CO Desorption and Absorption in Molten Steel: A Review

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(Received on August 27, 2020; accepted on December 9, 2020; J-STAGE Advance published date: January 23, 2021)

Previous work on the mechanism of carbon monoxide absorption and desorption from liquid steel/iron is reviewed. The experimental set-up employed in these studies is summarized and the characteristics of each methodology are discussed and compared. The reaction kinetics, particularly the rate-limiting step of the CO gas-molten steel/iron reaction is analysed with respect to experimental parameters, comprising temperature, CO partial pressure in the gas mixture, gas flow rate, crucible materials, and carbon and oxygen content in the steel/iron. To further understand the CO absorption and desorption mechanisms in liquid steel, suggestions for future work are provided.

KEY WORDS: steelmaking; CO absorption and desorption; gas-liquid reaction kinetics.

1. Introduction

The dissolved carbon and oxygen in molten steel to form carbon monoxide along with carbon monoxide absorption by liquid steel (*i.e.* carbon monoxide dissolving into liquid steel) are the most important gas-metal reactions in metallurgical processes, especially in iron and steelmaking operations.^{1–3)} For instance, the decarburization of steel in Basic Oxygen Furnace (BOF)^{4,5)} and Electric Arc Furnace (EAF) steelmaking⁶⁾ processes can be understood through the reaction

with equilibrium constant K

$$\log K = \log(P_{\text{CO}} / (a_{\text{C}} a_{\text{O}})) = 4882 / T + 8.65 \text{ kJ / mol}^7) \dots (2)$$

Where P_{CO} is the partial pressure of carbon monoxide in the atmosphere, and the activities a_{C} and a_{O} are taken equivalent to wt% $\underline{\text{C}}$ and wt% $\underline{\text{O}}$, respectively, at low solute concentrations. Similarly, ladle degassing relies on the formation of CO bubbles (by vacuum or by blowing inert argon gas) to provide efficient stirring for impurity removal,^{8,9)} while the production of rimming steel ingots depends upon the nucleation of CO bubbles at the advancing solid-liquid interface.^{10,11)} The direct smelting processes including HISMELT, COREX, DIOS, AISI direct steelmaking and Romelt processes¹²⁾ are also heavily influenced by the C–O reaction as gases such as CO, H₂, O₂, and CO₂ are injected into liquid melts in these processes.¹³⁾ In the Argon

Oxygen Decarburization (AOD) practice, the Ar/O₂ ratio in the injected gas is carefully controlled to increase with time.¹⁴⁾ The CO partial pressure in the Ar–O₂ gas bubble can increase with time due to the C–O reaction and an enhanced CO partial pressure can lead to the CO absorption in the liquid steel during bubble rising. Thus, a quantitative understanding of the CO absorption is required. Moreover, mathematical modelling and numerical simulation have become a powerful tool to understand and control metallurgical processes.^{15–21)} A comprehensive understanding of the C–O reaction is of great importance for the accurate simulation of industrial processes like the BOF operation.^{22–27)} Due to its importance, many efforts have been paid to understand the rate and mechanisms of this reaction (Eq. (1)). Different experimental methods, such as Sieverts' test,^{28,29)} levitated droplet,^{30–32)} isotope exchange technique³³⁾ and vacuum degassing,³⁴⁾ have been employed in CO absorption and/or desorption studies. However, the results are not always consistent and even contradict each other, particularly in the rate-limit step of the C–O reaction, *i.e.* carbon and/or oxygen diffusion in the liquid steel,^{28,29,34–38)} gaseous diffusion in the gas phase,^{30,31,39–45)} and interfacial reactions.^{33,46)} Moreover, in the literature it is constantly assumed that the CO absorption and desorption process are symmetrical, meaning the rate-limiting step of the two reactions is the same and the overall reaction rate is equivalent under the same experimental conditions. However, King *et al.*³⁷⁾ observed that for low carbon steel (~0.05 wt% C) the CO desorption rate was anomalously slower than the absorption rate. The difference in the mechanism of the two processes (CO absorption and desorption) is not yet clearly understood. Therefore, in order to supply data and knowledge for

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a fundamental understanding of the reaction mechanisms, a literature review on the carbon monoxide absorption into and desorption from a liquid steel is conducted.

