Rates of Nitrogen and Carbon Removal from Liquid Iron in Low Content Region under Reduced Pressures

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The kinetics of nitrogen and carbon removal from a liquid iron surface in low content regions by blowing Ar gas mixture under reduced pressures have been studied using the same vacuum induction furnace at 1 600°C, respectively. The results obtained are as follows:

(1) The nitrogen removal reaction is described as a second order reaction with respect to nitrogen content. The overall reaction rate constant, k_{ov}^N , decreases with the increase of total pressure, and oxygen and sulfur content.

Assuming that the nitrogen removal reaction progresses by a mixed control and that the chemical reaction for nitrogen gas formation is caused by adsorbed nitrogen atoms, the chemical reaction rate constant, k_r^N , and the adsorption coefficient of oxygen, κ_O , and of sulfur, κ_S , are estimated as follows:

$$\boxed{N} + \boxed{N} = \boxed{N_2} + \boxed{}$$

$$k_r^N (= k_{[N]} / f_N^2) \text{ cm/mass\%/sec} = 15 / (1 + \kappa_O \cdot a_O + \kappa_S \cdot a_S)^2,$$

$$\kappa_O = 161, \quad \kappa_S = 63.4$$

In the Fe–20mass%Cr–0.2mass%C–S system also, the value of k_r^N can be expressed by the same equation. It is thus concluded that, macroscopically, the mechanism of nitrogen removal is the same irrespective of whether or not the melt contains chromium.

(2) In the carbon content range below 200 ppm, the overall carbon removal reaction rate constant, k_{ov}^C , exhibits a maximum value against oxygen content, and decreases with the increase of sulfur content.

Assuming that the chemical reaction for CO gas formation caused by the adsorbed carbon and the adsorbed oxygen atoms as a following equation, the dependence of the chemical reaction rate constant on oxygen and sulfur content is explained by the values of the adsorption coefficients κ_O and κ_S , respectively.

The value of κ_O is equal to about 100–300 and that of κ_S is equal to about 40–65.

These values are in general accord with those determined from the nitrogen desorption reaction.

KEY WORDS: nitrogen removal; carbon removal; chemical reaction rate; adsorption coefficient; mixed control model; reduced pressure.

1. Introduction

To improve the quality of steel sheets, the carbon and nitrogen contents of the steel must be minimized. The ways to remove these impurities have been investigated vacuum degassing processes for secondary steel refining such as the RH and the DH processes.

Many fundamental studies have been reported about nitrogen removal^{1–6)} and carbon removal^{7,8)} from liquid iron under normal pressure, but only a few studies have been published on nitrogen removal^{9,10)} and carbon removal¹¹⁾ under reduced pressure and in an ultra low-content region. Consequently, many aspects of the mechanisms of nitrogen and carbon removal reactions

under these conditions remain unclear.

The present study measured the rates of nitrogen and carbon removal from the iron melt in low-nitrogen and low-carbon content regions under reduced pressures, using the same experimental apparatus. In the course of the study, the effects of oxygen and sulfur contents on the surface reaction rates were quantified, and the mechanisms of nitrogen and carbon removal reactions in low-content regions were examined.

2. Experimental Procedure

The experiments were carried out using a vacuum induction melting furnace (3 kHz) containing 12 kg of

iron melt in a magnesia crucible at 1600°C under reduced pressures. A schematic diagram of the experimental apparatus is shown in Fig. 1.

High purity electrolysis iron was used as raw material. The initial oxygen, sulfur, carbon and chromium content of the iron melt in each experiment was adjusted by adding iron oxide, sulfur, graphite and a metallic chromium, respectively. The initial nitrogen content was adjusted by controlling the nitrogen partial pressure, P_{N_2} , at about 10 mmHg.

To investigate the effect of sulfur content on nitrogen removal, the initial carbon content was controlled at 0.2 mass% to keep the oxygen content low and constant.

During the nitrogen and carbon removal experiment, argon mixed gas was blown against the liquid iron surface through a lance with a nozzle diameter of 7.5 mm in order to minimize the influence of mass transfer in the gas diffusion boundary layer. The mixed gas blow rate and height were 20 Nl/min and 150 mm, respectively. The total pressure, P_{total} , was controlled at 10 ± 2 mmHg.

A gas mixture of Ar-5mass%N₂ was used in the nitrogen removal experiments. Accordingly, the value of P_{N_2} was equal to 0.5 ± 0.1 mmHg.

