Influence of Copper on Decarburization Kinetics of Stainless Steel Melt at High Temperatures

Hoon Dong SHIN, Dong Joon MIN1) and Hyo Seok SONG2)

Formerly Graduate Student at Yonsei University, now at Tech-I. Ltd., Yokohama 225-0002 Japan. 1) Department of Metallurgical System Engineering, Yonsei University, Seoul 120-749, Korea. 2) Stainless Steel Research Group, Technical Research Laboratory, POSCO, Pohang 790-785, Korea. E-mail: chemical@yonsei.ac.kr

(Received on February 18, 2002; accepted in final form on April 29, 2002)

A kinetic study on the decarburization reaction of the Fe–Cr–Cu–C melts has been carried out at 1 873 K focusing on the effect of copper on the reaction rates. The decarburization rate of the Fe–C melt was preliminarily measured at 1 873 K. The result of the present work exhibits a good agreement with other studies. The addition of chromium to the Fe–C melt decreases the interfacial reaction rate. It is considered that the effect of copper on a retard of the reaction rate would have a relationship to the surface adsorption of chromium. The addition of copper to the Fe–Cr–C melt decreases the decarburization reaction rate. The delay of the interfacial reaction by copper at high concentrations of carbon could be responsible for the decrease in the overall reaction rate. The effect of copper on the reaction rate could be quantified by the following equation:

\[
\frac{k_{Fe-Cu}}{k_{FeCr}} = \frac{1}{1+0.09(\text{wt}\% \text{Cr})}
\]

From the results of the dependence of the interfacial rates on temperature for each alloy, it could be proposed that the presence of chromium on the reaction surface in the Fe–Cr–C melt would delay the reaction rate, which was originated from the additional reaction steps. However, it is suggested that copper would delay the decarburization rate by blocking a part of the reaction sites in the Fe–Cr–Cu–C melt.

KEY WORDS: decarburization; stainless steel; copper; (interfacial) reaction rate; reaction sites.

1. Introduction

Stainless steel is one of the most important materials and dominantly features corrosion resistance. Recently, it has been found that stainless steel containing copper would exhibit good corrosion resistance, formability, and an antibiotic property.1) However, it has been observed that the decarburization rate of stainless steel melt containing copper would be delayed in an AOD process.

Therefore, in the present study, the theoretical and experimental trials have been conducted to understand which is responsible for the delay of decarburization process: thermodynamics or kinetics. In view of thermodynamics, the interaction between carbon and other elements would be expected to affect the limit of decarburization from the melt. The overall reaction of decarburization can be expressed as follows2,3):

\[
\text{CO}_2(g) + [C] = 2\text{CO}(g), \quad \log K_{(1)} = -\frac{7560}{T} + 6.77 \quad (1)
\]

where \(K_{(1)}\) is the equilibrium constant of the reaction. The effect of alloying elements on the activity coefficient of carbon (\(\gamma_C\)) in molten steel at 1 873 K is given by Eq. (2).2,3)

\[
\log \gamma_C = -0.36 + 6.9X_C - 5.1X_{Cr} + 4.1X_{Cu} \quad (2)
\]

where \(X_i\) is the mole fraction of \(i\) in molten steel. From Eqs. (1) and (2), the limit of decarburization could be calculated as a function of the contents of chromium and copper (Fig. 1). Because the interaction coefficient between chromium and carbon (\(e_{Cr}^{C}\)) is negative, it is expected that the addition of chromium would retard the decarburization reaction in thermodynamic view.

On the other hand, the interaction coefficient between copper and carbon (\(e_{Cu}^{C}\)) is positive; thus, the decarburization reaction should be enhanced by addition of copper in view of thermodynamics. However, it has been observed that the reaction rate would be delayed by addition of copper in an actual decarburization operation. Consequently, the kinetic aspects rather than thermodynamics should be taken into account to explain the effect of copper on the decarburization reaction.