2. Literature Review

2.1. Methodology

In spite of many efforts, no consensus has been reached concerning the mechanism of CO-liquid iron/steel reaction. Some conclusions with respect to the rate-limiting step of the reaction are even contradictory. It is found in literature that the experimental set-up used in gas-metal reaction study varies with different researchers. Hence, it is meaningful to summarize these techniques and examine the advantages and limitations of each method.

2.1.1. Furnace Melting

One of the most widely used equipment in the study of gas-melt reaction is the high temperature furnace. As shown in the work of Suzuki and Mori,³⁴⁾ an induction melting furnace was used to measure the CO degassing rate from molten iron (**Fig. 1**). A magnesia crucible was placed in a quartz reaction tube and heated by high-frequency induction coils. 400 g of electrolytic iron was melted in the magnesia crucible in an argon atmosphere. Once the temperature was stabilized (1 550–1 677°C in this case), initial carbon and oxygen were regulated to be respectively 0.01–0.1 wt% $\underline{C}$ and 0.01–0.09 wt% $\underline{O}$ by blowing a CO–CO₂ gas mixture. After equilibrium was attained, the CO desorption process was started by replacing the furnace atmosphere with Ar, followed by sampling with silica tubes. The changes of carbon and oxygen concentrations during the CO degassing process were obtained by the LECO analysis of the steel samples with carbon and oxygen.

Some researchers also used the furnace melting method but with different experimental conditions. Rathke and Tarby⁴⁷⁾ studied the influence of reduced CO pressure on

the $\underline{C}$ – $\underline{O}$ reaction in an Fe-0.21 wt% $\underline{C}$ melt in a precision casting vacuum system (induction melting). This test simulates the industrial vacuum degassing practice, where liquid steel is suddenly exposed to a reduced pressure for a short duration while the CO desorption occurs. The molten bath was sampled by pouring the liquid metal into a block mold as a function of time during equilibrium (at a specific CO pressure). Bui *et al.*⁴⁸⁾ ran a similar test by evacuating the furnace chamber to ~0.79 atm with a vacuum pump and found the carbon content decreased from 2.615 wt.% (weight percentage) to 0.016 wt.% in 120 min at 1 500°C.

The furnace melting set-up is easy to access and flexible in terms of sample size, sample composition, temperature and initial gas composition. However, during the experiment, the gas flow rate is set as a fixed value. As shown in Suzuki and Mori's experiment, gas flow rate was optimized as 1 500 mL/min (in Ito's furnace melting experiment,³¹⁾ the flow rate was 2 000 mL/min) until the reaction rate was independent of the gas blowing rate. This means that the gas phase diffusion such as O₂/CO/CO₂ mass transfer from the gas boundary layer to the gas-melt interface is excluded from the discussion of the rate-limiting step. In this context, special attention in most furnace melting experiments was paid to the liquid phase diffusion.

2.1.2. Sieverts-type Apparatus

The Sieverts-type apparatus, also known as volumetric technique, has been widely used to measure gas sorption (*e.g.* hydrogen) on a material (*e.g.* hydrogen storage material).^{5,49)} The principle is to measure the variations in the volume of a gaseous system while keeping the pressure constant.⁵⁰⁾