The other hand, Ar-20mass%(CO-CO₂) gas mixture was blown in the carbon removal experiment. The value of CO/CO₂ mass ratio was 0.5-1.9. The purity of each gases used was above than 99.99 mass%.

For comparison with the results of the gas blowing experiment, some removal experiments were carried out under high vacuum pressure (2×10^{-3} mmHg) without

gas blowing.

The experimental conditions are listed in Table 1.

Metal samples were taken with a quartz tube, and nitrogen and carbon content in the samples was analyzed by the thermoconductometric method after melting in a current of inert gas, and by the infrared absorptiometric method after combustion in the current of oxygen (high sensitivity type).

3. Experimental Results

Under the experimental conditions used, no gas evolution was observed in the liquid iron. The nitrogen and carbon removal reaction sites could thus be surmised to be the gas/metal interface.

3.1. Nitrogen Removal Rate

The nitrogen removal rate from liquid iron can be approximated by a second-order reaction with respect to nitrogen content as Eq. (1) irrespective of the type of liquid iron.

$$-\frac{d[N]}{dt} = \left(\frac{A}{V}\right) \cdot k_{ov}^N \cdot ([N]_t^2 - [N]_e^2) \quad \text{.....(1)}$$

where A : gas-liquid iron contact area (cm²)

V : volume of liquid iron (cm³)

$[N]_t$: nitrogen content in liquid iron at time t (mass%)

$[N]_e$: equilibrium nitrogen content in liquid iron with nitrogen partial pressure (mass%)

k_{ov}^N : overall reaction rate constant for nitrogen removal (cm/mass%/sec)

t : time (sec).

Figure 2 shows the influence of total pressure, P_{total} , on the overall reaction rate constant, k_{ov}^N , in 0.2 mass%[C] iron melt by the gas blowing. Even with a

Fig. 1. Schematic diagram of experimental apparatus.

Table 1. Experimental conditions.

Metal temperature	1600°C	Metal weight	12 kg
Crucible (size)	MgO (120 mmφ × 250 mm)		
Gas flow rate	20 l/min	Lance height	150 mm
Nozzel diameter			7.5 mmφ
Nitrogen removal experiment		Carbon removal experiment	
Metal composition	① Fe-0.2mass%C-S ② Fe-O, Fe-O-S ③ Fe-0.2mass%C-S-20mass%Cr $a_N \leq 50$ ppm	① Fe-S-O-C $C \leq 200$ ppm $S \leq 0.082$ ppm	
Pressure	2×10^{-3} -12 mmHg	2×10^{-3} -12 mmHg	
Flow gas	Ar-1(l/min)N ₂	Ar-5(l/min)CO/CO ₂

Fig. 2. Influence of total pressure on overall reaction rate constant, k_{ov}^N , of nitrogen removal and on mass transfer coefficient, k_g , of N₂ in gas diffusion boundary layer.

Fig. 3. Influence of oxygen activity, a_O , and sulfur activity, a_S , on overall reaction rate constant of nitrogen removal, k_{ov}^N .

gas blowing rate of 20 (Nl/min), the value of k_{ov}^N decreases with the increase of P_{total} . This fact suggests that the value of resistance in the gas diffusion boundary layer including "the detachment reaction from the surface resistance of adsorbed nitrogen molecule at the metal surface"^{1,12)} is too large to be ignored at the pressure of 500 mmHg. For comparison, the value of k_{ov}^N measured under a high vacuum pressure without gas blowing is shown by open circles in Fig. 2. This value is slightly greater than that measured under the pressure of 10 mmHg with gas blowing.

Figure 3 shows the influence of activities of oxygen, a_O , and of sulfur, a_S , on k_{ov}^N observed under the pressure of 10 mmHg with gas blowing. The value of k_{ov}^N strongly depends on the value of a_O or a_S and decreases with the increase of a_O or a_S , respectively.

The degree of harmful influence of oxygen on the nitrogen removal rate is greater than that of sulfur, but the activities of both were calculated using the values of activity coefficient of each element based on thermochemical data.¹³⁾

The values of k_{ov}^N at low-oxygen and low-sulfur activity region observed in the present work are greater than those in previous studies.^{1-6,9)}

The relation between k_{ov}^N of Fe-20mass%Cr-0.2 mass%C-S system and a_S is shown in Fig. 3 as solid squares. The value of k_{ov}^N also decreases with the increase of a_S , and the actual value of k_{ov}^N is about 0.1 times smaller than the value of k_{ov}^N obtained no chromium containing system. However, the degree of harmful influence of the sulfur on k_{ov}^N is very similar to that observed in the Fe-0.2mass%C-S system.