Sain and Belton reported that the rate of decarburization of Fe–C melt was first-order with respect to the partial pressure of CO₂ at high carbon content and proposed that the dissociative chemisorption of CO₂ could be a rate-determining step of the decarburization reaction.4,5) These con-
Conclusions were supported by the isotope exchange experiments by Cramb and Belton.6) Fruehan et al. investigated the effects of sulfur, tin, phosphorus, lead, chromium, and nickel on the rate constant of CO₂ dissociation on liquid iron. 7,8) They showed that neither chromium nor nickel had a strong effect on the kinetics of CO₂ dissociation on the melt surface, while the sulfur significantly decreased the reaction rate. However, the effect of copper on the decarburization of stainless steel melt has never been reported yet.

Therefore, the aim of the present study is to find out how copper affects the rate of decarburization of the Fe–Cr–Cu–C melts.

2. Theoretical Considerations

The overall chemical reaction for the decarburization of iron melt can be given as Eq. (1). The CO₂ may react with carbon dissolved in liquid iron by the following elementary reaction steps:

\[ \text{CO}_2(g) = \text{CO}_2(ad) \] (3)

\[ \text{CO}_2(ad) = \text{CO}(ad) + \text{O}(ad) \] (4)

\[ \text{C}(ad) + \text{O}(ad) = \text{CO}(ad) \] (5)

\[ 2\text{CO}(ad) = 2\text{CO}(g) \] (6)

where (ad) indicates the species adsorbed on the surface.

It has generally been accepted that the dissociation of CO₂ (Eq. (4)) was the rate-determining step (RDS) in the overall mechanism of decarburization. The dissociation rate of CO₂ can thus be written as follows:

\[ \frac{dn_{\text{CO}_2}}{dt} = k(p_{\text{CO}_2} - p^E_{\text{CO}_2}) \] (7)

where \( n_{\text{CO}_2} \), \( k \), and \( p^E_{\text{CO}_2} \) is, respectively, the number of moles CO₂ per unit area, the forward rate constant (mol/cm²·s·atm), and the equilibrium partial pressure of CO₂. The value of \( p^E_{\text{CO}_2} \) is negligible compared to \( p_{\text{CO}_2} \) under present experimental conditions.

According to Langmuir adsorption isotherm, the surface coverage can be defined as a monolayer of sites having two parts: the fraction of sites covered by species \( i \), \( \theta_i \), and the fraction of vacant sites, \( 1 - \Sigma \theta_i \). The effect of surface-active species on the chemical rate constant can be expressed by Eq. (8).

\[ k = k_r \left(1 - \Sigma \theta_i \right) \] (8)

where \( k \) is the rate constant and \( k_r \) is the rate constant for a pure metal without surface-active elements. Rewriting Eq. (7) gives

\[ \frac{dn_{\text{CO}_2}}{dt} = k_r \left(1 - \Sigma \theta_i \right)(p_{\text{CO}_2} - p^E_{\text{CO}_2}) \] (9)

The relationship between surface coverage and the activity of adsorbed solutes can be given by

\[ \left(1 - \Sigma \theta_i \right) = \frac{1}{1 + \sum K_i \cdot a_i} \] (10)

where \( K_i \) and \( a_i \) are the equilibrium adsorption coefficient and the activity of an adsorbed solute \( i \), respectively. Therefore, the rate constant is given by Eq. (11).

\[ k = \frac{k_r}{1 + \sum K_i \cdot a_i} \] (11)

Hence, the rate constant would be decreased by the adsorbed solutes. On the other hand, Sain and Belton concluded that the reaction rate approached a constant value referred to the residual rate \( (k_r) \) at very high concentrations of sulfur.5) Thus, Eq. (11) could be rearranged as follows to take the residual rate into account:

\[ \frac{1}{k_a} = \frac{1}{k} + \frac{RT}{m} \] (13)

where \( k_a \) and \( m \) are, respectively, the apparent rate constant and the mass transfer coefficient. The mass transfer coefficient determined by the lance, crucible, and gas-jet geometry can be known by combining the empirical correlation for a fluid jet impinging on a reaction surface.4,10,11) Saito et al. proposed the following correlation between the mass transfer coefficient and experimental conditions11):

\[ \frac{1}{k_a} = \frac{1}{k} + \frac{RT}{m} \] (13)
where \( \text{Sh}, \text{Re}, \text{Sc}, r \) and \( d \) are, respectively, the Sherwood number, Reynolds number, and Schmidt number, and the radius of crucible and the diameter of lance.

