Effect of Silicon and Carbon on the Evaporation Rate of Copper in Molten Iron

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In order to increase the evaporation rate of copper in molten iron, the addition of silicon or carbon, which has a strong affinity with the solvent metal, iron, is considered to be effective, because the activity coefficient of copper can be expected to increase. Accordingly, the effects of silicon and carbon on the evaporation rate of copper in molten iron have been investigated. It is found that the rate constant of copper evaporation has a maximum value at the silicon content of about 3 mass%. The apparent rate constant at 3 mass% Si is about 1.4 times larger than that for Fe–Cu alloy. The apparent rate constant of copper evaporation for Fe–C–Cu alloy monotonically increases with increasing the carbon content. The rate constant at 2 mass% C is about 1.7 times larger than that for Fe–Cu alloy. At a practical reduced-pressure of 133 Pa, the rate constant of copper evaporation which is large enough to be equivalent to that in the case of the chemical reaction rate-limiting for Fe–Cu alloy was attained in the present study.

KEY WORDS: copper removal; evaporation; ferrous scrap; tramp element; steel.

1. Introduction

Most of ferrous scraps include tramp elements, such as Cu and Sn, which cause adverse effects on the mechanical properties of steel products, if their contents exceed certain levels. Although the recycling of the iron scraps is desirable to be repeated continuously, the contents of the tramp elements in the iron scraps certainly continue to increase, which will prevent the continuous recycling by a dilution method. On the other hand, the removal techniques of these elements from molten steel are not necessarily established, and the removal of the tramp elements is one of the most important problems in recycling the iron scraps. The vaporization processes are considered to be suitable for the efficient removal of Cu from ferrous alloys, and many studies have been conducted on the vaporization of Cu from iron melts. However, the evaporation rate of copper is generally limited by the gaseous mass transfer at the practical chamber pressure over 133 Pa, and the special techniques are required in order to attain the sufficiently large reaction rate.

In order to promote the vaporization, the addition of silicon or carbon, which has a strong affinity with the solvent metal, iron, is considered to be effective, because the activity coefficient of Cu can be expected to increase. Two studies were reported previously on the effect of silicon on the vaporization rate of Cu in molten iron. However, those results are not much in accord with each other, and the effect of Si on the vaporization rate of Cu shows different dependences on the silicon content between the two studies. In our previous study, the effect of silicon on the evaporation rate of Cu was examined from the activity coefficient of copper estimated from the thermodynamic data, and the validity of the two studies was discussed. It is concluded that the evaporation rate constant of Cu takes a maximum value at the specified Si content. However, the suitable Si content for the copper evaporation has not sufficiently been clarified. In the present study, the effects of silicon and carbon on the evaporation rate of copper in molten iron are investigated in order to know the silicon and carbon contents, at which the evaporation rate of copper is maximized.

2. Estimation of the Evaporation Rate of Copper in Fe–Si or Fe–C alloy

The reaction for the copper evaporation is expressed as follows:

\[ \text{Cu (mass\%, in Fe)} = \text{Cu (g)} \]

In the present work, the reaction is assumed to be controlled by both the gaseous mass transfer and the chemical reaction at the gas/metal interface. The profile of the activity or the partial pressure of Cu at the gas/metal interface is schematically shown in Fig. 1. The mass transfer rate of copper in the gaseous phase and the chemical reaction rate
At the gas/metal interface are represented by Eqs. (2) and (3), respectively.

\[
\frac{dn_{Cu}}{dt} = k_{Cu} \cdot A \cdot \frac{1}{RT} (P_{Cu,i} - P_{Cu})
\]  

(2)

\[
\frac{dn_{Cu}}{dt} = k_{Cu} \cdot A \cdot \frac{\rho_i}{M_{Cu}} (a_{Cu,i} - \frac{P_{Cu,i}}{K_{i1}})
\]  

(3)

On the basis of the mixed rate-limiting of them, the following equations can be obtained:

\[
\frac{dn_{Cu}}{dt} = k \cdot A \cdot \frac{P_i}{100M_{Cu}} \cdot 100 \frac{\gamma_{Cu} X_{Cu,i} - P_{Cu}}{K_{i1}}
\]  