3.2. Carbon Removal Rate

Figure 4 shows typical changes in the carbon and oxygen content of the ultra low sulfur iron melt during Ar-CO-CO₂ gas blowing. The carbon removal reaction behavior was divided into three regions.

(1) In the range of carbon content higher than about

Fig. 4. Changes in carbon and oxygen content in iron melt during Ar-CO-CO₂ blowing.

Fig. 5. Influence of oxygen content on k_{ov}^C at various times during Ar-CO-CO₂ blowing.

200 ppm, the rate of carbon removal was described as zeroth order reaction with respect to carbon content, and oxygen content remained constant at about 40 ppm, "Region-0".

(2) In the range of carbon content between about 10 and 200 ppm, the rate can be apparently approximated by a first-order reaction with respect to carbon content, and oxygen content was increased, "Region-I".

(3) With carbon content less than about 10 ppm, the rate is less than that in "Region-I", and the oxygen content is more than 150 ppm, "Region-II".

The carbon removal behavior in "Region-0" was previously explained,¹⁴⁾ so the details are abbreviated in this paper.

Kishimoto *et al.*¹¹⁾ reported that the overall reaction rate constant for carbon removal, k_{ov}^C , decreased with the decrease of carbon content at less than 0.005 mass%.

Figure 5 shows the effect of oxygen content on the value of k_{ov}^C , observed in melts with sulfur content of less than 5 ppm in Regions-I and -II. The value of k_{ov}^C was calculated by Eq. (2) from the carbon content between the analysis points.

$$-\frac{d[C]}{dt} = \left(\frac{A}{V}\right) \cdot k_{ov}^C \cdot ([C]_t - [C]_e) \quad \dots\dots\dots(2)$$

where, $[C]_t$: carbon content in liquid iron at time t

Fig. 6. Influence of sulfur content on change in carbon content in Region-I.

Fig. 7. Influence of sulfur content on k_{ov}^C .

(mass%)
 $[C]_e$: equilibrium carbon content in liquid iron with CO partial pressure and oxygen content in liquid iron (mass%)
 k_{ov}^C : overall reaction rate constant for carbon removal (cm/sec).

The value of k_{ov}^C becomes maximum when oxygen content is 0.01 to 0.02 mass% and decreases with further increase in oxygen content. Thus, progress of the carbon removal reaction from the surface of liquid iron in the low carbon content region is apparently retarded by the increase in oxygen content.

Figure 6 shows the changes in carbon content of liquid iron containing various sulfur during Ar-CO-CO₂ gas blowing under the pressure of 10 mmHg. The type of carbon removal behavior in this carbon content region corresponds to that in Region-I, and the value of minimum carbon content is not reached within 10 ppm. Namely, in this region, the rate of reaction is described as a first order reaction with respect to carbon content.

Figure 7 shows the influence of sulfur content on the average overall relation rate constant for the carbon removal, k_{ov}^C , this is determined from the slope of the straight line in Fig. 6. The value of k_{ov}^C decreases with the increase of sulfur content. In this case, the oxygen

Fig. 8. Change of oxygen content and $-\ln([C]_t/[C]_0)$ under high vacuum pressure.

Fig. 9. Influence of average oxygen content on k_{ov}^C under high vacuum pressure.

content increased from 50 to 150 ppm.

With Ar-CO-CO₂ gas blowing, oxygen content in Regions-I and -II increased. In order to prevent this increase, it was decided to perform a carbon removal experiment under a high vacuum pressure (2×10^{-3} mmHg) without Ar-CO-CO₂ gas blowing, and thereby to confirm the effect of oxygen content on the carbon removal reaction.

Figure 8 shows the change of $-\ln([C]_t/[C]_0)$ and $[O]$ in that experiment. The changes of $-\ln([C]_t/[C]_0)$ are in close agreement with the straight line against the time down to extremely low carbon content of 2 ppm. In this experiment, oxygen content was remained almost constant during the entire period of carbon removal.

The relation between k_{ov}^C as determined from the slopes of the straight lines in Fig. 8 and average oxygen content is shown in Fig. 9. Influence of oxygen content on k_{ov}^C is similar to that in the case of Ar-CO-CO₂ blowing, so, the value of k_{ov}^C becomes maximum relative to oxygen content.

