Decarburization and Denitrogenization of Iron and Iron-Chromium Alloys by Plasma Jet of Hydrogen-Argon Gas Mixture*

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Synopsis

Trials to enhance decarburization and denitrogenization of molten iron-chromium alloys were made by blowing plasma jet of hydrogen-argon gas mixtures onto the melt surface. The weight of melts was 1 to 3 kg, the gas blowing rate 8 l/min and the electric power consumption 15 to 30 kVA. The final concentrations of carbon and nitrogen obtained were as follows: $\underline{C} < 0.002\%$ for Fe, 18-8 stainless steel, 60%Cr-Fe alloy and Cr; $\underline{N} = 0.0015\%$ for Fe and $\underline{N} = 0.0065\%$ for 25%Cr-Fe alloy, values that would satisfy the known requirement for good intergranular corrosion resistance and ductility for ferritic stainless steel of $\underline{C} + \underline{N} < 100$ to 130 ppm.

By estimating the degree of dissociation of hydrogen in plasma jet at the metal interface, it was indicated that those hydrogen atoms in the plasma which were not thermally recombined into molecules should react with carbon and nitrogen in the molten metal. The mechanisms of decarburization and denitrogenization were also discussed.

I. Introduction

The use of high temperature plasma jet for practical refining of metals is receiving increasingly greater attentions.¹⁻⁴⁾ The plasma jet which produces very high temperatures is advantageous for: (1) melting of not only refractory metals but ordinary iron and steel owing to its high efficiency of heat conduction to the melt, (2) acceleration of the reaction rate of refining at the high temperatures achieved, and (3) enhancement of the chemical reaction which could not otherwise occur.

The authors have interested themselves in the fundamental studies on the refining of iron-chromium alloys by plasma jet of hydrogen-argon gas mixtures impinging on the melt surface. The most important characteristics of the hydrogen plasma refining are that hydrogen atoms in the plasma which are still dissociated and not yet thermally recombined to molecules at the reaction interface of the melt should react with impurities such as carbon, nitrogen or oxygen in alloys, and that the loss of alloying elements caused by oxidation in the conventional oxidation refining process should be prevented thanks to the reducing atmosphere. On the other hand, the removal of carbon and nitrogen from iron-chromium alloys down to a very low level without loss of chromium is very important to ensure good intergranular corrosion resistance and ductility for ferritic stainless steels.⁵⁾

In the present paper, the results of decarburization and denitrogenization of iron-chromium alloys by plasma jet of hydrogen-argon gas mixtures and of decarburization of iron by plasma jet of carbon-dioxide-argon gas mixtures will be described and dis-

cussed.

II. Experimental Apparatus

The reaction chamber for the plasma jet refining is shown schematically in Fig. 1. Argon was purified by flowing through calcium chrolide, then through a sponge titanium furnace heated at 850°C, while hydrogen by a hydrogen diffusion unit of the silver-paradium alloy. The cathode tip of the plasma torch was made of a tungsten rod of 5 mm diameter containing 1 to 2% thorium-oxide. The copper nozzle of the torch had a diameter of 5 to 6 mm, and was exchangeable when damaged. The plasma jet was generated between the tungsten-cathode and the metal in crucible serving as the anode at a nominal output of the rectifier of 40 kVA. The pillar of plasma arc was stable in 6 to 8 mm diameter. A copper pipe of 10 mm diameter was attached to the bottom of the crucible for electric contact with the metal.

A magnesia crucible of 85 mm of inner diameter was used for a 2 to 3 kg melt, and a 65 mm one for 1 kg. A pair of 30%Rh/Pt-6%Rh/Pt thermocouple was placed 5 mm inside of the crucible wall, so that the temperature indicated was approximately 150°C

Fig. 1. Reaction chamber equipped with plasma torch and crucible

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lower than the true temperature of the melt.

