.3	13.5	4.8	7.1	1.9	0.033	
CRP-6	0.91	0.078	43.2	14.4	16.0	12.4	4.3	8.0	1.4	0.037	
CRP-7	1.10	0.081	41.9	14.2	17.7	11.2	4.5	8.3	1.3	0.039	
CRPT1	0.43	0.053	45.4	15.6	16.4	11.5	3.8	4.6	2.0	0.022	1823K
CRPT2	0.44	0.017	43.1	15.0	15.8	12.8	4.0	4.1	3.2	0.021	1973K

experiments following removal of P and Cr. X-ray diffraction analysis of water-cooled slag samples just after the experiments, revealed strong peaks consistent with the presence of FeCr_2O_4 . NiCr_2O_4 was not observed in the present slag sample. Kanzaki *et al.*¹⁾ reported that the oxygen potential in the dephosphorization reaction of molten iron saturated with C and containing Cr depended upon the formation of CaCr_2O_4 . However, in the present slags, CaCr_2O_4 was observed merely as weak peak following X-ray diffraction analysis. Therefore, the oxygen potential in the dephosphorization reaction in the present system was taken to be controlled by the formation of FeCr_2O_4 as given by Eq. (2). The P-Cr equilibrium (Eq. (3)) has been derived from the reactions of P_2O_5 and FeCr_2O_4 as given by Eq. (1) and Eq. (2), respectively.

$$\Delta G^\circ(1) = -705422 + 556.5 \cdot T \quad (\text{J/mol})^{2)} \quad \dots\dots(1)$$

$$\Delta G^\circ(2) = -1022674 + 438.9 \cdot T \quad (\text{J/mol})^{3)} \quad \dots\dots(2)$$

$$\Delta G^\circ(3) = 572919 + 7.9 \cdot T \quad (\text{J/mol}) \quad \dots\dots(3)$$

Equation (4) can be derived from Eq. (3) by assuming the $a_{\text{FeCr}_2\text{O}_4} = 1$, i.e.

$$\log [\% \text{P}] = 1/2 \log a_{\text{P}_2\text{O}_5} - \log f_{\text{P}} + 5/4 \log a_{\text{Cr}} + 5/8 \log a_{\text{Fe}} + 14965/T + 0.205^{4)} \quad \dots\dots(4)$$

where $\log f_{\text{P}}$ is given by Eq. (5). In Eq (5), the value of e_{P}^{Ni} , 0.003, for liquid iron⁴⁾ and the value of e_{P}^{Cr} , -0.037, reported by Kanzaki *et al.*¹⁾ were used, because there is no data available in Fe-Ni alloy system.

$$\log f_{\text{P}} = 0.003 [\% \text{Ni}] - 0.037 [\% \text{Cr}] \quad \dots\dots(5)$$

And $\log a_{\text{Cr}}$ is assumed as Eq. (6), since the value of $e_{\text{Cr}}^{\text{P}} [\% \text{P}] + e_{\text{Cr}}^{\text{O}} [\% \text{O}] + e_{\text{Cr}}^{\text{Cr}} [\% \text{Cr}] + e_{\text{Cr}}^{\text{Ni}} [\% \text{Ni}]$ is negligibly small.

$$\log a_{\text{Cr}} = \log [\% \text{Cr}] \quad \dots\dots(6)$$

Moreover, the value of a_{Fe} , reported by Zellars *et al.*⁵⁾ was used.

Figure 2 indicates changes in measured contents of both P and Cr during oxidation refining at several temperatures, as compared with the values calculated from Eq. (4). The value of $a_{\text{P}_2\text{O}_5}$, which shows coin-

Fig. 2. Changes in both P and Cr contents during oxidation refining as compared with the P-Cr equilibrium in Cr-containing Fe-36%Ni melt.

cidence with the measured contents both P and Cr, was calculated from Eq. (4). As seen in Fig. 2, the removal of both P and Cr occurred along the P-Cr equilibrium (Eq. (4)). For reference, Fig. 2 also shows the values calculated from the P-Cr equilibrium¹⁾ controlled by CaCr_2O_4 formation. As can be seen, the temperature dependence of this reaction did not agree with that of the measured data, whereas that of Eq. (4) did.

3.2. Effect of Cr Content and Temperature on Removal of P in Cr-containing Fe-36%Ni Melt

Figure 3 shows the effect of Cr content on the phosphorus distribution ratio ($L_{\text{P}} = (\text{mass}\% \text{P})/[\text{mass}\% \text{P}]$). The measured L_{P} , at 1873 K, decreased with increasing Cr content in the metal. This behavior was investigated thermodynamically.

The value of L_{P} can be represented by Eq. (7) using the oxygen partial pressure, P_{O_2} , and the phosphate capacity of slag, $C_{\text{PO}_4^{3-}}$ ⁶⁾ as

$$\log L_{\text{P}} = -0.486 + \log C_{\text{PO}_4^{3-}} + \Delta G^\circ(8)/(19.144 \cdot T) + \log f_{\text{P}} + 5/4 \log P_{\text{O}_2}^{7)} \quad \dots\dots(7)$$

where P_{O_2} is obtained from Eq. (10) which is derived from Eqs. (2) and (9), and given in Eq. (11).