4. Discussion

In investigating the rate of gas/metal reaction between a liquid iron and a gas in the region where the element of interest is low in content, it is very important to estimate:

- 1) the value of mass transfer coefficient in the gas diffusion boundary layer, k_g ,
- 2) the value of mass transfer coefficient in the metal diffusion boundary layer, k_N , and
- 3) the value of the chemical reaction rate constant at the interface of the gas/metal, k_r .

Particularly when the content of the element to be removed is low, estimation of the chemical reaction rate constant is important to decide the rate controlling step of the reaction.

Assuming that the respective reaction proceeds as controlled by the mass transfer in the metal and gas phases and the chemical reaction at the gas/metal interface, the value of k_{ov}^N and k_{ov}^C is generally expressed by the following equations.

○ Nitrogen Removal (2nd order rate)⁹⁾

The nitrogen removal rates of three steps are expressed as follows:

- metal phase mass transfer

$$-n_M \left(\equiv \frac{dN_N}{dt} \right) = A \cdot k_N \cdot ([N]_b - [N]_i) \quad (\text{mol/sec}) \quad \dots (3)$$

- chemical reaction rate at the interface

$$-n_r \left(\equiv \frac{dN_N}{dt} \right) = A \cdot k_{[N]} \cdot ([N]_i^2 - [N]_i^2) \quad (\text{mol/sec}) \quad \dots (4)$$

- gas phase mass transfer

$$-n_g \left(\equiv \frac{dN_{N_2}}{dt} \right) = A \cdot k_g \cdot (P_{N_2}^i - P_{N_2}^b) \quad (\text{mol/sec}) \quad \dots (5)$$

- material balance equation

$$2n_g = n_r = n_M \quad \dots (6)$$

Considering the equilibrium nitrogen content in metal with the nitrogen partial pressure in gas phase, the value of k_{ov}^N is expressed by Eq. (7).

$$k_{ov}^N = k_N \cdot \left(\frac{2[N] + \phi - \sqrt{\phi^2 + 4[N] \cdot \phi + 4[N]_e^2}}{2([N]^2 - [N]_e^2)} \right) \quad (\text{cm}^4/\text{mol/sec}) \quad \dots (7)$$

$$\phi = k_N \cdot \left(\frac{K_{N_2}^2}{2k_g} + \frac{1}{k_{[N]}} \right) = \frac{([N] \cdot \lambda - 1)^2 - \lambda^2 \cdot [N]_e^2}{\lambda} \quad \dots (8)$$

$$\lambda = \frac{k_{ov}^N}{k_N} \quad \dots (9)$$

where, k_N : mass transfer coefficient of nitrogen atom (cm/sec)

$k_{[N]}$: apparent chemical reaction rate constant (cm⁴/mol/sec)

k_g : mass transfer coefficient of nitrogen molecule (mol/cm²/sec/atm)

K_{N_2} : equilibrium constant for $2[N] = N_2(g)$ (mol/

cm³/atm^{1/2})

$[N]_b$: nitrogen content in metal bulk (mol/cm³)

$[N]_i$: nitrogen content in metal at the interface (mol/cm³)

$[N]_i$: equilibrium nitrogen content in metal with the nitrogen partial pressure at the interface (mol/cm³)

$[N]_e$: equilibrium nitrogen content in metal with the nitrogen partial pressure of gas bulk (mol/cm³)

$P_{N_2}^b$: nitrogen partial pressure of gas bulk (atm)

$P_{N_2}^i$: nitrogen partial pressure at the interface (atm).

○ Carbon Removal (1st order rate)⁸⁾

The carbon removal rates of three steps are expressed as follows:

- metal phase mass transfer

$$-n_M \left(\equiv \frac{dN_C}{dt} \right) = A \cdot k_C \cdot ([C]_b - [C]_i) \quad (\text{mol/sec}) \quad \dots (10)$$

- chemical reaction rate at the interface

$$-n_r \left(\equiv \frac{dN_C}{dt} \right) = A \cdot k_r \cdot \left([C]_i \cdot [O]_i - \frac{P_{CO}^i}{K_{CO}} \right) \quad (\text{mol/sec}) \quad \dots (11)$$

- gas phase mass transfer

$$-n_g \left(\equiv \frac{dN_C}{dt} \right) = A \cdot k_g \cdot (P_{CO}^i - P_{CO}^b) \quad (\text{mol/sec}) \quad \dots (12)$$

- material balance equation

$$n_g = n_r = n_M \quad \dots (13)$$

Considering that the mass transfer rate of oxygen atom is much greater than that of carbon atom, the value of k_{ov}^N is expressed by Eq. (14).