When denitrogenization to yet lower levels was intended, a water-cooled copper mold was used because the final nitrogen contents refined in the magnesia crucible were limited to 50 ppm for iron and 110 ppm for 25%Cr ferroalloy, presumably owing to the air remaining in the stamped magnesia powders. In this case, however, only a melt pool of about 1.0 kg and 20 mm depth was obtained out of the 4 kg metal charge that was put into the copper mold.

III. Experimental Procedure

Electrolytic iron and chromium were heated first by blowing the argon plasma jet onto the metal. As the metal began to melt, the hydrogen-argon gas mixture was used in place of argon for possible removal of impurities in metal. When the metal was perfectly melted and the desired temperature reached, the initial concentrations of carbon and nitrogen were adjusted by adding graphite powders while stirring the melt mechanically or by blowing nitrogen gas onto the melt.

Immediately after this treatment, the decarburization or the denitrogenization was started with the plasma jet of hydrogen-argon gas mixture of a given composition. The flow rate of the gas was fixed at 8 l/min, and the partial pressure of hydrogen was varied from 0.052 to 0.8 atm.

The operational conditions at various hydrogen partial pressures are presented in Table 1 with the indicated temperatures. The power necessary to maintain the 1 kg metal pool out of 4 kg in the copper mold was 80 to 100 V and 300 to 400 A. When the plasma jet was impinged on the melt, a cavity of about 5 mm deep and 10 mm wide appeared at the impingement point, and it was observed that the melt was fairly well stirred.

For the chemical analysis a 10 to 20 g metal was taken by sucking into a quartz tube. Carbon and nitrogen in metal were determined by the coulometric titration method and the Kjeldahl method, respectively. The accuracies of analysis were within ± 6 ppm for carbon and ± 7 ppm for nitrogen.

IV. Experimental Result

1. Decarburization by H₂-Ar Plasma Jet

The results of decarburization of iron in the mag-

nesia crucible are shown in Fig. 2 for various hydrogen partial pressures. The weight of melts was 3 kg except for $p_{H_2}=0.5$ atm where it was 3.6 kg. The carbon concentration decreased from 0.5% to 0.1% within 20 min at $p_{H_2}=0.8$ and 0.65 atm, while 70 min were needed to decarburize from 0.3% to 0.1% at 0.1 atm. The rate increased with increasing hydrogen partial pressure, and for each hydrogen partial pressure it remained constant regardless of the carbon concentration in high carbon range but decreased gradually below about 0.3% carbon.

Figure 3 shows the results of 18-8 stainless steel at different hydrogen partial pressures. A 3 kg metal was melted in the magnesia crucible and the temperature was about 1 700°C. The rate was independent of the hydrogen partial pressure, and the carbon in metal was lowered from 0.15% to 0.002% within 100 min.

The results for 60%Cr-Fe alloys at different partial pressures are shown in Fig. 4 at about 1 750°C. Carbon decreased irrespective of the hydrogen par-

Fig. 2. Decarburization curves of iron by hydrogen-argon plasma with various partial pressures

Fig. 3. Decarburization behaviors of 18-8 stainless steel by hydrogen-argon plasma

Table 1. Operating conditions of plasma jet at various hydrogen partial pressures and temperatures of molten iron

p_{H_2} (atm)	Voltage (V)	Current (A)	Output (kVA)	Temperature (°C)
0.1	68	180	12.2	1 650
0.2	70	200	14.0	1 660
0.35	76	250	19.0	1 590
0.5	84	190	16.0	1 670
0.65	90	220	19.8	1 620
0.8	78	280	21.8	1 640

tial pressure from 0.08% to 0.002% within 130 min. The rate was comparatively smaller than the case of 18-8 stainless steel.

The electrolytic chromium ($C=0.007\%$) was decarburized at $p_{H_2}=0.75$ atm using the water-cooled copper mold. An electric power of 87 V and 355 A was supplied to the metal, producing 1 kg melt pool out of 4 kg. The carbon content of the melt decreased to 0.004% after 10 min and to 0.002% after 30 min.