Fig. 3. Effect of Cr content in Fe-36%Ni melt on the phosphorus distribution ratio.

Fig. 4. Effect of temperature on the phosphorus distribution ratio.

$$1/2 P_2 = [P]$$

$$\Delta G^\circ(9) = -157851 + 5.39 \cdot T \quad (\text{J/mol})^8) \quad \dots\dots\dots(8)$$

$$1/2 O_2 = [O]$$

$$\Delta G^\circ(9) = -117152 - 2.89 \cdot T \quad (\text{J/mol})^9) \quad \dots\dots\dots(9)$$

$$\Delta G^\circ(10) = -1491282 + 427.35 \cdot T \quad (\text{J/mol}) \quad \dots\dots\dots(10)$$

$$\log P_{O_2} = 1/2(\Delta G^\circ(10)/19.144 \cdot T) - \log a_{\text{Cr}} - 1/2 \log a_{\text{Fe}} \quad \dots\dots\dots(11)$$

The value of L_P for each Cr content was calculated from Eq. (7) by using the values of $C_{\text{PO}_3^{3-}}$ in the system of $\text{CaO-SiO}_2\text{-FeO-P}_2\text{O}_5$.¹⁰⁾ This was done because there is little data for $C_{\text{PO}_3^{3-}}$ in the system employed in the present study. Figure 3 shows the comparison between the measured and calculated values of L_P . It also gives Cr_2O_3 contents of the slag. The calculated value of L_P shown by the solid line coincided with the measured values. This means that L_P was not significantly influenced by Cr_2O_3 content in the slag in the present experiment. Moreover, the decrease in L_P with increasing Cr content can be explained by the reduction of the oxygen partial pressure with increasing Cr content, because it has a slight influence shown by the dotted line in Fig. 3 to neglect e_P^{Cr} in $\log f_P$. For reference, the values of L_P in the range of the present Cr contents calculated from Eq. (7) using the values of $C_{\text{PO}_3^{3-}}$ in the system of $\text{CaO-CaF}_2\text{-SiO}_2$ ¹¹⁾ were of the order of 1000, which did not agree with that of the measured data.

Figure 4 shows the effect of temperature on L_P . The value of L_P increased with increasing temperature. The

temperature dependence of measured L_P coincided approximately with that of L_P calculated from Eq. (11) by using the value of $C_{\text{PO}_3^{3-}}$ and f_P assuming regular solution behavior.

3.3. On the Assumption of $a_{\text{FeCr}_2\text{O}_4} = 1$

In the above discussion, it was conveniently assumed that the activity of FeCr_2O_4 was unity. There are few phase diagrams on the same system as the present slag containing Cr oxide. Therefore, it is unknown whether or not the present slag melts were saturated with FeCr_2O_4 at 1873 K.

When $a_{\text{FeCr}_2\text{O}_4}$ is not unity, Eq. (7) becomes

$$\begin{aligned} \log L_P = & -0.486 + \log C_{\text{PO}_3^{3-}} + (\Delta G^\circ(8) + 5/8 \Delta G^\circ(10)) / \\ & (19.144 \cdot T) + \log f_P - 5/4 \log a_{\text{Cr}} - 5/8 \log a_{\text{Fe}} \\ & + 5/8 \log \gamma_{\text{FeCr}_2\text{O}_4} + 5/8 \log N_{\text{FeCr}_2\text{O}_4} \quad \dots\dots\dots(12) \end{aligned}$$

where $\gamma_{\text{FeCr}_2\text{O}_4}$ and $N_{\text{FeCr}_2\text{O}_4}$ are the activity coefficient relative to Raoult's Law and the molar fraction of FeCr_2O_4 , respectively. The value of $N_{\text{FeCr}_2\text{O}_4}$ was shown in Table 2. With the value of Fe_iO which was obtained by subtracting the Cr_2O_3 concentration from the Fe_iO concentration in the present slag, the Cr_2O_3 concentration, and the concentration of other compositions, the mole fraction of Cr_2O_3 was determined, and this value was taken as $N_{\text{FeCr}_2\text{O}_4}$. Assuming that the value of $\gamma_{\text{FeCr}_2\text{O}_4}$ is constant in the range of $N_{\text{FeCr}_2\text{O}_4}$ in the present slags, Eq. (13) can be derived from Eq. (12), the data in Table 2, as follows.