(4)

\[
\frac{d[mass\%Cu]}{dt} = -k \cdot A \cdot V \frac{1}{100} \frac{\gamma_{Cu} X_{Cu}}{X_{Cu,0} - P_{Cu}} = 0
\]  

(5)

where

\[
k = \left( \frac{1}{k_{Cu}} + \frac{\rho_i RT}{M_{Cu} K_{i1}} \right) \frac{1}{k_{Cu,0}}
\]  

(6)

Accordingly, the apparent rate constant of copper evaporation, \(k_{Cu,0}\), defined by Eq. (6), is derived by Eq. (7).

\[
\frac{d[mass\%Cu]}{dt} = -k_{Cu,0} \frac{A}{V} (mass\%Cu)
\]  

(7)

where \(A\) denotes the reaction area (m²), \(a_{Cu,i}\) the copper activity relative to the pure liquid at the gas/metal interface, \(K_{i1}\) the equilibrium constant for Eq. (1), \(k_{Cu}\) the chemical reaction rate constant (m/s), \(k_{Cu,0}\) the mass transfer coefficient of copper in the gaseous phase (m/s), \(n_{Cu}\) the mole number (mol), \(P_{Cu}\) and \(P_{Cu,i}\) the vapor pressures of Cu in the bulk metal and at the interface (Pa), respectively, \(R\) the gas constant (8.314 J/(mol·K)), \(T\) the temperature (K), \(t\) the time (s), \(V\) the metal volume (m³), \(\gamma_{Cu}\) the activity coefficient of Cu in the alloy and \(\rho_i\) the density of the alloy (kg/m³). From Eq. (7), the apparent rate constant of copper evaporation, \(k_{Cu,0}\), is first order with respect to the activity coefficient of copper in molten iron, \(\gamma_{Cu}\), at the constant temperature and pressure \((k=\text{const})\), and \(k_{Cu,0}\) changes linearly as a function of \(\gamma_{Cu}\). In our previous study, \(9\) the activity coefficient of copper in Fe–Si–Cu alloy, \(\gamma_{Cu,Fe-Si-Cu}\), was estimated from the activity coefficients of Cu in Fe–Cu and Si–Cu binary alloys by the regular-solution model in a ternary system \(12,13\) as follows:

\[
\ln \gamma_{Cu,Fe-Si-Cu} = \ln \gamma_{Cu,Fe-Cu} \frac{X_{Fe}}{X_{Fe} + X_{Si}} - \ln \gamma_{Cu,Si-Cu} \frac{X_{Si}}{X_{Fe} + X_{Si}} \frac{\Delta H_m^{Fe-Si}}{RT}
\]  

(8)

where \(\Delta H_m^{Fe-Si}\) denotes the enthalpy change of mixing for Fe–Si alloy (J/mol), \(X_i\) the mole fraction of component \(i\), and \(\gamma_{Cu,Fe-Cu}\) and \(\gamma_{Cu,Si-Cu}\) the activity coefficients of Cu in molten iron and in molten silicon, respectively. The estimation of \(\gamma_{Cu,Fe-Si-Cu}\) is also conducted using the FactSage thermochemical software and databases. \(16\) The activity coefficient of copper in Fe–C–Cu alloy is calculated by the following equation:

\[
\ln \gamma_{Cu,Fe-C-Cu} = \ln \gamma_{Cu,Fe-Cu} + \frac{\Delta H_m^{Fe-C}}{RT}
\]  

(9)

(at the dilute solution)

where \(\Delta H_m^{Fe-C}\) denotes the interaction coefficient of Fe for Cu. \(17\) The relationship between \(\gamma_{Cu,Fe-M-Cu}/\gamma_{Cu,Fe-Cu}\) and the M (=Si or C) content at 1 873 K is shown in Fig. 2. Koros et al. \(15\) measured the activity coefficient of copper in Fe–C–Cu alloy at 1 873 K, and the results are also shown in Fig. 2(b). Although Eq. (9) is generally applicable only to the dilute solution, the activity coefficient of copper in Fe–C–Cu alloy by Koros et al. is in reasonable agreement with Eq. (9), which shows that the extrapolation of Eq. (9) to the higher carbon content is valid. It is also found that the rate
3. Experimental