Solar and Guthrie²⁹⁾ employed the Sieverts-type method to investigate the CO absorption kinetics into liquid iron with a CO pressure ranging from 0.1 to 1.5 atm at 1 600°C. A 4 cm long rod iron (diameter = 2 cm) sample was introduced into an alumina tube with a closed end. The diffusion cell was placed in the measuring system, which was evacuated and flushed with pure argon (see **Fig. 2**). Subsequently, the cell was lowered into the furnace, heated up to the test temperature (1 580–1 700°C in this case), and then evacuated, maintaining the low pressure for 3 hours by closing stopcock S5, as illustrated in **Fig. 2**. The vacuum in the diffusion cell is preserved, while the left part of the apparatus was filled with CO. The initial carbon and oxygen concentrations in the metal bulk are homogenous and equal to C_C^∞ and C_O^∞ , respectively. At time $t = 0$, stopcock S8 was opened. The evacuated space (on top of the melt) is then quickly filled with CO at pressure P (0.1–1.5 atm at 1 600°C). It was assumed that the dissociation (CO absorption into liquid steel) reaction $\text{CO} = \underline{C} + \underline{O}$ was instantaneous at the melt-gas interface. C_C^* and C_O^* (carbon and oxygen concentration at gas-melt interface) then immediately reached the equilibrium level so that $C_C^* \cdot C_O^* = KP^0$ (K : reaction constant). 10 seconds later, the differential pressure transducer shunt S4 was closed. As CO is absorbed by molten iron, the absorption rate is measured by monitoring the pressure drop in the gas phase at constant volume using the differential pressure transducer (measure the differential pressure change between its two sides) or monitoring the volume change while fixing the pressure value. Once the

Fig. 1. Experimental set-up for CO desorption from liquid iron.³⁴⁾ (Online version in color.)

Fig. 2. Schematic of Sieverts-type apparatus. A - DEOXO catalytic gas purifier, B - DRIERITE tower; C - mercury manometer; D - reference volume; E - differential pressure transducer; F - absorption micro-burette (in volume method apparatus only); G - molybdenum furnace; H - leveling mechanisms; I - O-ring connector; J - polyethylene tubing; K - diffusion cell assembly; R1, R2, R3 – water-jacket thermistors; R4 - Gas phase thermistors; S1, S2, ... S9 - high-vacuum stopcocks; T1 - travelling thermocouple; T2, T3, T4 - control thermocouples.⁵⁰⁾

absorption experiments were completed for a given sample, the crucible assembly was taken out of the furnace and quenched in cold water. The absorption kinetics of CO by stagnant liquid iron was then explained in terms of a simplified mass transfer model involving simultaneous diffusion of the dissolved carbon and oxygen.

Parlee *et al.*³⁶⁾ examined the CO absorption and desorption rates into/from the inductively stirred melts with a Sieverts-type apparatus. The experimental procedure consisted of equilibrating the liquid steel with an initial CO pressure and then rapidly altering the pressure to a required value. The pressure was kept constant at this value by changing the volume of the system. To estimate the rate of CO desorption from Fe-O-0.15–4.4 wt% C melt and the rate of the reverse reaction (*i.e.* CO absorption into the melt), the volume changes as a function of time was recorded. Similarly, King *et al.*³⁷⁾ used the Sieverts' type equipment in studying the CO-iron melt reaction. However, instead of using an inductively stirred melt, they performed the experiment in a naturally-convection iron melt.

Although the measuring system is complicated with respect to the furnace melting method, one of the important features of the Sieverts-type set-up is to exactly quantify the pressure/volume change of the gas with time, *i.e.*, the quantity of the absorbed CO by liquid alloy with time. Hence, the kinetic data of carbon and oxygen diffusion in liquid phase can be determined.

2.1.3. Levitated Droplet Experiment

In the experiment with the Sieverts type apparatus or the furnace melting set-up, the reaction between refractory/crucible materials and liquid alloys was found to significantly influence the results. For example, in Parlee *et al.*'s experiment³⁶⁾ with a Sieverts' type apparatus, the reaction between the alumina crucible and carbon in liquid iron was observed in the high carbon-containing sample, as shown in Eq. (3).

Fig. 3. Schematic of levitated method.⁴¹⁾ (Online version in color.)

