Effect of the Chromium Content and Argon Bubbling in the Carbon Removal Rate from Low Carbon Liquid Steel under Reduced Pressure Condition

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A fundamental investigation of the carbon removal rate in the low-carbon-content region using a vacuum induction furnace (12 kg-scale, 600 kg-scale, and 7 t-scale) was carried out and the following results were obtained:

1) A 12 kg-scale experiment aimed at elucidating the adsorption element effect in the decarburization reaction was carried out. The kinetic analysis of the experimental results obtained by using high-chromium steel and a former experimental study of low alloy steel showed that the reaction rate can be estimated using an integrated reaction rate. Moreover, by using this estimation method, the reaction rate of different scale experimental results can also be well predicted.

2) Argon bubbling experimental results using a 7 t-scale vacuum induction furnace showed that the bubble burst under highly reduced pressure conditions can be considered to take place at the shallow depth of 40 mm. Furthermore, a major factor of reaction promotion in both 17 mass% Cr steel and low alloy steel can be estimated by the surface expansion and mass transfer promotion effect of bubble bursting.

KEY WORDS: reaction rate; surface active element; decarburization; gas bubbling; ultra-low carbon steel; reduced pressure; chromium steel.

1. Introduction

Ultra-low carbon steel is required for high-performance steel products. Nowadays, the demand of progress in the both of amount and quality is strongly required. At a steelmaking shop, the vacuum degassing process is used as a ladle refining process, e.g., RH and tank degasser. In such processes, the decarburization rate of the vacuum degassing treatment, according to the decreasing carbon content, decreases because of the setting down of the CO boil formation.

Kraus1) studied the critical condition of CO bubble formation theoretically, and, in addition, several experimental studies were reported.2-5) Their results showed the supersaturation of CO partial pressure during CO bubble formation, and its value was reported as 1–16 (kPa). Therefore, it is common practice to perform the decarburization under the low CO partial pressure condition.

Sain et al.5) showed the inhibiting effect of the solute sulfur adsorption on the carbon removal reaction. Further, Harashima et al.2,6) reported that the decarburization reaction is disturbed both of sulfur and oxygen. Mukawa et al.9) also studied using different experimental set up, and the result was almost identical to those of former studies.7,8) In addition, the hydrogen plasma adding method was studied in laboratory experiments. The results showed that the decarburization reaction was promoted through hydrocarbon formation by the chemical reaction of the dissolved carbon and activated hydrogen.10,11) The above studies were carried out to elucidate and take advantage of the interface reaction phenomena.

Argon bubbling is a significant method for reaction promotion.12) Kitamura et al. showed that as a result of the gas bubbling into the molten steel the decarburization reaction is promoted at the perturbed metal surface by the argon bubble burst position;13) based on this result, a simulation model of the industrial decarburization process (RH-type, new type degassing: REDA15)) was created. The primary feature of this model is dividing the reaction site into three parts: the bath surface, the argon bubble surface, and the inner site where CO boiling occurs. Kirihara et al.16) estimated the contribution of the metal/refractory interface by basic experiments and numerical simulations, and the results showed the effect of the interface can be considered negligible (less than 5% of total reaction rate). Using the above

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concept, several process models were produced,\textsuperscript{17–22} and studies attempted to select fitting parameters using experimental results and numerical simulation models. Further, some studies of surface perturbation phenomena using a water model experiment were also reported.\textsuperscript{23,24}

Recently, authors reported the decarburization rate of argon bubbling effect under normal pressure conditions using several grades of steel and examined the effect of different CO partial pressure conditions by measuring the activity differences of carbon and oxygen due to the effect on the contained alloy.\textsuperscript{25}

Kunagai et al.\textsuperscript{26} studied the behavior of injected bubbles under reduced pressure using cold model experiments, and showed that near the reduced pressure surface, bubbles expand sharply as thin shape and hardly burst.

Therefore, during the decarburization treatment under reduced pressure conditions, physical and chemical phenomena are considered to be quite complicated, and the fundamental knowledge is insufficient.