The high purity electrolytic iron (mass ppm O/15–20) and Si (purity 99.9999%) were inserted in an alumina crucible (38-mm o.d., 45-mm height and 30-cm³ volume) and were inductively heated up to 1 873 K in Ar–H₂ atmosphere. Then, copper (purity 99.0%) was added, and the content was adjusted to about 0.6 mass%. After holding about 5 min, the sample was cooled rapidly, and the Fe–0–20mass%Si–0.6mass%Cu alloys were prepared. Similarly, the Fe–0–4mass%C–0.6mass%Cu alloys were made by adding carbon and copper after the electrolytic iron was inductively heated and was melted at 1 873 K. The preliminary prepared Fe–Si–Cu or Fe–C–Cu alloy weighing about 60 g was put in the alumina crucible and was inductively heated to 1 923 or 1 973 (±5) K. After reaching the experimental temperature, the chamber pressure was adjusted to a fixed value ranging from 133 to 10⁵ Pa, and the hydrogen gas (purity 99.9999%) was blown onto the surface of the metal at a fixed flow rate of 0.1 to 1 L/min (s.t.p.). After holding for a fixed time, the sample was quickly cooled, and 1 to 2 g of the sample was taken for chemical analysis. The similar procedure was repeatedly carried out using the remaining sample, and the variations of Si, C and Cu contents of metal with time were investigated. The copper and silicon contents of metal were analyzed by the inductively coupled plasma (ICP) emission spectrometry. The carbon content was analyzed by the combustion method using a carbon analyzer. The experimental conditions are summarized in Table 1.

4. Results

4.1. Evaporation of Copper from Molten Fe–Si–Cu or Fe–C–Cu Alloy

The variations of Si and Cu contents of Fe–Si–Cu alloy or C and Cu contents of Fe–C–Cu alloy with time are shown in Figs. 3 and 4, respectively, under the chamber pressure of 133 Pa at 1 923 K. In the present study, assuming that the evaporation rate of copper in molten iron is a first order with respect to the copper content of the alloys, the apparent rate constant of the copper evaporation, \( k_{Cu} \), is determined on the basis of Eq. (10), which is derived from the integration of Eq. (6).

\[
\ln\left(\frac{[\text{mass%Cu}]}{[\text{mass%Cu}_0]}\right) = -k_{Cu} \left(\frac{A}{V} t\right) \quad \text{………………(10)}
\]

where [mass%Cu]₀ denotes the initial copper content of metal.

4.2. Effect of Silicon on the Evaporation Rate of Copper

The dependence of the apparent evaporation rate con-
stant of copper in Fe–Si–Cu alloy on the initial silicon content, [mass%Si]₀, is shown in Fig. 5. At the other chamber pressures except for 10⁴ Pa (Fig. 5(b)), the largest evaporation rate constant of copper is attained when the initial silicon content is about 3 mass%, and the maximum rate constant is about 1.4 times as large as that for Fe–Cu alloy. On the other hand, under the chamber pressure of 10⁴ Pa, the evaporation rate constant of copper takes a maximum value at the silicon content of about 10 mass%. At this time, the evaporation rate constant is about twice as large as that for Fe–Cu alloy, and the promoting effect of copper evaporation by the addition of silicon is the largest in comparison with those at the other chamber pressures.

4.3. Effect of Carbon on the Evaporation Rate of Copper

The dependence of the apparent evaporation rate constant of copper in Fe–C–Cu alloy on the carbon content is shown in Fig. 6. It is found that the evaporation rate of copper increases with increasing the carbon content, regardless of the variation of the chamber pressure. The apparent rate constant of the copper evaporation, \( k_{Cu} \), is about 1.7 times as large as that for Fe–Cu alloy at 2 mass% C. It can be said that the promoting effect of copper evaporation by the carbon addition is larger than that by the silicon addition from the present results.