This reaction markedly increases the CO desorption rate. Similarly, Ito *et al.*³¹⁾ measured the CO degassing/desorption rate from liquid iron by crucible melting. They found that the change in the oxygen/carbon concentration ratio during degassing is lower than the stoichiometrical relations. This was explained by metal/crucible (MgO) interface reactions: *i.e.* crucible corrosion leads to an increase in oxygen content in the liquid iron (see Eq. (4)).

In order to eliminate the effect of crucible/steel interaction, several researchers^{30,39,51)} employed the levitated droplet method in the gas-melt study. Ito *et al.*⁴¹⁾ measured the rate of carbon and oxygen transfer between CO–CO₂ mixtures and iron using the levitated droplet method, as shown in **Fig. 3**. An iron-droplet (electrolytic iron, Fe > 99.97%) was melted in a silicon tube flushed with pure Ar. The sample was heated by an induction heating coil. After reaching the desired temperature (1 870–2 070°C), the atmosphere was quickly replaced by a CO–CO₂ mixture

with a specific composition (CO₂: 0–5 vol.%) at various flow rates (270–3 000 mL/min). Once reaching the scheduled reaction time, the furnace power was switched off and a water-cooled copper mold was raised up to quench the liquid droplet. The carbon and oxygen content of the quenched sample were further analyzed to determine the evolution of carbon and oxygen concentration with time at various conditions (temperature, gas composition and flow rate), corresponding to the CO absorption rate.

Baker *et al.*³⁹⁾ measured the decarburization of levitated Fe–0 to 5.5 wt% C alloy droplets at 1 660°C flushed by 1, 10, and 100% O₂–He gas mixtures. An equation was derived to predict the rate of oxygen diffusion to the droplet through the gas boundary layer, as shown in Eq. (5).

$$N_{O_2} = \frac{D(O_2 - X)_f P \overline{Nu'}}{RT_f d_p} y_{O_2} \dots\dots\dots (5)$$

where N_{O_2} is the flux oxygen (mol·cm⁻²s⁻¹), D is the gas diffusion coefficient (cm²s⁻¹), T is the temperature of gas film (K), P is the total pressure (atm), R is the gas constant (82.06 cm³ atm·K⁻¹·mol⁻¹), d_p is the spherical diameter (cm), Nu' is the Nusselt number for mass transfer based on the total surface of a sphere. X is the inert component in the gas mixture.

Distin *et al.*³⁰⁾ conducted a similar levitation experiment by blowing O₂, CO₂, O₂ + H₂O, and H₂O gas mixtures and found that the decarburization rate increased significantly at more elevated gas flow rates.

Simento *et al.*^{42–44)} systematically investigated the decarburization kinetics using the levitated droplet method, by blowing inert gas (N₂ and/or He) with O₂, CO₂, O₂ + CO₂, and O₂ + H₂O, respectively. The key findings are: (1) the decarburization rate with 10% oxygen at 1 450°C is limited by the transport of oxygen in the bulk gas to the melt surface; (2) the experiment with CO₂ at 1 450°C shows that the decarburization is jointly controlled by gas phase mass transport and dissociative chemisorption of CO₂; (3) for the decarburization with O₂ + CO₂, the rate is limited by the O₂ and CO₂ transport in the gas phase with additional resistance from the interfacial reaction kinetics of CO₂; (4) in the case of simultaneous decarburization by O₂ + H₂O, the basic mechanism of decarburization is similar to that of O₂ + CO₂, but the reaction between O₂ and CO to produce CO₂ occurs in the vicinity of the interface, lowering the decarburization rate.

Widlund *et al.*⁴⁵⁾ investigated the decarburization of Fe–4%C alloys containing silicon in the 0.3 to 0.7% range under a He + O₂ gas mixture. The results show that at high carbon content (>0.5%), the decarburization rate is not dependent on the carbon concentration in the liquid steel. Instead, the decarburization rate is controlled by the O₂ partial pressure in the gas mixture (Si = 0.37–0.71%, T = 1 400–1 700°C), indicating a gas mass transfer-controlled mechanism in this experimental condition (C > 0.5%, Si = 0.37–0.71%, T = 1 400–1 700°C).