In this report, kinetic studies were carried out based on three kinds of experimental results: 1. estimation of chemical reactions of high-chromium molten steel by 12 kg-scale experiment, 2. effect of the pressure on argon bubbling condition by 7 t-scale experiment, 3. effect of argon flow rate under highly reduced pressure condition by 600 kg-scale experiment. The results aimed to reveal the unknown mechanism of carbon removal phenomena in low carbon condition without CO bubble formation.

2. Experimental Conditions

As described above, three kinds of induction furnaces were used. In each experiment, metal sampling was started after confirmation that no CO bubbles were present by observation through a heat-resistant windowpane. In the present experiments, CO boiling was observed at the surface without bottom bubbling, so the distinction between argon bubble and CO bubbles was evident. Therefore, every experiment could be carried out without considering the CO boiling condition.

The metal temperature was measured by a batch-type thermocouple: Pt–Rh (6, 30 mass%), and the initial oxygen content was controlled by iron oxide (mainly hematite) addition and zirconia-type solute oxygen sensor measurement.

During the experiment, periodic sampling was carried out using a dipping sampler (12 kg-scale: quartz grass type: ID = 8 mmϕ, 600 kg-, 7 t-scale: stainless steel: ID = 30 mmϕ), the carbon and oxygen (as [t.O]) contents were measured by a combustion analyzer. The oxygen content of each experiment was significantly higher than the carbon content or slightly increased during the experiment because of oxygen separation from the crucible. Therefore, the present experiment was carried out without considering the effects of oxygen mass transfer.

As a general consideration in the high-chromium steel experiment, the chromium oxide formation during measurement must be taken into account. Metal surface observation confirmed that no chromium oxide was present, and this phenomena is demonstrated by the thermodynamic estimation ([t.O] < 0.04 mass%).

Tables 1 and 2 summarize experimental conditions for each experiment.

### Table 1. Experimental conditions without argon gas bubbling.

| Experiment | Metal temperature | Inner diameter of the bath | Metal grade | Composition (mass%) |
|------------|-------------------|----------------------------|-------------|---------------------|
| 12 kg-scale | 1 873 K           | 120 mm                     | 17 mass%Cr steel, 24 mass%Cr steel | [C]: 0.001–0.01, [O]: 0.007–0.025 |
|            |                   |                            |             | [Si] < 0.001, [Mn] < 0.001, [P] < 0.001, [S] < 0.0005 |

### Table 2. Experimental conditions of argon bubbling test.

| Experiment | Atmosphere | Metal temperature | Inner diameter of the bath | Metal grade | Composition (mass%) |
|------------|------------|-------------------|----------------------------|-------------|---------------------|
| 7 t-scale  | <133–101 300 Pa (normal pressure) | 1 843–1 893 K       | 1 100 mm                   | low alloy steel | [C]: 0.01, [Si]: 0.05, [Mn]: 0.1, [P]: 0.02, [S]: 0.004, [O]: 0.03–0.08 |
| 600 kg-scale | <133 Pa               | 1 833–1 883 K       | 380 mm                     | low alloy steel | [C]: 0.01, [Si]: 0.05, [Mn]: 0.1, [P]: 0.02, [S]: 0.004 |

2.1. 12 kg-scale Experiment

Since the details of the 12 kg-scale experimental setup are described in another report on nitrogen removal,\textsuperscript{27} only the experimental conditions are explained in this section. Electrolytic iron and metallic chromium was used as raw material. After the setting, coil current was induced to melt under an argon atmosphere (270–400 kPa) and temperature was held within 1 873 ±10 K by controlling the induction current and performing batch thermocouple measurements. The initial carbon and oxygen contents were controlled by the addition of shot carbon (<5 mm) and iron oxide (high-purity mill-scale) with measurements of carbon content and solute oxygen. Then, the pressure was reduced to the experimental condition (<13 Pa). During the experiment, the chromium content decreased slightly (within 0.5 mass%) likely due to vaporization in the highly reduced pressure condition, but there was no significant composition change without carbon content.