In the present study, the mass transfer coefficient was obtained by employing Eq. (14). Then, the chemical rate constant could be calculated from the apparent rate constant and Eq. (13).

3. Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 2. A high frequency induction furnace was used. The reaction chamber was enclosed in a quartz tube with sealed brass end-caps. An R-type (Pt–Pt/13 Rh) thermocouple was inserted into a hole drilled through the bottom of the graphite holder to contact the bottom of the alumina crucible (inner diameter: 14 mm, height: 41 mm). The temperature was controlled by combining thermocouple and a proportional-integral-differential (PID) controller.

Using an electric resistance furnace, the Fe–Cr–C alloys were pre-melted by mixing electrolytic iron and reagent grade chemicals and then cut into appropriate sizes. The initial concentration of carbon in the alloys was adjusted to about 4 mass%. Some amounts of copper and iron powders were added to make up each experimental condition.

Most of the experiments were carried out at 1 873 K. After heating to the desired temperature, the Ar gas was switched to the gas mixture of CO/CO\(_2\). The reaction gas was blown through an alumina lance (inner diameter: 4 mm, outer diameter: 6 mm) at a distance of 5 mm from the surface of the melts. The gas flow rate was controlled by a mass flow controller (MFC, Matheson model 8284) and the total amount of gas mixture was maintained to be 1 000 Nml/min. Finally, the rate of decarburization was determined by measuring the change in the ion-current ratio of CO/CO\(_2\) by using an in-line Mass Spectrometry (Balzers Quadstar 422).

4. Results and Discussion

4.1. Decarburization of Fe–C Melt by CO\(_2\)

Figure 3 exhibits the changes in the concentration of carbon in the Fe–C melt with time due to decarburization reaction by the CO\(_2\) gas at temperatures of 1 773–1 873 K. At an initial stage of decarburization (up to about 150 sec), the concentration of carbon linearly decreases with time, indicating the zero-order reaction with respect to carbon content. In this case, the rate equation is given by Eq. (15).\(^{12}\)

\[
\frac{dC_C}{dt} = k \quad \text{(15)}
\]

where \( C_C \) is the concentration of carbon. It has been known that the gas phase mass transfer and the interfacial reaction could be considered to be a zero-order reaction. By combining Eqs. (13) and (14), the interfacial reaction rate constant could be estimated from the apparent rate constant, which is shown in Fig. 4 as a function of temperature. The rate constant, which corresponds to the rate of CO\(_2\) dissociation, exhibits the following dependence on temperature:

\[
\log k = -\frac{4 490}{T} - 0.72 \quad \text{(16)}
\]

This is relatively in good correspondence to the experimental result reported by Sain and Belton (Eq. (17)).\(^{4}\)

\[
\log k = -\frac{5 080}{T} - 0.21 \quad \text{(17)}
\]
4.2. Effect of Chromium on Decarburization Rate of Fe–Cr–C Melt

The effect of chromium on the interfacial reaction rate in the Fe–Cr–C melt at 1 873 K is shown in Fig. 5 as a function of chromium content. The reaction rate significantly decreases with increasing content of chromium up to about 6 mass%, followed by nearly constant reaction rate. These results are somewhat different from those of Petit and Fruehan who found that the chromium would not have any strong effect on the interfacial reaction rate.

Recently, Song et al. measured the effect of chromium content on the surface tension of the Fe–Cr alloys under an Ar atmosphere at 1 823 K (Fig. 5). The surface tension decreases by increasing the content of chromium, followed by constant value of about 1 600–1 620 mN/m. Thus, it can be suggested that the effect of chromium on retard of the interfacial reaction would have strong correlation to the surface adsorption of chromium from the similar tendency between the surface tension and decarburization rate shown in Fig. 5. The effect of chromium on the interfacial reaction rate can quantitatively be examined by employing the adsorption coefficient as follows.