It is clear that in the levitated droplet experiment, no crucible contamination/corrosion occurs. Additionally, both gas and liquid phase diffusion can be taken into account while analyzing the rate-limiting step.

2.1.4. Isotope Exchange Technique

In the discussion of the CO absorption and desorption, it is constantly assumed that the chemical reaction at the gas-melt interface is instantaneous. To quantify the interfacial reaction rate, the isotope exchange method was used by a number of researchers.^{33,46,52)} The measurement is made at chemical equilibrium, so that the isotope reaction is not influenced by liquid phase mass transfer. Kim *et al.*⁴⁶⁾ used an isotope exchange technique to investigate the kinetics of CO dissociation/absorption into the molten iron. As shown in Fig. 4, a graphite crucible serving as both heating element and protective crucible was placed in the induction furnace. An alumina crucible with iron specimen was introduced into the graphite crucible. The furnace was heated up to the desired temperature (1 100–1 500°C) in an argon atmosphere. After temperature stabilization, the argon gas was replaced by a CO + ¹³CO gas mixture. The distance between the end of the lance (for gas injection) and the crucible was minimized to prevent the leakage of reaction gases. The exit gas composition was measured by a quadrupole mass spectrometer. In the preliminary test prior to the measurement, the gas flow rate was increased above the critical value in such a way that gas phase mass transfer could be excluded from the rate-limiting steps. Thus, the CO/melt interfacial reaction rate (on the molten iron surface) at different temperatures could be measured.

To study chemical kinetics of CO on liquid iron alloys, Fruehan and Antolin³³⁾ have also employed the isotope exchange technique by using a double isotope of CO containing C¹³ and O¹⁸ (C¹³O¹⁸). Taking into account the overall isotope exchange reaction for C¹³O¹⁸ dissociation,

the rate constant, k , for the reaction can be derived as Eq. (6).

$$k = -\frac{\bar{V}}{A} \ln \left\{ \frac{F_{31}^0 - F_{31}^{eq}}{F_{31}^i - F_{31}^{eq}} \right\} \dots\dots\dots (7)$$

Where $\bar{V}$ is the gas flow rate, A is the surface area of liquid iron alloys, F_{31} is the fraction of the C¹³O¹⁸ isotope in the gas phase. The superscript 0, i and $eq.$ refer to the moment, respectively, at the start of experiment, time i and

Fig. 4. Schematic diagram of isotope exchange technique.⁴⁶⁾
(Online version in color.)

the equilibrium state. According to the experiment, the reaction rate constant is estimated to be $1.5 \times 10^{-5} \text{ mol} \cdot \text{cm}^{-2} \text{ s}^{-1}$ at 1 600°C.

Fan *et al.*⁵³⁾ studied the decarburization rate of Fe–C melts with a CO₂–O₂ mixture by employing the isotope tracing technique. Their results indicate that the utilization rate of CO₂ exceeds 97%. However, only approximately 52% of the oxygen reacted with C to form CO and 17% of the oxygen reacted to form CO₂. The rest of oxygen (31%) was reacted during post combustion. Fan *et al.*'s work focuses on the source of CO₂ formed in the decarburization, while no analysis on the mechanism of the C–O or C–CO₂ reaction was performed.

2.2. Kinetics of CO Absorption and Desorption

Kinetic studies, particularly the determination of their rate-limit step, are critical in metallurgical processes involving CO absorption and desorption, such as CO degassing, carburization by CO, and decarburization by ejecting oxygen-inert gas mixture or CO₂ into molten steel/iron. Although the controlling step of the reaction (CO absorption and desorption) has been discussed in many studies, no consensus has been achieved yet. According to literature, the possible rate-limiting step for CO absorption and desorption includes (a) mass transfer in the liquid phase; (b) mass transfer in the gas phase; (c) chemical reaction at the interface; and (d) bubble nucleation in the liquid phase.