2. Denitrogenization by H_2 -Ar Plasma Jet

The denitrogenization behaviors of iron melted in the magnesia crucible are shown in Fig. 5 for various hydrogen partial pressures. The weight of melt was 2 kg and the temperature was about 1 600°C. The denitrogenization proceeded even with a plain argon plasma jet, but it was accelerated with increasing hydrogen partial pressure and reached a constant beyond 0.1 atm. The rate was also dependent on the nitrogen content of the melt. Nitrogen was removed from 0.04% to the final concentration of 0.005% within 10 min. The result of the final concentration

Fig. 4. Decarburization behaviors of 60%Cr-Fe alloy by hydrogen-argon plasma

Fig. 5. Denitrogenization curves of iron by argon and hydrogen-argon plasmas with various partial pressures

refined in the copper mold is presented in Table 2. Nitrogen was lowered from 0.005% to 0.0015% within 10 min.

Figure 6 shows the results of 25%Cr-Fe alloy at different hydrogen partial pressures. The rate was independent of the hydrogen partial pressure, but dependent on the nitrogen concentration of the melt. Nitrogen was decreased from 0.04% to the final concentration of 0.011% within 20 min. Taking account of the findings of Ban-ya, *et al.*⁶⁾ that the denitrogenization did not proceed under flowing argon when the chromium content of alloy exceeded 12% and also considering that the denitrogenization by the reaction of nitrogen in metal with molecular hydrogen is thermodynamically hard to proceed, the present results prove that hydrogen plasma effectively work for the denitrogenization of high chromium alloys. The result in the copper mold is also presented in Table 2: nitrogen was removed from 0.011% to 0.0065% within 40 min.

In Fig. 7, the results of 60%Cr-Fe alloy melted in the magnesia crucible are shown for different hydrogen partial pressures. The rates were greatly dependent both on the hydrogen partial pressure and on the concentration of nitrogen. The time required to denitrogenize from 0.15% to the final concentration of 0.04% was 30 min at $p_{H_2}=0.7$ atm, whereas 60 min was needed at 0.5 atm.

3. Decarburization by CO_2 -Ar Plasma Jet

Iron of 720 or 840 g was melted at 1 600°C in a magnesia crucible of 65 mm inner diameter. The oxidation of tungsten-cathode of the torch was so serious that the experiments at higher carbon-dioxide partial pressures were discontinued.

	N_{lowest} (ppm)	$N_{initial}$ (ppm)	Refining time (min)	p_{H_2} (atm)
Fe	15	50	10	0.75
25%Cr ferroalloy	65	110	40	0.75

Fig. 6. Denitrogenization curve of 25%Cr-Fe alloy by hydrogen-argon plasma

Fig. 7. Denitrogenization curves of 60%Cr-Fe alloy by hydrogen-argon plasma with various partial pressures

Fig. 8. Decarburization curves of iron by carbon-dioxide-argon plasma with various partial pressures

The results are shown in Fig. 8 for different carbon-dioxide partial pressures. The decarburization rate is proportional to the partial pressure, and if the decarburization can be assumed to proceed by the chemical reaction $\text{CO}_2 + \text{C} = 2\text{CO}$, the utilization efficiency of carbon-dioxide is 100% in the high carbon concentration range above 0.08%.

V. Discussion

1. Estimation of Reaction Products and Reaction Temperatures by Thermodynamic Consideration

When a hydrogen-argon gas mixture is ionized in the plasma jet, it reaches a temperature of higher than 10 000°C, when hydrogen exists as atom or ion.⁷⁾ However, when the jet is impinging on the melt surface, where the temperature is relatively low, it is unlikely that the hydrogen will reach the metal surface in the ionic state. At the interface of the melt, the temperature of gas drops rapidly and further, the positively charged ion will be repelled and neutralized by the metal which acts as an anode. Therefore, it must be considered that hydrogen will participate in

Fig. 9. Partial pressures of possible product gases on decarburization for $h_{\text{C}} = 0.2$ (0.2% C for iron)

the interfacial reaction as atom or molecule.