$$k_{ov}^C = \frac{(k_{gr} \cdot [O]) \cdot k_C}{(k_{gr} \cdot [O] + k_C)} \quad \dots (14)$$

$$k_{gr} = \frac{(K_{CO} \cdot k_g) \cdot k_r^C}{(K_{CO} \cdot k_g) + k_r^C} \quad \dots (15)$$

where, k_C : mass transfer coefficient of carbon atom (cm/sec)

k_r^C : chemical reaction rate constant for carbon removal (cm⁴/mol/sec)

K_{CO} : equilibrium constant for $[C] + [O] = CO(g)$ (mol²/cm⁶/atm)

k_g : mass transfer coefficient of CO molecule (mol/cm²/sec/atm)

$[O]$: oxygen content (mol/cm³)

$[C]_b$: carbon content in metal bulk (mol/cm³)

$[C]_i$: carbon content in metal at the interface (mol/cm³)

$[C]_e$: equilibrium carbon content in metal with the value of P_{CO} at the gas bulk and oxygen content (mol/cm³)

P_{CO}^b : partial pressure of carbon monoxide in gas bulk (atm)

P_{CO}^i : partial pressure of carbon monoxide at the interface (atm).

4.1. Estimation of the Mass Transfer Coefficient of the Gas Diffusion Boundary Layer under Reduced Pressures in Gas Blowing

Choh *et al.*⁹⁾ conducted experiments using a furnace of practically the same type and size as that used in the present experimental work, and reported 0.050–0.068 cm/sec as the value of the mass transfer coefficient of nitrogen atom, k_N . Hence, the value of k_N is adopted as 0.050 cm/sec and is also used to determine the mass transfer coefficient of nitrogen molecules.

Under high vacuum pressure, the mean free path of the nitrogen molecule is considered sufficiently larger than the length from liquid iron surface to the top of the crucible. So, assuming that the rate determining step of the nitrogen removal reaction under the condition of 2×10^{-3} mmHg is mixed control of the mass transfer of nitrogen atom and chemical reaction at the gas/metal interface described by Eq. (17), the average value of $k_r = k_{[N]}$ plotted in Fig. 2 as open circles can be decided as 8.1 (cm/sec/mass%) = 1 620 (cm⁴/sec/mol). The value of $k_{[N]}$ was calculated by using the value of $[N] = 0.0020$ mass% = 1.0×10^{-5} mol/cm³. The unit was unified in the calculation to decide the value of $k_{[N]}$. Substituting those values into Eqs. (7)–(9), the values of k_g under each pressure can be calculated. Figure 2 shows the relation between k_g and P_{total} . The value of k_g is inversely proportional to P_{total} . Generally, the value of k_g is expressed as

$$k_g = D_{\text{Ar-N}_2} / \delta, \quad D_{\text{Ar-N}_2} \propto 1/P_{\text{total}}^{1.5} \quad \text{.....(16)}$$

where, $D_{\text{Ar-N}_2}$: diffusivity of nitrogen molecule in Ar.

As the value of gas blowing rate is constant, it is considered that the thickness of gas diffusion boundary layer, δ , is maintained as a constant value.¹⁵⁾ Accordingly, the dependence of the value of k_g on P_{total} is a reasonable result. So, in the condition of a 20 (Nl/min) gas blowing rate under 10 mmHg pressure, the value of k_g is equal to 2.0×10^{-4} (mol/cm²/sec/atm).

It should be noted that even when the gas is blown at the rate of 20 Nl/min, the gas phase presents resistance equivalent to about 1×10^{-5} (mol/cm²/sec/atm) under the vicinity of normal pressure.

4.2. Influence of Oxygen and Sulfur Content on Chemical Reaction Rate

Assuming that the chemical reaction of nitrogen desorption and of CO gas formation at the liquid iron surface are described by Eqs. (17)¹⁾ and (19), and that the value of $(1 + \kappa_S \cdot a_S + \kappa_O \cdot a_O)$ is so much greater than the value of $(\kappa_C \cdot a_C + \kappa_N \cdot a_N)$, the chemical reaction rate constants are expressed by Eqs. (18)¹⁾ and (20), respectively.

$$k_r^N = \frac{k_{[N]}}{f_N^2} = \frac{k_{ro}^N}{(1 + \kappa_S \cdot a_S + \kappa_O \cdot a_O)^2} \quad \text{.....(18)}$$

$$k_r^C = \frac{k_{ro}^C}{(1 + \kappa_S \cdot a_S + \kappa_O \cdot a_O)^2} \quad \text{.....(20)}$$

where, $\square$: adsorption site

k_{ro}^N : chemical reaction rate constant for nitrogen removal from pure liquid iron

k_{ro}^C : chemical reaction rate constant for carbon removal from pure liquid iron

κ_X : adsorption coefficient of element X in liquid iron

a_X : activity of X element in liquid iron.