The initial composition for each experiment was confirmed using the OES (Optical Emission Spectrometry) method and by using the combustion analyzer.
2.2. 7 t-scale Experiment

The details of 7 t-scale experimental setup are described in a previous report on the kinetic study of carbon removal in the decreasing-pressure stage.\(^5\) For this experiment, cut pieces from high-purity industrial cast slabs were used as the raw material. During the melting process, the initial carbon content was controlled using an argon-sealed induction furnace. Then, 7 t of molten metal was poured into the vacuum induction furnace. The experimental atmosphere was maintained by controlling the argon injection valve and vacuum valve. The experiment began after the fixed pressure condition and temperature measurements were confirmed. During the experiment, metal sticking was generated and the metal weight loss was within 5%; in the present study, for the kinetic analysis, the metal weight was treated as constant (7 t).

2.3. 600 kg-scale Experiment

The experimental apparatus and method for the 600 kg-scale experiment are similar to those for 7 t-scale experiment. A high-purity porous magnesia crucible (ID = 380 mm, purity $\geq 98$ mass%, porosity $\approx 15\%$) was fixed in the magnesia chromite refractory by MgO stamping. The raw material was also the same as that in the 7 t-scale experiment, and for the high-chromium steel experiment, metallic chromium was used as the alloy material.

The inner diameter is smaller than that in the 7 t-scale experiment, so the average weight loss due to metal sticking was about 10% of the initial weight. Therefore, in this experimental analysis, the metal weight was considered to be constant at 550 kg.

3. Experimental Results

Table 3 shows the list of results for each experiment. In this table, $[O]$ ave (ppm) and $kr$ (1/min) and kov (cm/s) indicate average $t,O$ and first-order reaction rate coefficients obtained by following Eq. (1), respectively.

$$\frac{-d[C]}{dt} = kr([C] - [C]e) = 60 \cdot A \cdot V \cdot kov \cdot ([C] - [C]e) ... (1)$$

\*therefore, kov = $kr \cdot V / (60 \cdot A)$

$kr$: total reaction rate coefficient (1/min), kov: overall reaction rate coefficient (cm/s)

A: metal surface area ($cm^2$), V: volume of metal ($cm^3$)

$[C]$: carbon content in the metal (mass%), $[C]e$: equilibrium carbon content ($\equiv 0$)

$[Cr]o$ (mass%) is the initial chromium content in the 12 kg-scale and 600 kg-scale experiments. $P$ (Pa) is the experimental pressure in the 7 t-scale experiment.

In addition, the gas metal interfacial area A (without argon bubbling) is estimated by parabolic shape fitting of convex height at the center position of a metal-free surface that is affected by electromagnetic effects.\(^27\) In the case of the 12 kg-scale experiment, the estimated value is 138 $cm^2$; and in the 600 kg-scale experiment, the A is calculated to be 1 230 $cm^2$. On the other hand, interfacial area in the 7 t-scale and 600 kg-scale experiments with argon bubbling cannot be estimated because there is no standard shape, so only the reaction rate coefficient values $kr$ (1/min) are listed.

As described above, the following experimental results were obtained under a no-CO-boiling condition. Activity of oxygen and carbon decreases with chromium content significantly, so CO boiling was not observed in high-chromium steel experiments.

The CO boiling was observed only in the beginning of

\[\begin{array}{cccccccc}
\text{ch.No} & 17Cr-1 & 17Cr-2 & 17Cr-3 & 17Cr-4 & 17Cr-5 & 17Cr-6 & 24Cr-1 & 24Cr-2 \\
[Cr]o \text{ (mass%)} & 17.2 & 17.2 & 17.6 & 17.0 & 17.5 & 17.6 & 24.0 & 24.0 \\
[O] \text{ ave} \text{ (ppm)} & 152 & 154 & 160 & 178 & 84 & 84 & 185 & 153 \\
kr \text{ (1/min)} & 0.0582 & 0.0475 & 0.0603 & 0.0602 & 0.0329 & 0.0283 & 0.0365 & 0.0627 \\
kov \text{ (cm/s)} & 0.0120 & 0.0098 & 0.0125 & 0.0125 & 0.0068 & 0.0059 & 0.0076 & 0.0130 \\
\end{array}\]