Provided that the atomic hydrogen participates in the reaction, the species of possible gaseous product of the decarburization must be such hydrocarbons as CH , CH_2 , CH_3 , CH_4 , C_2H_2 , etc. Figure 9 shows the relation between temperature and partial pressures of these gases with p_{H} as a parameter, calculated on thermodynamic data for these reactions^{8,9)} with $h_{\text{C}} = 0.2$ ($\text{C} = 0.2\%$ for iron).

In the case of $p_{\text{H}} = 0.1$ atm, CH_4 has the highest partial pressure below 2 670K, and the partial pressures of CH_3 , C_2H_2 , CH_2 and CH decrease in this order. The ratio of p_{CH_4} to other molecules increases with increasing p_{H} , and at $p_{\text{H}} = 0.9$ atm p_{CH_4} becomes the highest below 3 000K. The partial pressure of CH_4 calculated by assuming that carbon in metal should react with the molecular hydrogen is also shown in Fig. 9 for $p_{\text{H}_2} = 0.8$ atm. Obviously this partial pressure is far lower than the pressures which are calculated on the basis of atomic hydrogen.

The circular marks in Fig. 9 are the partial pressures of product gas estimated from the measured decarburization rate using the following equation:

$$p_{\text{CH}_4} = (d\text{C}/dt) \cdot (22\,400/Q) \cdot (T/273)$$

assuming a molecule of product gas has one carbon atom, where $d\text{C}/dt$ (mol/min) is the measured decarburization rate, Q (8 000 cc/min) is the gas flow rate, $T = 300\text{K}$ and at $\text{C} = 0.2\%$. These values are never lower than the actual partial pressures at the metal interface. In plotting the marks in Fig. 9, the hydrogen partial pressures at the reaction interface p_{H}^*

are assumed to be $p_H^\circ - 4p_{CH_4}$, where p_H° is the partial pressure which fully dissociated hydrogens would have under the total pressure of 1 atm.

Naturally the actual p_H would be lower owing to the partial recombination of hydrogen atoms, and so the temperature be lower than that estimated above. In other words, the temperature of 2 300 to 2 350K should be regarded as the maximum estimation. Further, because the temperature of the cavity on the melt surface right under the jet is probably higher than this estimation, this temperature should be interpreted as the mean temperature of the whole reaction zone including the cavity. Thus the estimated mean temperature, *i.e.*, that which does not exceed 2 350K, seems not very wrong from the observation that the melt never boils even at the plasma impingement area.

From the discussions stated above, it will be safe to say that the reactant gas is not hydrogen molecules but atoms. This means that hydrogen atoms in the plasma react directly with carbon in metal, freezing the recombination reaction $2H \rightarrow H_2$. The main product species is most possibly CH_4 , though it will depend on the hydrogen partial pressure and the reaction temperature. No confirmation of this by gas analysis was attempted in the present research, however, because CH_4 being more stable at lower temperatures, the gas composition would have inevitably changed during cooling. It would appear, therefore, that, at the present time at least, because of the limitations of experimental technique, the thermodynamic estimations should give more precise and reliable information on the plasma reactions.

The thermodynamic calculations for denitrogenization was made similarly to decarburization as presented in Fig. 10. Among the possible gaseous products of NH , NH_2 and NH_3 , the species which shows the highest partial pressure is NH_3 under any condition. However, in this case, attentions must be paid to the formation of molecular nitrogen ($2N=N_2$) which is also possible to occur. The calculated partial pressures of the nitrogen molecule are presented together in Fig. 10.

Comparing the partial pressures of each molecule in this figure, the relation $p_{N_2} > p_{NH_3}$ holds above 2 100K at $p_H=0.1$ atm and above 2 400K at $p_H=0.5$ atm, both for $h_N=0.02$ ($N=0.02\%$ for iron). Thus, it is apparent that the main product for iron is the molecule N_2 near the jet impingement area, and the formation of NH_3 contributes slightly to denitrogenization as p_H increases.