5. Discussion

5.1. Effect of Silicon on the Evaporation Rate of Copper

The variation of the silicon content of Fe–Si–Cu alloy with time is shown in Fig. 7 under the chamber pressure of 10⁴ Pa at 1973 K.
tents did not change with time at the other chamber pressures (see an example at 133 Pa shown in Fig. 3). For this reason, in Fig. 5, the result at the chamber pressure of 10^4 Pa is considered to be different from the results at the other chamber pressures. In the present study, the experiments were conducted in the reduced atmosphere by introducing hydrogen, and the progress of desiliconization by the oxidation reaction can be hardly considered. The possibility is examined on the desiliconization by the formation of SiH$_4$, written as

$$\text{Si}(l) + 2\text{H}_2(g) \rightleftharpoons \text{SiH}_4(g)$$ ..............(11)

The standard Gibbs energy for Eq. (11) at 1 973 K is given by

$$\Delta G^{\circ}_{11} = -227 \text{kJ/mol} \quad \text{(at 1 973 K)} ..............(12)$$

Here, the activity of silicon in Fe–5mass%Si alloy is estimated to be $a_{\text{Si}} = 1.06 \times 10^{-3}$, relative to the pure liquid. The equilibrium partial pressure of SiH$_4$ is calculated under the conditions of 1 973 K and $P_{\text{H}_2} = 1.013 \times 10^5$ Pa. The partial pressure of SiH$_4$, $P_{\text{SiH}_4}$, is derived to be $1.1 \times 10^{-9}$ Pa. This value corresponds to about $7 \times 10^{-10}$ times as large as the vapor pressure of copper in Fe–0.5mass%Cu alloy, 16 Pa, and it can be thermodynamically concluded that the formation of SiH$_4$ is not the main cause of the progress of the desiliconization. Only at the chamber pressure of $10^4$ Pa, the formation of a compound, which seemed to be SiO$_2$, was observed at the internal wall of the crucible and the tips of the gas inlet tube after the experiments, which implies the possibility of the progress of the desiliconization by

$$\text{Si} \left(\text{mass\%}, \text{in Fe–Si alloy} \right) + \Omega \left(\text{mass\%}, \text{in Fe–Si alloy} \right) \rightleftharpoons \text{SiO}_2(g)$$ ..............(13)

It may be expected that the consumed oxygen in the desiliconization reaction was supplied by the H$_2$ reduction of Al$_2$O$_3$, which was used as the crucible and the gas inlet tube. However, the reason has not been clarified enough that the desiliconization proceeds only at the specified chamber pressure of $10^4$ Pa. As well as the case by Matsuo et al., the copper removal was promoted by increasing the reaction area in combination with the decarburization, it can be expected that the evaporation rate of Cu increases by the turbulence of the gas/metal interface, which is caused by the formation of SiO gas. Under the chamber pressure of $10^4$ Pa at 1 973 K, the dependence of the apparent evaporation rate constant of copper on the initial and final silicon contents in the present study is shown in Fig. 8. The desiliconization proceeds fastest in the experiment plotted by the triangle in Fig. 8, and the silicon content decreased to about 3 mass%, at which the evaporation rate of Cu was confirmed to be maximized at the other chamber pressures. For this reason, namely by the combination effects of the silicon addition and the desiliconization, the promotion of Cu evaporation is considered to become largest in comparison with that at the other chamber pressures. At the other chamber pressures except for $10^4$ Pa, the evaporation rate of copper becomes smaller than that for Fe–Cu alloy when the silicon content exceeds about 7 to 10 mass%. On the other hand, at the chamber pressure of $10^4$ Pa, the promoting effect of copper evaporation by the addition of silicon was appeared over the whole silicon composition range in the present study. From this viewpoint, the desiliconization is also considered to contribute to the promotion of the copper evaporation, in addition to the effect of the silicon addition. The effect of Si on the evaporation rate of Cu, which was examined by Morales et al. and by Esimai based on a levitation technique, and is shown in Fig. 9. From the result by Morales et al., the optimum Si content exists, at which the evaporation rate of Cu is maximized. On the other hand, from the result by Esimai, it is found that the evaporation rate monotonically increases with the increase of the silicon content. The effect of silicon on the evaporation rate of copper was thermodynamically discussed in our previous study, and the result by Morales et al. was concluded to be more valid than those by Esimai. The present experimental results also show the same qualitative tendency as the result by Morales et al. and by the thermodynamic evaluation. From the present study, it is found that the silicon content, at which the evaporation rate constant of copper takes a maximum value, is about 3 mass%.

5.2. Effect of Carbon on the Evaporation Rate of Copper

Morales et al. also investigated the effect of carbon on the evaporation rate of copper in Fe–Cu alloy by the levitation technique. From the result by Morales et al. in Fig. 6, the apparent evaporation rate constant of copper linearly

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**Fig. 8.** Dependence of the apparent evaporation rate constant of copper on the initial and final silicon contents in the present study under the chamber pressure of $10^4$ Pa at 1 973 K.