The chemical reaction rate constant k_r^N is first discussed. Substituting the following values into Eqs. (7)–(9), the value of the apparent chemical reaction rate constant, $k_{[N]}$, can be calculated from the value of k_{ro}^N at the pressure of 10 mmHg.

$$k_g = 2 \times 10^{-4} \text{ (mol/cm}^2\text{/sec/atm)}, \quad k_N = 0.050 \text{ (cm/sec)}$$

Accordingly, the value of k_r^N can be determined by Eq. (18) from the activity coefficient, f_N .¹³⁾

When the method of least squares is applied to the data of the Fe–O and Fe–S–0.2mass% C system according to Eq. (21), the values of κ_O , κ_S and k_{ro}^N can be determined.

$$\frac{1}{\sqrt{k_r^N}} = \frac{(1 + \kappa_O \cdot a_O + \kappa_S \cdot a_S)}{\sqrt{k_{ro}^N}} \quad \text{.....(21)}$$

The respective values of κ_O and of κ_S were:

$$\kappa_O = 161, \quad \kappa_S = 63.4, \quad k_{ro}^N = 15 \text{ (cm/mass%/sec)}$$

Figure 10 shows the relation between k_r^N and Y , where,

$$Y \equiv 1 + 161 \cdot a_O + 63.4 \cdot a_S$$

The relations between the value of k_r^N obtained by three systems and Y can be closely resembles a straight line with a slope of -2.0 . The value of k_{ro}^N is considerably larger than that of previous studies^{1,4,5)} made at 1 atm, and similar to the value reported by Harada and Janke.¹⁰⁾

The values of k_r^N in Fe–20mass%Cr–0.2mass% C system are indicated by solid squares in Fig. 10. These values are plotted just a little above the straight line with an overall slope of -2.0 . Using the value reported by

Fig. 10. Relation between chemical reaction rate constant, k_r^N , of nitrogen removal and Y .

Wada and Pehlke¹⁶⁾ for f_N calculation, the relation between k_r^N and Y is in good agreement with this straight line. Macroscopically, the nitrogen removal reaction is presumed to proceed by the same mechanism, irrespective of chromium content.

A discussion of the chemical reaction rate constant for carbon removal follows. Blowing the Ar-CO-CO₂ mixture to the liquid iron surface, resulted in an oxygen content increase in Regions-I and -II. It is therefore not reasonable to conclude that the carbon removal reaction is controlled by the mass transfer of oxygen in the liquid iron, particularly in regions where the carbon content is 100 ppm or lower. It is, rather, assumed that the reaction progresses in the regions through the mixed control of the mass transfer of carbon and CO and the chemical reaction expressed as Eq. (19).

Substituting the following values into Eqs. (14) and (15), the value of k_r^C can be determined from k_{ov}^C in the ultra low-sulfur liquid iron at the pressure of 10 mmHg. The unit was unified in the calculation to decide of the value of k_r^C .

$$k_g = 2 \times 10^{-4} \text{ (mol/cm}^2\text{/sec/atm)}, \quad k_C = 0.048 \text{ (cm/sec)}$$

The value of k_C was compensated by Eq. (22)¹⁵⁾ using the value of D_X ,¹⁷⁾ and the value of k_g was equal to that of the nitrogen removal because the conditions of gas blowing were the same:

$$k_C = \left(\frac{D_C}{D_N} \right)^{4/3} \cdot k_N \dots\dots\dots(22)$$

where, D_X : diffusivity of X element in liquid iron.

$$D_C = 8.5 \times 10^{-5} \text{ (cm}^2\text{/sec)}^{17)}$$

$$D_N = 9.0 \times 10^{-5} \text{ (cm}^2\text{/sec)}^{17)}$$

Figure 11 shows the relation between k_r^C and oxygen content. The value of k_r^C decreases with the increase of oxygen content.

The curves in the figure indicate the oxygen content

Fig. 11. Relation between chemical reaction rate constant, k_r^C , of carbon removal and oxygen content at various times.

dependence of k_r^C , the value of which is calculated by Eq. (20) substituting the following values:

$$k_{ro}^C = 40 \text{ (cm/mass\%/sec)}$$

$$\kappa_O = 50\text{--}350.$$

The calculated value of k_r^C when κ_O is 100 to 300 can roughly explain the oxygen content dependence of the experimental values.