On the melt surface apart from the plasma impinging spot, on the other hand, it is reasonable that hydrogen atoms should no longer be dissociated but are recombined to molecules, so that nitrogen is removed as N_2 as the usual denitrogenization under inert gases. Consequently, the condition to form NH_3 is not satisfied.

As for the case of 60%Cr-Fe alloy, the relation $p_{NH_3} > p_{N_2}$ below 2 200K at $p_H=0.1$ atm and below 2 530K at 0.5 atm, both for $h_N=0.002$ ($N=0.1\%$ for

Fig. 10. Partial pressures of possible product gases on denitrogenization for $h_N=0.02$ (0.02%N for iron) and 0.002 (0.1%N for 60%Cr-Fe alloy)

60%Cr-Fe alloy), was obtained as shown in Fig. 10. This critical temperature becomes higher with increasing p_H and with decreasing h_N . In view of the temperature of the plasma impingement spot of about 2 400 to 2 600K estimated from the foregoing decarburization results and also by the fact that the denitrogenization does not occur under argon atmosphere, it is believed that only the formation of NH_3 contributes to the denitrogenization of 60%Cr-Fe alloy.

In the case of 25%Cr-Fe alloy, both N_2 and NH_3 have the possibility to be the reaction products in the present condition of $h_N=0.004$ ($N=0.04\%$ for 25%Cr-Fe alloy).

2. Discussion of Reaction Mechanism

The following discussions of the reaction mechanism are restricted by lack of precise knowledge of the reaction interface, the reaction temperature and the degree of dissociation of hydrogen. In the present investigation of the plasma jet refining, further, strictly controlled experiments to elucidate the reaction mechanism could not be made because the proportion of hydrogen in the working gas could not be changed without changing the power consumption. Therefore, many of the numerical values used in calculations are necessarily assumed ones.

The gas-metal reaction is generally rate-controlled by one or combination of the steps of (1) mass transfer on the gas side, (2) chemical reaction and (3) mass transfer on the metal side. Of these steps, the step of chemical reaction including the recombination reaction of hydrogen atoms which are unstable at lower temperatures can be very fast at sufficiently high temperatures. Therefore, this step was left out of consideration unless it became indispensable in interpreting the results.

1. Reaction of Decarburization

(1) Decarburization of Iron

(i) Mass Transfer on the Gaseous Side

From the results of the sublimation rate of naphthalene blown with nitrogen gas and subsequently of the combustion rate of graphite by CO_2 , Taniguchi, *et al.*¹⁰⁾ obtained empirical equations for the mass transfer rate of the gas jet. Their equations are modified and expressed by Eq. (1) for easier application to the present conditions.

$$Sh = (0.0537 \sim 0.0839) \cdot Re \cdot Sc^{0.5} \cdot (r/d)^{-0.25} \cdot (H/d)^{-0.5} \quad \dots\dots\dots (1)$$

where, $Sh = (kd/D)$

$$Re = (\rho u d) / \mu$$

$$Sc = (\mu / \rho D)$$

k : mass transfer coefficient (cm/sec)

D : diffusion coefficient (cm^2/sec)

μ : viscosity (poise)

u : gas velocity (cm/sec)

ρ : density of the gas (g/cm^3)

H : distance between nozzle tip and metal surface (cm)

d : representative length, here, the nozzle diameter (cm)

r : radius of the reaction zone of the melt (cm)

As the area of reaction is not known in the application of Eq. (1), the calculation was made with r as a variable, and with $H=2.5$ cm, $d=0.5$ cm, $p_{\text{H}_2}=0.5$ atm, the gas flow rate 8 l/min (300K) and $T=2400$ K. The hydrogen was assumed to be fully dissociated, and values of $p_{\text{H}}=0.66$ atm and $\rho=1.17 \times 10^{-4}$ g/cm³ were used. The diffusion coefficient $D=26.11$ cm²/sec and the viscosity $\mu=9.28 \times 10^{-4}$ poise were used for Ar-H₂ system. The gas velocity u is 6 000 cm/sec. Substitution of above values into Eq. (1) yields:

$$Sh = (3.81 \sim 5.96) \cdot r^{-0.25}$$

Then the quantity:

$$\dot{n}_{\text{H}} = (0.106 \sim 0.0165) \cdot r^{1.75} \cdot \Delta p_{\text{H}}$$

gives the mass transfer rate (mol/sec) of hydrogen atoms to the reaction surface πr^2 (leaving the particulars of the shape of the cavity out of consideration for the time being).