**Fig. 9.** Effect of silicon on the apparent evaporation rate constant of copper reported by Morales et al. and by Esimai.
The value for $e_{Cu}$ of the copper evaporation in Fe–Cu alloy was estimated by Morales et al. In the present study, the value is also estimated by a similar method. The following equation can be derived from Eqs. (7) and (9).

$$k_{Cu} = C \cdot e^{e_{Cu} \cdot X_C} \quad (C=\text{const.}) \quad (14)$$

The value for $e_{Cu}$ was determined by fitting the experimental results to Eq. (14) and is shown in Table 2. The values for $e_{Cu}$ in Table 2 are positive, which reasonably agrees with the fact that the solubility of carbon in molten copper is much smaller than that in molten iron. Moreover, the following relationship is derived from Eq. (7):

$$\frac{\gamma_{Cu(Fe-Cu)}}{\gamma_{Cu(Fe-Cu)}} = k_{Cu(Fe-Cu)} \quad \frac{k_{Cu(Fe-Cu)}}{k_{Cu(Fe-Cu)}} \quad (15)$$

where $k_{Cu(Fe-Cu)}$ and $k_{Cu(Fe-Cu)}$ denote the apparent rate constants of the copper evaporation in Fe-Cu alloy and in Fe-C–Cu alloy, respectively. Using Eq. (15), the relationship between $\gamma_{Cu(Fe-Cu)}/\gamma_{Cu(Fe-Cu)}$ and the carbon content is shown in Fig. 10 from the present experimental results and the previous ones by Morales et al.5) The experimental values reasonably agree with Eq. (9), which shows that the evaporation rate of copper in molten iron is affected by the activity coefficient of copper.

5.3. Effect of the Chamber Pressure on the Evaporation Rate of Copper

The dependence of the chamber pressure on the apparent evaporation rate constant of copper is shown in Fig. 11. The minimum value at each error bar, which represents the range of the present results, shows the $k_{Cu}$ value for Fe–Cu alloy. The maximum value shows the largest evaporation rate constant of copper at each chamber pressure attained by the addition of Si or C in the present study. It is found that the evaporation rate of copper from molten ferrous alloys is affected by the chamber pressure under the present experimental conditions, which implies the influence of the gas phase mass transfer. Savov et al.4) also reported that the copper evaporation is greatly influenced by the chamber pressure and is not much affected by the liquid phase mass transfer under the chamber pressure of 10 to 10^5 Pa. Accordingly, the assumption that the evaporation rate of copper in molten iron is not controlled by the liquid phase mass transfer is considered to be valid. The result by Matsuo,3) which is shown by a closed square in Fig. 11, shows the apparent rate constant of copper removal when the copper evaporation is promoted by the decarbonization using the weak oxidizing agents, such as SiO$_2$ and MgO. The other results show the apparent evaporation rate constant of copper in Fe–Cu alloy. The apparent rate constant of copper evaporation obtained in the present study is larger at each chamber pressure, irrespective as to whether the silicon (or carbon) addition or not, than the value in the previous studies. Although the cause cannot be specified clearly, the ingoing hydrogen gas may promote the copper evaporation by removing the surface active element, oxygen, at the metal surface, or by facilitating the gaseous diffusion of copper for the smaller atomic size of hydrogen. Moreover, the possibility is also considered that the copper can be removed in the form of some hydride compounds. At the practical reduced-pressure of 133 Pa, the present results are larger than the result by Matsuo, in which the copper removal was promoted by the decarbonization using the weak oxidizing agents. The apparent evaporation rate constants of copper obtained in the present study are about 2.4 to 3.5 times larger than the previous ones, and only a little smaller than those at the chamber pressure under 10 Pa for Fe–Cu alloy. That is, the evaporation rate of copper, which is large enough to be equivalent to that in the case of the chemical reaction rate-limiting for Fe–Cu alloy, was attained at the practical reduced-pressure of 133 Pa in the present study.