The Eq. (12) can be rewritten by Eq. (18) in the case of i = Cr.

\[
\frac{k_{Fe-Cr}}{1 + K_{Cr}[mass\%Cr]} + k_i \quad \text{(18)}
\]

where, \( k_{Fe-Cr} \) is the interfacial rate constant of the Fe–Cr–C melts and \( k_i \) is the interfacial rate constant of the Fe–C melt \( (k_i = 3.20 \times 10^{-4}) \). The residual rate constant \( (k_r) \) could be determined from the constant value observed at chromium content greater than about 10 mass% in Fig. 5 \( (k_r = 7.09 \times 10^{-5}) \). The Eq. (18) was modified into Eq. (19) and thus the value of \( K_{Cr} \) could be obtained to be about 2.89 from the slope of the straight line in Fig. 6.

\[
\frac{1}{k_{Fe-Cr}} - k_i \quad \frac{1}{k_r} = \frac{K_{Cr}[wt\%Cr]}{k_r} \quad \text{.........(19)}
\]

Therefore, the interfacial rate constant for the Fe–Cr–C melt could be described by Eq. (20) from the present experimental results.

\[
k_{Fe-Cr} = \frac{3.20 \times 10^{-4}}{1 + 2.89[wt\%Cr]} + 7.09 \times 10^{-5} \quad \text{.........(20)}
\]

4.3. Effect of Copper on Decarburization Rate of Fe–18(mass%)Cr–Cu–C Melt

The effect of copper on the rate of decarburization of the Fe–18(mass%)Cr–Cu–C melt at 1 873 K was shown in Fig. 7 as a function of reaction time at different copper contents. At high concentrations of carbon greater than about 1.5 mass%, the straight lines are observed, which are similar to the results of the decarburization of the Fe–C melt as shown...
in Fig. 3. This means that the zero-order reaction with respect to the content of carbon would be going on. However, approaching at low concentrations of carbon, the slopes of the lines change with reaction time, probably indicating that there would be different reaction mechanisms in the relatively high and low carbon content regions.

Fruehan investigated the decarburization kinetics of stainless steel melt and suggested that the mass transfer of carbon in the melt, which is a first-order reaction with respect to the carbon content, could be a rate-determining step when the content of carbon would relatively be low. Fruehan investigated the decarburization kinetics of stainless steel melt and suggested that the mass transfer of carbon in the melt, which is a first-order reaction with respect to the carbon content, could be a rate-determining step when the content of carbon would relatively be low. Fruehan investigated the decarburization kinetics of stainless steel melt and suggested that the mass transfer of carbon in the melt, which is a first-order reaction with respect to the carbon content, could be a rate-determining step when the content of carbon would relatively be low. Fruehan investigated the decarburization kinetics of stainless steel melt and suggested that the mass transfer of carbon in the melt, which is a first-order reaction with respect to the carbon content, could be a rate-determining step when the content of carbon would relatively be low. Fruehan investigated the decarburization kinetics of stainless steel melt and suggested that the mass transfer of carbon in the melt, which is a first-order reaction with respect to the carbon content, could be a rate-determining step when the content of carbon would relatively be low.

Fruehan investigated the decarburization kinetics of stainless steel melt and suggested that the mass transfer of carbon in the melt, which is a first-order reaction with respect to the carbon content, could be a rate-determining step when the content of carbon would relatively be low.

In case of the first-order reaction with respect to carbon content, the rate equation can be given by Eq. (21). In case of the first-order reaction with respect to carbon content, the rate equation can be given by Eq. (21). In case of the first-order reaction with respect to carbon content, the rate equation can be given by Eq. (21).

\[ -r = -\frac{dC_C}{dt} = kC_C \]  \hspace{1cm} (21)

where \( C_C \) is the concentration of carbon. The rate constant in Eq. (21) can be calculated from the experimental results at low carbon content region and is shown in Fig. 8 as a function of copper content. The rate constant slightly decreases with increasing copper content and exhibits a similar order of magnitude with the result of Fruehan's work.

Therefore, it is suggested that the mass transfer of carbon in the melt could be a rate-determining step at low carbon content region.

On the other hand, the interfacial reaction rate should be discussed by taking the effect of copper into account at high concentrations of carbon. Figure 9 exhibits the effect of copper on the interfacial reaction rate. The rate constant decreases by increasing the content of copper with no residual rate in the range of copper content investigated.

The quantitative effect of copper on the interfacial reaction rate could be examined by employing the adsorption coefficient of copper as in the case of chromium discussed in Sec. 4.2. The Eq. (11) was modified into Eq. (22) and thus the value of \( K_{Cu} \) could be obtained to be about 0.09 from the slope of the straight line in Fig. 10.