7 t-scale experiment ($F_{Ar} = 15 Nl/min$)

\[\begin{array}{cccccccc}
\text{ch.No} & 7t-1 & 7t-2 & 7t-3 & 7t-4 & 7t-5 & 7t-6 & 7t-7 & 7t-8 \\
P \text{ (Pa)} & <133 & 266 & 2660 & 6650 & 3300 & 26000 & 10100 & 557 \\
[O] \text{ ave} \text{ (ppm)} & 482 & 512 & 402 & 184 & 583 & 604 \\
kr \text{ (1/min)} & 0.0512 & 0.0403 & 0.0402 & 0.0463 & 0.0321 & 0.0384 & 0.0213 & 0.0111 \\
\end{array}\]

600 kg-scale experiment (<133 Pa)

\[\begin{array}{cccccccc}
\text{ch.No} & 17Cr0L & 17Cr1L & 17Cr2L & 17Cr4L & 0Cr0L & 0Cr2L \\
[Cr]o \text{ (mass%)} & 17.1 & 17.4 & 17.4 & 17.3 & – & – \\
[O] \text{ ave} \text{ (ppm)} & 290 & 346 & 216 & 184 & 583 & 604 \\
kr \text{ (1/min)} & 0.0228 & 0.0302 & 0.0793 & 0.0994 & 0.0177 & 0.0399 \\
kov \text{ (cm/s)} & 0.0243 & – & – & – & 0.0188 & – \\
F_{Ar} \text{ (Nl/min)} & 0.0 & 1.0 & 2.0 & 4.0 & 0.0 & 2.0 \\
\end{array}\]
highly reduced pressure conditions (<133 Pa) in the 600 kg-scale experiment, and obtained data with CO-boiling was cancel outed from examination data. The oxygen content in the present experiments was 460–670 ppm, and carbon content of samples after cessation of CO boiling was about 30 ppm. Therefore, supersaturation CO partial pressure of present experiments was estimated to be about 6–8 (kPa). This value is in agreement with those reported in previous studies.\textsuperscript{2–5)}

3.1. 12 kg-scale Experiment
The advanced examination in the different pressure condition (about 650 Pa) using 17mass\%Cr steel showed there was no difference of carbon removal rate in the high reduced pressure condition. Therefore, present experimental results can be treated as mixing rate determined, without accounting for any CO mass transfer effect.

Figures 1 and 2 show the change in carbon content from the 12 kg-scale experiment and the data is linearly fit according to Eq. (1). Figure 3 shows the relation between the kov value and average oxygen content. In this figure, open circles are the experimental results for low-alloy steel experiments using same experimental apparatus.\textsuperscript{8)}

3.2. 7 t-scale Experiment
Figure 4 shows the change in the carbon content for several pressure conditions.

The straight lines were obtained by numerical fitting based on the first-order reaction rate as per Eq. (1). Figure 5 shows the relationship between experimental pressure and kr (1/min). Reaction rate is observed to increase with pressure reduction.

This result can be considered as occurring for the following reasons: 1) promotion of CO molecule mass transfer in the gas phase boundary layer, 2) increasing CO absorption into the argon bubbles, and 3) expansion of surface area by bubble expansion.

However, there is no acceleration effect in low pressure
region (<2.660 Pa), so the result suggests that even in the highly reduced pressure condition, injected bubbles should burst at a 40 mm depth (metal weight stress ≈ 2 660 Pa).

3.3. 600 kg-scale Experiment
Figures 6 and 7 show the change in the carbon content of low alloy steel and 17 mass%Cr steel, respectively. Straight lines in these figures are obtained by first-order reaction rate fitting, as previously described. The relationship between argon bubbling flow rate and kr is shown in Fig. 8. Carbon removal rate is promoted by increasing the argon bubbling flow rate significantly, and its effects appear to be on the same order in both experiments.

4 Discussion
4.1. Effect of Surface Active Element
As described in section 1, a kinetic study on the effects of surface active elements (oxygen and sulfur) showed that not only nitrogen removal but also decarburization reaction, are affected by the obstruction effect.7–9) In their reports, the value of adsorption coefficient of oxygen (κo) is much higher than that of sulfur (κs), and this is in agreement with several former studies of the nitrogen removal phenomenon.