2.2.1. Oxygen and/or Carbon Mass Transfer in Liquid Metal Phase

One of the earliest investigations was made by Parlee *et al.*³⁶⁾ using a Sieverts' type apparatus. As seen in Fig. 5, the rate constant of C–O reaction in the investigated system (Fe–0.2 to 4.5 wt% C) is almost constant when the carbon content is in excess of 0.2 wt%. It was concluded that the reaction rate was primarily controlled by oxygen diffusion in the metal at C > 0.2 wt%.

King *et al.*³⁷⁾ studied the absorption and desorption of CO in naturally-convecting iron melts. They found that the absorption rate of CO for all carbon contents, and the CO desorption rate for medium carbon content (~0.2 wt% C), were controlled by the mass transport of oxygen in liquid steel. However, they observed that the CO desorption rate from low carbon steel (~0.05 wt% C) were anomalously

Fig. 5. Effect of carbon content (wt.%) on rate constants at 1 630°C.³⁶⁾ (Online version in color.)

low. The low CO desorption rate was attributed to a slow surface reaction as the available sites are limited by strong adsorption of oxygen.

Solar *et al.*²⁹⁾ performed a Sieverts' type measurement for CO absorption in stagnant iron, where vacuum was initially maintained at the top of the melt and then the evacuated space is filled with CO gas. The absorption rate of CO is recorded by the pressure drop in the gas phase at a constant volume. It was found that the pressure drop (ΔP) can be expressed as a function of root time (*i.e.* $\Delta P = \alpha \sqrt{t}$). Mass transfer equations developed to describe the absorption were adapted to define an 'apparent diffusion coefficient' of carbon monoxide by essentially taking both carbon and oxygen diffusivity in the liquid phase into account. Over the temperature range from 1 570 to 1 700°C, the apparent diffusion coefficient of CO at 1 atm in liquid iron (initially containing approximately 80 ppm of both carbon and oxygen) was given by:

$$D_{CO} = 3.51 \cdot 10^{-3} \exp \left(-\frac{13\,872 \pm 8\,455}{RT} \right) \dots \dots \dots (8)$$

The measured D_{CO} values was $9.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ on average, while carbon and oxygen diffusivities were calculated to be 41.2×10^{-5} and $5.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, respectively.

Schenck *et al.*^{28,38)} and Knuppel *et al.*⁵⁴⁾ measured CO desorption rates from liquid iron under reduced pressure. The influence of the experimental parameters such as temperature, chromium content and surface-active elements on the desorption rate of CO were determined.²⁸⁾ It was concluded that sulfur had no effect on the CO desorption rate. They also reported that the chemical reaction rate in the CO desorption process was very fast and that the overall CO desorption rate was controlled by liquid phase mass transfer. The CO desorption rate was significantly affected by carbon and oxygen concentrations in the liquid iron. In case of low initial carbon contents, the generated amount of CO gas increases linearly with initial carbon content. In case of high carbon content, however, the released CO increases with the reciprocal value of the initial carbon content. The mass transfer coefficient of oxygen in the liquid iron was derived as Eq. (8):

$$k_o = 18.5 \exp \left(-\frac{20\,200}{RT} \right) \dots \dots \dots (9)$$

At 1 600°C, effective diffusion coefficient of oxygen (D_o) in the liquid iron was estimated to be $22 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. This value is in the same order of magnitude of the estimation by Solar *et al.*²⁹⁾

Suzuki *et al.*³⁴⁾ studied the kinetics of CO desorption by measuring concentration changes of carbon and oxygen with reaction time in an inductively stirred bath. The experimental data highlight that: (a) for carbon higher than 0.03 wt%, the rate is controlled by oxygen mass transfer in the metal only; the value of k_o (mass transfer coefficient of oxygen in liquid iron) is approximately 0.035 cm s^{-1} ; (b) for oxygen higher than 0.06 wt%, the rate is controlled by mass transfer of carbon, and the value of k_c (mass transfer coefficient of carbon in liquid iron) is approximately 0.051 cm s^{-1} ; (c) the changeover from oxygen mass transfer control to carbon mass transfer control occurs at a ratio of $C_c/C_o = 0.69$, as shown in Fig. 6; (d) mixed mass transport control