In the case of various sulfur content, the value of k_{ov}^C in Region-I is also calculated for comparison with that of the observed values. The calculated value is shown by the curved line in Fig. 7.

The calculated values used are as following values and the value of κ_S is used as a parameter.

$$[O]_{ave.} = a_O = 0.0075 \text{ mass\%},$$

$$k_{ro}^C = 40 \text{ (cm/mass\%/sec)},$$

$$\kappa_O = 160.$$

The observed value of k_{ov}^C thus agree well with the calculated one when the κ_S is approximately equal to 40–60.

Figure 9 shows the oxygen content dependence of k_{ov}^C observed in the experiments conducted under high vacuum pressure at an almost constant oxygen content. In this case, k_{ov}^C is calculated by assuming that k_g is much larger than k_{ro}^C and the carbon removal reaction proceeds controlled by the combination of the mass transfer of carbon and the interfacial chemical reaction. In this case, the value of k_{ro}^C used is equal to 40 (cm/mass%/sec) and κ_O is used as parameter.

The observed value of k_{ov}^C thus agree roughly with the calculated one when the value of κ_O is equal to 160–200. Also, in this case, the value of k_{ov}^C assumes a maximum value relative to oxygen content.

Accordingly, when the chemical reaction for CO product described by Eq. (19) is the rate controlling step, the value of k_{ov}^C is given by Eq. (23), and if a_O and a_S are approximated by mass%[O] and mass%[S], respectively, the oxygen content at which k_{ov}^C assumes a maximum value is given by Eq. (24).

$$k_{ov}^C = \frac{k_{ro}^C}{(1 + \kappa_S \cdot a_S + \kappa_O \cdot a_O)^2} \dots\dots\dots(23)$$

$$\text{mass\%[O]}^{\text{Max.}} = \frac{1 + \kappa_S \cdot \text{mass\%[S]}}{\kappa_O} \dots\dots\dots(24)$$

The mechanisms of nitrogen and carbon removal through the surface of liquid iron have been studied on the basis of the influence of oxygen and sulfur content on the overall reaction rate constants in low-nitrogen and low-carbon regions.

Since the overall reaction rates of nitrogen and carbon removal depend on oxygen and sulfur content, both chemical reactions are considered to proceed according to the combination of the adsorbed elements. Then, dependence of both chemical reaction rate constants on a_O and on a_S can be satisfactorily explained by using the respective values of the adsorption coefficients κ_O and κ_S . The value of κ_O is 100 to 300 and of κ_S is 40 to 65.

Fig. 12. Relation between $\sigma_{\text{Fe-O}}$ and $\ln(a_{\text{O}})$.

The values of κ_X were respectively reported by Cramb and Belton¹⁸⁾ and Sain and Belton¹⁹⁾ as the following equations:

$$\log(\kappa_{\text{O}}) = 11\,370/T - 4.09^{18)} \quad (25)$$

$$\log(\kappa_{\text{S}}^{\text{[C]sat.}}) = 3\,600/T - 0.57^{19)} \quad (26)$$

where, $\kappa_{\text{S}}^{\text{[C]sat.}}$: the value of κ_{S} in carbon saturated iron.

According to these equations, the value of κ_X in 1 600°C is calculated as follows, but the value of $\kappa_{\text{S}}^{\text{[C]sat.}}$ is corrected with the activity coefficient of sulfur, f_{S} ,¹³⁾ in comparison with that in low carbon content iron melt.

$$\kappa_{\text{O}} = 96,$$

$$\kappa_{\text{S}} = \kappa_{\text{S}}^{\text{[C]sat.}}/f_{\text{S}} = 56.$$

The value of κ_{O} estimated in the present work was 1.7–2.1 times greater than this value, but the estimated value of κ_{S} in present work was in good agreement with that of the corrected value.

Based on the relation between the surface tension of liquid iron, $\sigma_{\text{Fe-O}}$, and a_{O} ,^{20–23)} the value of κ_{O} is now discussed.