For the estimation of Δp_{H} the relation:

$$\begin{aligned} \dot{n}_{\text{H}} / \pi r^2 &= (k_{\text{H}} / RT) \Delta p_{\text{H}} = 4 \dot{n}_{\text{CH}_4} / \pi r^2 \\ &= 4 (k_{\text{CH}_4} / RT) p_{\text{CH}_4}^* = 4 \dot{n}_{\text{C}} / \pi r^2 \\ (k: \text{mass transfer coefficient}) \end{aligned}$$

is used, and this yields an approximate expression:

$$\Delta p_{\text{H}} = 4 (k_{\text{CH}_4} / k_{\text{H}}) p_{\text{CH}_4}^* = 4 p_{\text{CH}_4}$$

where, p_{CH_4} is the mean partial pressure of CH_4 in the waste gas previously calculated in V. I. by the measured decarburization rate.

The calculation from the measured value of $\dot{n}_{\text{C}} = 6.78 \times 10^{-3}$ mol/sec using this relation gives a radius

$r=1.1 \sim 1.5$ cm. The r , thus evaluated on the assumption that the rate-determining step be the mass transfer on the gaseous side, corresponds to the radius of the reaction zone, which is a little greater than 0.4 to 0.5 cm of the observed radius of the cavity formed by the plasma jet but far smaller than the crucible diameter of 4.25 cm, indicating that the reaction does not occur over the whole melt surface but is limited to near the jet impingement area.

This is in accord with the fact that the temperature of the impingement area is much higher than the average melt temperature and can be around 2 300 to 2 350 K as is previously estimated. Besides, the finding that the decarburization rate at high carbon concentration is independent of the carbon concentration (Fig. 11) strongly suggests that the mass transfer on the gaseous side be the rate-determining step in the range of these concentrations, a conclusion which is consistent with the ordinary conventional decarburizations by O_2 and CO_2 gases.

(ii) Mass Transfer on the Metal Side

To estimate the strength of stirring by the plasma jet in comparison with the non-plasma gas flow, equations due to Davenport, *et al.*¹¹⁾ and to Matsushima and Mori,¹²⁾ as expressed by Eq. (2), are used.

$$\dot{M} / \rho' g H = (\pi / 2 \alpha K^2) \cdot (L/H) \cdot (1 + L/H) \quad \dots\dots\dots (2)$$

where, $\dot{M} = (\pi/4) \rho u^2 d^2$: the jet momentum per unit time (g·cm/sec²)

ρ' : density of the melt (g/cm³)

g : gravitational acceleration (cm/sec²)

L : depth of cavity (cm)

K : jet constant depending on Re and assumed to be 6.2¹²⁾

α : energy loss ratio related to the shape of the cavity and assumed to be 0.36¹²⁾

Using the values for the non-plasma gas flow at $p_{\text{H}_2}=0.5$ atm, $\rho=1.17 \times 10^{-4}$ g/cm³, $u=5.44 \times 10^3$ cm/sec, $d=0.5$ cm, $\rho'=6.5$ g/cm³ and $H=2.5$ cm, the jet momentum $\dot{M}=6.78 \times 10^2$ g·cm/sec² and the depth of cavity for the non-plasma jet $L=0.14$ cm are obtained. This calculated depth is consistent with the observation. The momentum of the plasma jet was found 4 times as great as for the non-plasma jet for the

Fig. 11. Plots of the measured decarburization rates of iron against carbon concentration with various hydrogen partial pressures

observed depth $L=0.5$ cm. This enhanced momentum is a measure of the stirring effect by plasma.