Because the decarburization reaction occurs via reaction between oxygen and carbon, oxygen is a necessary element for carbon removal. Moreover, it is quite difficult to carry out the decarburization experiment at low oxygen activity conditions without considering oxygen mass transfer as the rate-determining step, because the quantitative analysis limit is not reliable at the lower carbon content region of previous studies.

The effect of chromium alloy on the main physical properties (density, viscosity, and surface tension) of molten steel is not significant at lower than 25 mass% content.28) In addition, Choh et al.29) showed the effect of chromium content on the mass transfer coefficient of impurity by considering the study of Pehlke et al.30) Following their conclusion, the effect of chromium content on the mass transfer coefficient can be considered as a minor factor under the present experimental conditions. Furthermore, the adsorption coefficient of chromium is much lower than that of oxygen or sulfur,29) so chromium atoms do not affect the surface active element significantly.

On the other hand, activity coefficients of oxygen and carbon (fo and fc) calculated by the interaction parameter (εOCr = –0.0519, εCCr = –0.023, λOCr,Cr = 0.0005831) are much lower than the low alloy steel’s value (∈1.0). Therefore, one of the features of the present study is the quantitative estimation of oxygen adsorption effect at low oxygen activity conditions.

Figure 9 shows the relation between average oxygen activity and kov (cm/s) obtained by each experiment, instead of Fig. 3. In Fig. 9, kov values are plotted against oxygen activity, and the area surrounded by the dotted line...
indicates the estimated value from low alloy steel experiments.\textsuperscript{8) } kov values obtained from high-chromium experiments (solid points) can be considered as extrapolated from the area.

The overall reaction coefficient (kov: cm/s) can be obtained from the mixing rate determination equation, and expressed by following equations:

\begin{align}
&\text{mass transfer rate in the molten steel}\nonumber \\
&-d[C]/dt = 60 \cdot A / V \cdot km \cdot |[C] - [C]^*| \tag{2} \\
&\text{chemical reaction rate at the surface}\nonumber \\
&-d[C]/dt = 60 \cdot A / V \cdot kc \cdot ac^* \cdot ao = 60 \cdot A / V \cdot kc \cdot fc[C]^* \cdot fo[O] \tag{3}
\end{align}

km: mass transfer coefficient of carbon in the metal (cm/s)

[C]: carbon content in the bulk (mass%)

[C]^*: carbon content at the surface (mass%)

ac*: activity of the carbon at the surface (Henry’s 1 mass% standard(-) (=fc[C]^*)

ao: activity of oxygen in the bulk (Henry’s 1 mass% standard(-) (=fo[O]))

km value is estimated as 0.048 cm/s, which is evaluated by considering several induction furnaces.\textsuperscript{7) }

Then, in this experiment, the oxygen content is much higher than the sulfur content, so for the estimation of the chemical reaction rate coefficient at the surface, kc (cm/mass%) only the oxygen effect was considered. The estimated value from low alloy steel experiments for the chemical reaction rate coefficient is expressed as follows (by Eq. (4)).\textsuperscript{8) }

\begin{equation}
kc = kro / (1 + kO \cdot ao)^2 \tag{4}
\end{equation}

kro: ideal pure iron chemical reaction rate coefficient 40 (cm/mass%·s)

kO: oxygen adsorption coefficient 100–300(-)

Based on Eqs. (2) and (3), [C]^* (which cannot be measured) is canceled by simultaneous equation, and the reaction rate of carbon can be expressed by following equation:

\begin{align}
&-d[C]/dt \\
&= 60 \cdot A / V \cdot (kc \cdot km \cdot fc \cdot fo[O]) / (km + kc \cdot fc \cdot fo[O]) \cdot [C] \tag{5} \\
&= 60 \cdot A / V \cdot kov \cdot [C]
\end{align}