The relation between $\sigma_{\text{Fe-O}}$ and a_{O} is expressed by Gibbs's adsorption equation as Eq. (27).

$$\sigma_{\text{Fe-O}} = \sigma_{\text{Fe}} - \Gamma_{\text{O}} \cdot R \cdot T \cdot \ln(1 + \kappa_{\text{O}} \cdot a_{\text{O}}) \quad (27)$$

where, Γ_{O} (mol/cm²) = $1.92 \pm 0.24 \times 10^{-9}$ ²⁰⁾

$$\sigma_{\text{Fe}} \text{ (dyn/cm)} = 1\,890.^{20)}$$

Figure 12 shows that the relation between the value of $\sigma_{\text{Fe-O}}$ and a_{O} , and the curved lines show the calculated values according to Eq. (27) when κ_{O} is used as a parameter.

The dependence of $\sigma_{\text{Fe-O}}$ observed values on a_{O} is in good agreement with that of the calculated lines when κ_{O} is about 96 to 200. Those values are similar to that of estimated in the present work. However, the value of κ_{O} can not be determined as a specific value.

Oxygen is an element that reacts with carbon in the carbon removal reaction. The behavior of oxygen in this carbon removal reaction must be further investigated through more accurate experiments.

5. Conclusions

The kinetics of nitrogen and carbon removal through a liquid iron surface by blowing argon gas mixture under reduced pressure have been studied using a vacuum induction furnace at 1 600°C.

The results obtained are as follows:

(1) In the range of nitrogen content less than 50 ppm, the nitrogen removal reaction was described as a second-order reaction with respect to nitrogen content in liquid iron. The overall reaction rate constant, k_{ov}^{N} , decreased with the increase of total pressure and oxygen and sulfur content.

(2) Assuming that the nitrogen removal reaction progresses by a mixed control and that the chemical reaction for nitrogen gas formation is caused by adsorbed nitrogen atoms, the chemical reaction rate constant, k_{r}^{N} , and the adsorption coefficient of oxygen, κ_{O} , and of sulfur, κ_{S} , are estimated as follows:

$$k_{\text{r}}^{\text{N}} = 15 \text{ (cm/mass\%/sec)}, \quad \kappa_{\text{O}} = 161, \quad \kappa_{\text{S}} = 63.4.$$

In the Fe–20mass%Cr–0.2mass%–S system, the value of k_{r}^{N} is expressed macroscopically by the same equation estimated in the system of Fe–O–S. It is concluded that the mechanism of nitrogen removal was the same irrespective of chromium content.

(3) With carbon content of less than 200 ppm, the overall reaction rate constant, k_{ov}^{C} , assumes a maximum value relative to oxygen content with or without the gas blowing, and k_{ov}^{C} decreases with the increase of sulfur content under Ar–CO–CO₂ blowing.

(4) It is therefore concluded that the chemical reaction for CO gas formation at the interface is caused by the adsorbed carbon and adsorbed oxygen. Dependences of the chemical reaction rate constant on oxygen and sulfur content could thus be explained by the value of the adsorption constants of κ_{O} and κ_{S} , respectively, the value of κ_{O} is about 100 to 300 and of κ_{S} is about 40 to 65, respectively. Those values are similar to those estimated in the nitrogen desorption.

Nomenclature

- A : area of gas/metal interface
- D_X : diffusivity of element X or molecule X
- K : equilibrium constant
- P_{total} : total pressure
- P_X^b : partial pressure of X molecule in gas phase
- P_X^i : partial pressure of X molecule at the interface
- R : gas constant
- T : temperature
- V : volume of liquid iron
- $[X]_b (= [X])$: content of element X in liquid iron bulk
- $[X]_e$: equilibrium content of element X in liquid iron with gas phase
- $[X]_i$: content of element X in liquid iron at the surface
- $[X]_l$: equilibrium content of element X in liquid iron at the surface with P_X^i
- $[X]_o$: initial content of element X in liquid

	iron
$[X]_t$	content of element X in liquid iron at time t
a_X	activity of element X in liquid iron
f_X	activity coefficient of element X in liquid iron
k_g	mass transfer coefficient in gas diffusion boundary layer
k_X	mass transfer coefficient of element X in metal diffusion boundary layer
k_{ov}^X	overall removal reaction rate constant of element X from liquid iron
k_{ro}^X	chemical reaction rate constant at the surface of element X in pure liquid iron
k_r^X	chemical reaction rate constant at the surface of element X in liquid iron
$k_{[N]}$	apparent chemical reaction rate constant for nitrogen removal
κ_X	adsorption coefficient of element X in liquid iron
$\boxed{X}$	adsorption atom or adsorption molecule of X
σ_{Fe}	surface tension of pure liquid iron
Γ_O	surface excess of oxygen

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