Table 2. The estimated values for the interaction coefficient of carbon for copper in liquid iron.

| Temperature (K) | $e_{Cu}$ | Morales et al. | The recommended value by JSPS (1) |
|----------------|----------|----------------|----------------------------------|
| 1973           | 3.28     | 2.92           | 5.40                             |
| 2073           | 4.06     | 2.92           | 5.40                             |

Fig. 10. Relationship between $\gamma_{Cu(Fe-Cu)}/\gamma_{Cu(Fe-Cu)}$ and the carbon content.

Fig. 11. Dependence of the chamber pressure on the apparent evaporation rate constant of copper.
6. Conclusions

The effects of silicon and carbon on the evaporation removal of copper in molten iron have been investigated. The following conclusions are obtained:

1) The silicon content at which the rate constant of copper evaporation is maximized is about 3 mass%. The silicon content, 3 mass%, is smaller than that estimated from the thermodynamic calculation. The apparent rate constant at 3 mass% Si is about 1.4 times as large as that for Fe–Cu alloy.

2) The apparent rate constant of copper evaporation for Fe–C–Cu alloy smoothly increases with increasing the carbon content. The rate constant at 2 mass% C is about 1.7 times larger than that for Fe–Cu alloy.

3) At the practical reduced-pressure of 133 Pa, the rate constant of copper evaporation which is large enough to be equivalent to that in the case of the chemical reaction rate-limiting for Fe–Cu alloy was attained in the present study.

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REFERENCES

1) T. Matsuo, K. Maya, T. Nishi, K. Shinme, A. Ueno and S. Anezaki: ISIJ Int., 36 (1996), Supplement, S62.

2) T. Nishi, S. Fukagawa, K. Shinme and T. Matsuo: ISIJ Int., 39 (1999), 905.

3) T. Matsuo: Tetsu-to-Hagané, 86 (2000), 741.

4) K. Ono, E. Ichise, R. O. Suzuki and T. Hidani: Steel Res., 65 (1995), 372.

5) T. Hidani, K. Takemura, R. O. Suzuki and K. Ono: Tetsu-to-Hagané, 82 (1996), 135.

6) R. D. Morales and N. Sanoe: Ironmaking Steelmaking, 9 (1982), 64.

7) C. N. Estimai: Scand. J. Metall., 16 (1987), 267.

8) L. Savov and D. Janke: ISIJ Int., 40 (2000), 95.

9) H. Ono-Nakazato, K. Taguchi and T. Usui: ISIJ Int., 43 (2003), No. 7, 1105.

10) JANAF Thermochemical Tables, 3rd ed., eds. by M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frup, R. A. McDonald and A. N. Syverud: J Phys. Chem. Ref. Data, 14 (1985), Suppl. No. 2, 971, 973.

11) Handbook of Physico-chemical Properties at High Temperature, ed. by Y. Kawai and Y. Shiraishi, ISIJ, Tokyo, (1988), 13, 49.

12) F. D. Richardson: Physical Chemistry of Melts in Metallurgy, 1st ed., Part I, Pergamon Press, London, (1974), 143.

13) H. Ono-Nakazato, D. Hirai and T. Usui: J. High Temp. Soc., 26 (2000), 139.

14) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelly and D. D. Wagman: Selected Values of the Thermodynamic Properties of Binary Alloys, ASM, Metals Park, Ohio, (1973), 479, 671.

15) V. S. Sudavtsova and V. K. Kudom: Inorganic Mater., 37 (2001), 319.

16) C. W. Bale, P. Chartrand, S. A. Degterov, G. Eriksson, K. Hack, R. Ben Mahfoud, J. Melaniecon, A. D. Pelton and S. Petersen: Calphad, 26 (2002), 189.

17) The 19th Committee on Steelmaking: Steelmaking Data Sourcebook, The Japan Soc. for the Promotion of Science, Gordon and Breach Science Publishers, New York, (1988), 283.

18) P. J. Koros and J. Chipman: J. Met., 8 (1956), 1102.

19) I. Barin and O. Knacke: Thermochemical properties of inorganic substances, Springer-Verlag, Berlin, (1973), 679.

20) Y. Nakajima, T. Okimura and J. Hirama: The Report of Committee on Separation of Circulative Elements, ISIJ, Tokyo, (1993).

21) N. Tokumitsu and H. Hirata: CAMP-ISIJ, 3 (1990), 1184.