4.2. Consideration of Scale Factor

In Fig. 7 (kr value in the 600 kg-scale experimental result), the total reaction rate coefficients without argon bubbling are obtained. As described in section 3, the sulfur content is lower than 40 ppm, and this amount is significantly lower than the oxygen content. However in the case of the high-chromium experimental condition, the reduction in the activity coefficient of oxygen is lower than that of sulfur (in the case of 17 mass%Cr steel, fo = 0.19, fs = 0.67). On the other hand, Harashima et al. showed that the adsorption coefficient of sulfur is much lower than that of oxygen (ks = 63.4, kO = 161).\textsuperscript{8) } In the present experimental conditions, adsorption effects estimated by the above factors indicate that the effect of sulfur is not higher than 25% of that of oxygen, so the surface active element is considered to be only oxygen, as in the case of the 12 kg-scale experiment.

Choh et al. showed the experimental study using a small induction furnace (ID = 38 mm). The kinetic analysis was applied penetration theory by the following equations:\textsuperscript{29) }

Us = 1 / (2(2 · g · h)\frac{1}{2}) \tag{6}

\begin{equation}
kv = 2(Dx \cdot Us / \pi \cdot r)^{\frac{1}{2}} \tag{7}
\end{equation}

Us: typical metal surface velocity (m/s)

g: gravity (9.8 m/s²)
h: convex height of surface center position (m),

kv: mass transfer coefficient of x (m/s)

Dx: diffusion constant of x (m²/s)

r: radius of crucible (= 0.19 m)

The 600 kg-scale experiments were carried out using a large crucible (ID = 380 mm) and measured value of h, obtained by rod dipping test, was 0.015 m. Then, the estimated value of the mass transfer coefficient with the above penetration theory becomes 0.0148 (cm/s). Therefore, the calculated carbon removal coefficient kov using Eqs. (4) and (5) becomes 0.00733 (cm/s) for the low alloy steel and 0.00854 (cm/s) for the 17 mass%Cr steel. However, experimental results (Table 3) obtained without the argon bubbling condition gave 0.0188 (cm/s) for the low alloy steel and kov = 0.0243 (cm/s) for 17 mass%Cr. Consequently, experimental results cannot be explained by the penetration theory, because present experiments were carried out under turbulent conditions.

To account for this, the surface renewal theory was applied for estimation of the present experimental results. Kataoka et al. showed the equation for estimation of mass transfer coefficients under turbulent conditions based on the results of cold model experiments and former theoretical analysis, giving Eq. (10):\textsuperscript{32) }

\begin{equation}
km = (Dc \cdot Us^3 \cdot \rho_m / \sigma)^{\frac{1}{2}} \tag{8}
\end{equation}

ρ_m: molten steel density (= 7000 kg/m³),

σ: surface tension (= 1.6 N/m)

Dc: diffusion coefficient of carbon (= 1.2 \times 10^{-8} m²/s)

The calculated result of kov under turbulent condition using Eq. (8) is 0.102 (cm/s), so calculated results by substitution using Eqs. (4) and (5) and experimental conditions for 600 kg-scale experiment are as follows: low alloy steel: kr = 0.0127 (cm/s) and 17 mass%Cr steel: kov = 0.0169 (cm/s).

Figure 10 shows the relationship between the measured values of kov and calculated values, kovcal, by using Eq. (5), where the kO value is selected as the center value of 200(-). In this figure the kovcal value of the 600 kg-scale experiment was the estimated result from the above surface renewal theory. As shown in this figure, good correlation can be obtained, as its standard deviation is 0.0023(cm/s) (around 10% of the experimental value).

Additionally, Fig. 11 shows the relationship between kr (cm/s) and calculated kov (cm/s). Open symbols on the plot signify the result of 600 kg-scale experiments without argon bubbling (A = 1230 cm², V = 78 570 cm³). It should be apparent that the kO value should not increase more than this experimental stirring condition because estimated kov value does not increase with increasing kO value. Therefore, the reaction rate is controlled only by the chemical reaction rate at the metal surface under strong stirring conditions, and, moreover, significant promotion of carbon removal rate
can be obtained by increasing argon flow rate (see Fig. 8) as a result of the surface expansion effect.