![Graph](image1)

**Fig. 7.** Decarburization reaction of the Fe–18(mass%)Cr–Cu–C melts by CO2 gas at 1 873 K.

![Graph](image2)

**Fig. 8.** Rate constants of decarburization at low concentrations of carbon in the Fe–18Cr–Cu–C system.

![Graph](image3)

**Fig. 9.** Effect of copper on the interfacial reaction rate in the Fe–18Cr–Cu–C melts at 1 873 K.

![Graph](image4)

**Fig. 10.** Determination of the adsorption coefficient of copper, \( K_{Cu} \) by the graphical method.
\[ \frac{1}{K_{Fe-Cr-Cu}} - \frac{1}{k_{Fe-Cr}} = \frac{K_{Cu}}{k_{Fe-Cr}}[\text{mass}\%Cu] \quad \ldots \ldots (22) \]

where, \( k_{Fe-Cr-Cu} \) is the interfacial rate constant of the Fe–Cr–Cu–C melt. Therefore, the interfacial rate constant for the Fe–Cr–Cu–C melt could be described by Eq. (23) from the present experimental results.

\[ k_{Fe-Cr-Cu} = k_{Fe-Cr} \frac{1}{1+0.9[w\%\text{Cr}]} \quad \ldots \ldots (23) \]

However, because Eq. (23) has been deduced from the experimental results for the Fe–18(mass\%)Cr–Cu–C melts, further investigation would be required to establish a general rate equation applicable to a wide content of chromium.

Consequently, in the present study, it has been proposed that the addition of copper could affect the mass transfer of carbon in the melt at low concentrations of carbon and affect an interfacial reaction at high carbon contents, respectively. Thus, the dominant factor affecting the overall reaction rate of decarburization of the Fe–Cr–Cu–C melt can be determined by employing the concept of shifting order as follows.

Supposing that the reaction is of zero-order with the rate constant \( k_1/k_2 \) at high concentrations of carbon and of first order with rate constant \( k_C \) at low carbon content region, the overall rate equation can be expressed by Eq. (24).12)

\[ -r = \frac{dC_C}{dt} = \frac{k_C C_C}{1+k_C C_C} \quad \ldots \ldots (24) \]

Using Eq. (24), the reaction rate is shown in Fig. 11 through the entire contents of carbon. It is of interest that the reaction rate at high concentrations of carbon decreases with increasing copper content, while the effect of copper addition on the reaction rate would be negligible in the composition of low carbon contents during decarburization process. Therefore, it is probably concluded that the addition of copper in the stainless steel melt could affect the interfacial reaction, resulting in retard of the overall reaction rate.

4.4. Dependence of Reaction Rate on Temperature

The dependence of decarburization reaction on temperature has been investigated for the Fe–18(mass\%)Cr–C and Fe–18(mass\%)Cr–4(mass\%)Cu–C melts at 1 773–1 923 K to compare the differences in an activation energy between each alloy (Fig 12). For the Fe–18Cr–C melts, the rate constant is obtained as a function of temperature as follows:

\[ \log k_{Fe-Cr} = \frac{-2.780}{T} - 2.42 \quad \ldots \ldots (25) \]

Comparing Eq. (25) with Eq. (16), it is found that the activation energy is changed due to chromium, indicating the effect of chromium on an interfacial reaction. That is, chromium may take part in the decarburization reaction as a reaction medium. Fruehan reported that the chromium was oxidized much faster than carbon in an AOD process and that most of the oxygen would be consumed by an oxidation of chromium.14,15) He also concluded that the rising Cr₂O₃ particles by Ar/O₂ bubbling in steel bath would behave as an oxidizer in the following reactions:

\[ 2Cr + \frac{3}{2}O_2(g) = Cr_2O_3(s) \quad \ldots \ldots (26) \]

\[ Cr_2O_3(s) + 3C = 2Cr + 3CO(g) \quad \ldots \ldots (27) \]

Hence, it can be proposed that the presence of chromium on the reaction surface could retard the interfacial reaction by the above reaction steps. Also, the interaction between chromium and carbon could decrease the activity of carbon in view of thermodynamics as discussed in Sec. 1.