$$\begin{aligned} \log L'_P(\text{Cr} = 1.1\%) - \log L'_P(\text{Cr} = 0.2\%) \\ = \log L_P(\text{Cr} = 1.1\%) - \log L_P(\text{Cr} = 0.2\%) \\ + 5/8(\log N_{\text{FeCr}_2\text{O}_4}(\text{Cr} = 1.1\%) \\ - \log N_{\text{FeCr}_2\text{O}_4}(\text{Cr} = 0.2\%)) \quad \dots\dots\dots(13) \end{aligned}$$

where L'_P is $(\%P)/[\%P]$ when $a_{\text{FeCr}_2\text{O}_4}$ is not unity, and $L_P(\text{Cr} = i\%)$ and $N_{\text{FeCr}_2\text{O}_4}(\text{Cr} = i\%)$ are L_P and $N_{\text{FeCr}_2\text{O}_4}$, respectively, at $[\text{Cr}] = i$ mass%. According to Eq. (13), a difference of $\log L'_P$ is lowered only by about 0.3. Therefore, the conclusion in Sec. 3.2 may be slightly influenced in case that $a_{\text{FeCr}_2\text{O}_4}$ is not taken as unity. Moreover, similarly, the conclusion in Sec. 3.1 also may be only slightly influenced.

3.4. Effect of Ni Content on the Removal of P in Fe-Ni Melt

Table 3 shows the chemical composition range of metal and slag samples which were taken just after the experiments on removal of P in Fe-Ni melt. As shown in Fig. 5, the measured values of L_P increased with increasing Ni content. This may be explained thermodynamically as follows:

The oxygen potential is considered to be controlled by Eq. (14) in removal of P in a Cr free Fe-Ni melt, and is obtained from Eq. (14), since FeO was identified of X-ray diffraction analysis of water-cooled slag sample just after the experiments.

$$\Delta G^\circ(14) = -117809 + 49.87 \cdot T \quad (\text{J/mol})^9) \quad \dots\dots\dots(14)$$

The value of L_P for each Ni content was calculated from Eq. (15), which was derived from Eqs. (7), (8), (9) and (14).

Table 3. Chemical composition range of metal and slag samples taken just after the experiments following removal of P in Fe-Ni melt. (mass%)

Heat No.	[Ni]	[P]	[Cr]	CaO	SiO ₂	CaF ₂	FeO	MgO	P ₂ O ₅	Temperature
Ni-1	5.1	0.013	<0.01	43.5	14.3	16.1	16.1	4.0	3.7	1873K
Ni-2	9.8	0.012	<0.01	42.5	14.3	17.3	16.8	3.9	4.1	
Ni-3	20.2	0.009	<0.01	41.8	13.5	17.0	18.4	4.4	2.8	
Ni-4	29.8	0.008	<0.01	44.1	14.1	16.5	17.3	4.0	3.0	
Ni-5	36.1	0.008	<0.01	43.7	14.9	16.8	16.0	4.5	3.3

Fig. 5. Effect of Ni content in the Fe-Ni melt on the phosphorus distribution ratio.

$$\log L_P = \log C_{PO_4^{3-}} + \log f_P - 5/2 \log a_{Fe} + 5/2 \log a_{FeO} - 38976/T + 5.94 \quad (15)$$

where $\log f_P$ is given by Eq. (5) at $[\%Cr]=0$. In this expression, the value of a_{FeO} was calculated at each slag composition in the present experiments from the iso-activity diagram of FeO in the system of CaO-SiO₂-FeO.¹²⁾ In addition, the values of $C_{PO_4^{3-}}$ and a_{Fe} were calculated in the same way as mentioned above. The comparison between the measured and calculated values of L_P is shown in Fig. 5.

The calculated L_P coincided approximately with the measured ones. The calculated values of a_{FeO} and $C_{PO_4^{3-}}$ were almost constant through the experiments, because $(\%CaO)$, $(\%SiO_2)$ and $(\%FeO)$ in the slag were nearly constant. The values of a_{Fe} and f_P are changed with increasing Ni content. However, the change in a_{Fe} with increasing Ni content is about four times greater than that in f_P . Therefore, the increase in L_P with increasing Ni content is considered to be due to the increase in the oxygen partial pressure with decreasing a_{Fe} mainly.

4. Conclusions

Attempts have been made to clarify the characteristics of removal of both P and Cr in Cr-containing Fe-36%Ni melt. The oxygen potential of the dephosphorization reaction was taken to be controlled by the formation of FeCr₂O₄. Removal of both P and Cr occurred along the P-Cr equilibrium controlled by FeCr₂O₄ formation,

and high temperature treatment was effective in lowering P content in the range of the present Cr contents.

The phosphorus distribution ratio (L_P) decreased with increasing Cr content in the metal. This reason was considered to be that the oxygen partial pressure in the reaction was lowered by increasing the content of Cr. Moreover, L_P increased with increasing Ni content in the metal. This is believed to occur because the increase in the oxygen partial pressure with increasing Ni content mainly.

Nomenclature

- T : temperature (K)
 a_i : activity of component i in a liquid alloy with respect to an infinite dilute of one mass percent standard state
 f_i : activity coefficient of component i in a liquid alloy with respect to an infinite dilute of one mass percent standard state
 γ_i : activity coefficient of component i relative to Raoult's Law
 N_i : molar fraction of component i
 e_i^j : interaction parameter between component i and j
 $C_{PO_4^{3-}}$: phosphate capacity of slag
 P_{O_2} : partial pressure of gas O₂

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