4.3. Evaluation of Reaction Site Contribution under Highly Reduced Pressure with Argon Bubbling Conditions

As described in section 3.2, the bubble bursting depth can be estimated at a shallow bath position (within 40 mm depth). In this section, CO absorption effect in the total reaction rate is discussed.

The maximum adsorbing volume of CO can be estimated as per the CO saturated condition (CO partial pressure in the metal $P_{\text{CO}}$ in the bubble at 40 mm depth).

$$\text{CO} + \text{O} \rightarrow \text{CO}_2$$ (9)

Therefore, CO partial pressure in the metal is expressed by Eq. (10)

$$P_{\text{CO}} = \frac{P_{\text{CO}} \cdot \rho \cdot g \cdot h}{V_{\text{CO} \text{gas}} \cdot V_{\text{Ar}}}$$ (10)

By using preceding equations, CO saturation ratio ($\eta_{\text{Ar}}$) can be defined at the bubble bursting position, and carbon content change estimated using a fixed $\eta_{\text{Ar}}$ value.

The carbon removal reaction can be expressed as follows:

$$\eta_{\text{Ar}} = \frac{P_{\text{CO in bubble}}}{P_{\text{CO in metal}}} = (P_0 + \rho \cdot g \cdot h / 1000)$$

$$V_{\text{CO}} / (V_{\text{CO} + V_\text{Ar}}) / (\text{fc} \cdot \text{for} \cdot [\text{C}] \cdot [\text{O}] \cdot 10^{1.60/2.003}) \cdot 101 \cdot 300$$

$$P_{\text{CO in bubble}}: \text{CO partial pressure in the argon bubble at depth} = h$$

$$P_{\text{CO in metal}}: \text{CO partial pressure of molten steel}$$

$P_0$: pressure in the metal surface (Pa),

$\rho$: density of molten steel (7 000 kg/m$^3$)

$V_{\text{CO}}$: CO gas volume absorbed at bubble bursting position (l/min)

$V_{\text{Ar}}$: argon gas volume at bubble bursting position (l/min)

Figure 12 shows this concept schematically.

In Fig. 13, change in the carbon content of 17 mass%Cr steel (experimental data) and maximum carbon reaction rate by CO saturated argon bubbles ($\eta_{\text{Ar}}=1.0$, $h=40$ mm) at an argon flow rate of 4 (Nl/min) are shown. The estimated lines were fit for a first order reaction rate coefficient, $k_{\text{r bub}}$ (1/min), the value of which indicates the maximum reaction
rate into the argon bubble. Therefore, the bubble reaction rate cannot exceed 30% of total reaction rate, and almost all contributions to reaction rate should be from surface reaction effect.

As shown in Fig. 8, the reaction rate with argon bubbling is promoted by an increase in the flow rate, and, as described before, mass transfer of carbon does not lead to an increase in the reaction rate. Further, in the argon bubbling experimental conditions, the surface area can be estimated as same between low alloy steel experiments and 17 mass%Cr steel experiments for the same argon bubbling flowrate.

Consequently, for not only 17 mass%Cr steel but also the low alloy steel, the major factor of reaction promotion by argon bubbling condition is estimated by the surface area expansion of the bubble bursting effect, and this result is almost in agreement with former studies.

5. Conclusion

The carbon removal rate in the low-carbon-content region was examined using a vacuum induction furnace (12 kg-scale, 600 kg-scale, and 7 t-scale); based on experiments and theoretical examination, the following results were obtained:

Adsorption element effects in the decarburization reaction were thoroughly examined by performing previously reported experiments involving high-chromium steel and low alloy steel by using a 12 kg-scale induction furnace. As a result, the carbon removal rate was well expressed by using a chemical reaction model. Moreover, by using this estimation method, the reaction rate for different scale experimental conditions can also be well predicted.

Argon bubbling experiments using a 7 t-scale vacuum induction furnace showed that bubble bursting under highly reduced pressure conditions can be considered to take place at the shallow depth of 40 mm.

Further, the results of kinetic examination in the 600 kg-scale experiments demonstrated that a major factor for the reaction promotion in both 17 mass%Cr steel and low alloy steel can be estimated by the surface expansion of bubbles, and that the mass transfer promotion factor is not effective factor.

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