The following is an estimation of the decarburization rate, assuming the mass transfer of carbon in metal is the rate-determining step, by applying the rate equation of the oxygen mass transfer in metal, derived by Matsushima and Mori,¹²⁾ who blew the oxygen jet onto the molten silver. They gave the equation for the apparent mass transfer coefficient k^* as:

$$k^* = 4.3 \cdot (L/R^*)^{2.5} \dots\dots\dots(3)$$

where, R^* is the radius at which the jet momentum is reduced to 1% of that at the center of metal surface and given as $R^*=1.07 \cdot K^{0.5} \cdot (H+L)$ with $K=6.2$. Then the decarburization rate $\dot{n}_C$ (mol/sec) is expressed as:

$$\dot{n}_C = \pi R^{*2} \cdot k^* \cdot \Delta C = 32.5 \cdot L^2 \cdot (L/(H+L))^{0.5} \cdot \Delta C \dots\dots(4)$$

where, ΔC is the concentration difference between the interface and the bulk (mol/cm³), and the reaction sites are assumed to be confined to the cavity. These equations yield $R^*=0.52$ cm using $H=2.5$ cm and $L=0.5$ cm, and $\dot{n}_C=7.2 \times 10^{-3}$ mol/sec using $\Delta C=0.4\%$ (2.2×10^{-3} mol/cm³).

The calculated $\dot{n}_C$ is larger than the maximum rate of 1.3×10^{-3} mol/sec at $p_{H_2}=0.8$ atm. If $L=0.3$ cm, for an observation error is inevitable, $R^*=0.5$ cm and $\dot{n}_C=2.1 \times 10^{-3}$ mol/sec are obtained, but the value for $\dot{n}_C$ is still larger than the measured rate, even though R^* is in accord with the observed radius (0.5 cm) of the cavity. However, the calculated value $\dot{n}_C$ would become larger, if the area of reaction were to be considered to extend to outside of the cavity.

Here, it is to be remembered that in applying the Eq. (4) to the present experiment, there are at least two factors that should have been taken into consideration but were not. Namely, the first factor is that the Schmidt number for the iron system is about 10 times larger than the silver system, and this would correct the calculation positively. On the other hand, the second factor, which would negatively correct, is that the ratio of the crucible radius to the melt depth is about half of the silver system so that in the present experiments the stirring was relatively insufficient in the bottom part of the melt. Besides, the difference of gas momentum used between the present work and Matsushima and Mori's should be taken into account.

In the later stage of the reaction below $\Delta C=0.3\%$, the decarburization rates are roughly proportional to the carbon concentration, so that Eq. (4) is applicable. It may safely be said then that the carbon mass transfer in metal takes part in the rate-determination in the low carbon range. However, the mass transfer in gaseous phase as mentioned above cannot be ignored because the dependence of the rate on hydrogen partial pressure was observed (Fig. 11). Accordingly, it is believed that the mass transfer in both gas and metal are important in the rate-determination of decarburization of the iron-carbon system.

(2) Decarburization of 18-8 Stainless Steel and 60%Cr-Fe Alloy

In case of 18-8 stainless steel, the mass transfer in metal may be the rate-determining step, since the decarburization rate is not dependent on the hydrogen partial pressure and the logarithm of the carbon content shows a linear relation to the refining time as illustrated in Fig. 12. The slope of the straight line is 0.017 min^{-1} , which is considerably smaller than the calculated values of 0.054 min^{-1} ($L=0.3$ cm) and 0.183 min^{-1} ($L=0.5$ cm) using Eq. (4), probably by the reasons described above. The diffusion coefficient of carbon for the Fe-Cr system, as estimated from the data of the solids,¹³⁾ could be about 40% of that for iron. Consequently, the mass transfer of carbon for the Fe-Cr-C system is expected to be slower than for the Fe-C system so that the contribution of the gaseous mass transfer may be negligible, contrary to the Fe-C system.