As 4 mass\% copper is added to the Fe–Cr–C melt, the graph shifted downward as shown in Fig. 12. The rate constant can be expressed as a function of temperature by the following equation:
In Eqs. (25) and (28), the values of the activation energy are nearly identical to each other. This means that the decarburization reaction in both cases would be occurred based on a unique mechanism. It is considered that the difference in the intercepts between each case could be originated from the changes in the physical environment on the reaction surface. As in the case of chromium, copper also occupies a certain fraction of the reaction sites depending on its surface activity. However, because of the more noble characteristics of copper than chromium and iron, it would not take part in the decarburization reaction. Thus, it is suggested that the copper could delay the decarburization reaction by blocking a part of the reaction sites.

5. Conclusions

A kinetic study on the decarburization reaction of the Fe–Cr–Cu–C melts has been carried out at 1 873 K focusing on the effect of copper on the reaction rates. The results of this study can be summarized as follows:

(1) The decarburization rate of the Fe–C melt was preliminarily measured at 1 873 K. The result of the present work exhibits a good agreement with other studies.

(2) The addition of chromium to the Fe–C melt decreases the interfacial reaction rate. It is considered that the effect of chromium on a retard of the interfacial reaction would have a relationship to the surface adsorption of chromium.

(3) The addition of copper to the Fe–Cr–C melt decreases the decarburization reaction rate. The delay of the interfacial reaction by copper at high concentrations of carbon could be responsible for the decrease in the overall reaction rate. The effect of copper on the reaction rate could be quantified by the following equation:

\[
\log k_{Fe-Cr-Cu} = - \frac{2.640}{T} - 2.63 \quad \ldots \ldots \ldots \ldots (28)
\]

\[
k_{Fe-Cr-Cu} = \frac{k_{Fe-Cr}}{1 + 0.09[\text{wt}\%\text{Cr}]}
\]

(4) From the results of the dependence of the interfacial rates on temperature for each alloy, it could be proposed that the presence of chromium on the reaction surface in the Fe–Cr–C melt would delay the reaction rate, which was originated from the additional reaction steps. However, it is suggested that copper would delay the decarburization rate by blocking a part of the reaction sites in the Fe–Cr–Cu–C melt.

Acknowledgment

This work was financially supported by the 99th research grant program of POSCO. Also, one of the authors (HDS) was supported by the Brain Korea 21 Project.

REFERENCES

1) Y. D. Lee: Trends Met. Mater. Eng., 13 (2000), 53.
2) C. H. P. Lupis: Chemical Thermodynamics of Materials, Prentice Hall, New York, (1993), 523.
3) The Japan Society for the Promotion of Science (19th Committee on Steelmaking): Steelmaking Data Sourcebook, Revised Ed., Gordon and Breach Science Publishers, New York, (1988), 59.
4) D. R. Sain and G. R. Belton: Metall. Trans. B, 7B (1976), 235.
5) D. R. Sain and G. R. Belton: Metall. Trans. B, 9B (1978), 403.
6) A. W. Cramb and G. R. Belton: Metall. Trans. B, 12B (1981), 699.
7) F. J. Mannion and R. J. Fruehan: Metall. Trans. B, 20B (1989), 853.
8) C. P. Petit and R. J. Fruehan: Metall. Mater. Trans. B, 28B (1997), 639.
9) R. J. Fruehan and S. Antolin: Metall. Trans. B, 18B (1987), 415.
10) S. Taniguchi, A. Kikuchi and S. Maeda: Tetsu-to-Hagané, 62 (1976), 191.
11) H. Saito, A. Yoshizawa and T. Soma: Tetsu-to-Hagané, 70 (1984), 58.
12) O. Levenspiel: Chemical Reaction Engineering, 3rd ed., John Wiley & Sons, New York, (1999), 38.
13) H. S. Song, D. S. Kim, Y. H. Kim and A. W. Cramb: Bull. Korean Inst. Met. Mater., 12 (1999), 412.
14) R. J. Fruehan: Ironmaking Steelmaking, 3 (1976), 153.
15) R. J. Fruehan: Metall. Trans. B, 6B (1975), 573.