The decarburization of 60%Cr-Fe alloy is similar to that of 18-8 stainless steel, but the slope of the straight line in Fig. 12 shows 0.012 min^{-1} which is yet smaller than the value for 18-8 stainless steel due to decrease in the diffusion coefficient of carbon with increase in chromium content.

2. Reaction of Denitrogenization

(1) Denitrogenization of Iron

The reaction product of the denitrogenization of iron may be N_2 as already discussed in V.1. The reaction rates increased with increasing hydrogen partial pressure until it reached 0.1 atm and remained constant beyond that pressure (Fig. 5). Moreover, the relation between the logarithm of nitrogen content and refining time is linear as shown in Fig. 12. These facts indicate that the denitrogenization in the present experiment was retarded by the adsorbates such as oxygen which is removed as hydrogen partial

Fig. 12. Logarithms of the carbon and nitrogen concentrations against the refining time

pressure increases, and finally above 0.1 atm, it is controlled only by the nitrogen mass transfer in metal.

The calculation of the denitrogenization rate by use of Eq. (4), confining the reaction site within the cavity, yields 0.081 min^{-1} ($L=0.3 \text{ cm}$) and 0.275 min^{-1} ($L=0.5 \text{ cm}$). These values are not far different from the measured value of 0.097 min^{-1} under conditions of $p_{\text{H}_2} > 0.1 \text{ atm}$. But, if the reaction is taken to occur over the whole free surface of the melt, the rate constant, calculated on the basis of the formation of nitrogen molecules, becomes far larger than the measured.

(2) Denitrogenization of 25%Cr-Fe Alloy

The denitrogenization is independent of hydrogen partial pressure, and a linear relation between the logarithm of nitrogen content and refining time was obtained as shown in Fig. 12. The slope of the line is 0.018 min^{-1} which is smaller than that of iron, corresponding to the diffusion coefficient of nitrogen¹⁴⁾ lowered by an addition of chromium, *e.g.*, while the diffusion coefficient of 25%Cr-Fe alloy is about one third of iron, the observed rate is a fifth.

Both N_2 and NH_3 are possible as a product, but regardless of the product species the mass transfer of nitrogen in metal was found to control the reaction rate.

(3) Denitrogenization of 60%Cr-Fe Alloy

As described in *V.I.*, only NH_3 is the possible reaction product gas for 60%Cr-Fe alloy. The reaction rates decreased further compared with that of 25%Cr-Fe alloy and showed again dependency on the hydrogen partial pressure (Fig. 7). The final nitrogen concentration was not lower than 0.04%. The reaction rate calculated by Eq. (4), assuming the nitrogen concentration at the reaction interface 0.04% and taking account of nitrogen diffusion coefficient decrease, agrees fairly well with the measured value at $p_{\text{H}_2}=0.5 \text{ atm}$. The dependence of denitrogenization rates on the hydrogen partial pressure should be explained in such a manner that the higher p_{H} makes the concentration gradient for N diffusion greater, lowering the nitrogen concentration at the reaction interface.

VI. Conclusion

(1) The hydrogen-argon plasma jet is effective for decarburization and denitrogenization of iron and iron-chromium alloys; this leads to technical pos-

sibility of the direct production of iron-chromium alloys from chromite ores.

(2) In the case of 25%Cr-Fe alloy, the final concentrations of carbon and nitrogen refined are $\text{C} < 0.002\%$ and $\text{N} = 0.0065\%$, satisfying the requirements for good intergranular corrosion resistance and ductility.

(3) The reaction mechanisms of decarburization and denitrogenization are concluded as follows:

(i) The decarburization product is likely to be CH_4 and the reaction is controlled by gaseous mass transfer in higher carbon concentrations and by metallic mass transfer in lower carbon concentrations for any metals studied in the present work.

(ii) The denitrogenization product is mostly N_2 except for 60%Cr-Fe alloy in which NH_3 should be the predominant species. The reaction for three metals studied is controlled by mass transfer of nitrogen in metal.

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