Fig. 6. Mass transfer coefficients of carbon and oxygen in iron with the ratio of carbon and oxygen contents (mol/cm³).³⁴⁾ (Online version in color.)

and mixed control (chemical reaction plus mass transfer in liquid phase), when assumed as the rate-limiting step, do not fit with the observed results. The experimental data in Fig. 6 also show that for $C_C/C_O < 0.69$, the k_C value is constant and for $C_C/C_O > 0.69$, the k_O value is constant. The former implies that the reaction is controlled by mass transport of oxygen, while the latter suggests mass transport of carbon controls the reaction rate. Hence, the overall kinetics of CO desorption during argon blowing could be determined by initial carbon or oxygen content and the mass transfer coefficient (k_C , k_O). However, as commented by Ito *et al.*,³¹⁾ the increased CO desorption in Suzuki *et al.*'s experiment was due to the reaction between refractory materials (MgO crucible) and molten iron. It is suggested that the crucible melting method is not suitable for the kinetics study of CO degassing, provided that the rate of crucible-melt reaction is not quantitatively determined. Ito *et al.*^{31,40)} measured the rates of CO degassing for liquid iron containing 0.025–0.095 wt% C and 0.03–0.09 wt% O by using the levitation method. The CO desorption proceeds stoichiometrically, as shown in $C + O = CO$, until carbon or oxygen is depleted, indicating a carbon and/or oxygen mass transfer-controlling step in the liquid phase. Wang *et al.*³⁵⁾ blew O₂–CO₂ gas mixtures into the Fe–Cr–C melts and found that the decarburization is controlled by the mass transfer in the liquid iron. Kim *et al.*⁷³⁾ calculated the forward and backward reaction rate constant of the C–O reaction (Eq. (1)), based on the experimental data reported by Dancy⁵⁵⁾ and Lloyd *et al.*⁵⁶⁾ They obtained the following equations:

Forward reaction rate constant,

$$k = 1.33 \times 10^8 \exp(-250\,000 / RT), \text{ mol / (m}^2\text{s)}$$

Backward reaction rate constant,

$$k = 2.40 \times 10^{11} \exp(-277\,000 / RT), \text{ mol / (m}^2\text{s)}$$

2.2.2. Mass Transfer in Gas Phase

Baker *et al.*³⁹⁾ studied the decarburization of a levitated Fe–0 to 5 wt% C alloy droplet flushed by O₂–He gas mix-

tures with various O₂ fractions (1, 10 and 100%). It was found that for high carbon concentrations, the decarburization rate of the levitated drop at 1 660°C was completely controlled by the rate of O₂ diffusion to the droplet through the gas boundary layer. For low carbon content Fe–C alloy, where CO nucleates homogeneously in the droplet, the decarburization decreased with carbon content of the liquid steel. In this case, local carbon diffusion control became significant.

Distin *et al.*³⁰⁾ conducted a similar levitation experiment by blowing O₂, CO₂, O₂ + H₂O, and H₂O gas mixtures. The measured decarburization rates were significantly influenced by the oxygen gas flow rate, suggesting that the reactions were controlled by the mass transfer in the gas phase. They also estimated the rate of oxygen absorption to the liquid droplet during the tests, and the oxygen mass transfer coefficient, k_O , of 0.002 to 0.003 cm s^{−1} was determined.

Whiteway *et al.*⁵⁷⁾ studied the kinetics of decarburization of iron melts (1.3 to 1.4 wt% C) by blowing argon-oxygen gas mixtures (0.1 to 1.2 vol.% O₂). They concluded that under their experimental conditions the decarburization process was controlled by the diffusion of oxygen in the gas phase. In the experiment of Ito *et al.*,⁴⁰⁾ using the levitation melting technique, it was found that in the initial stage the CO absorption is not dependent on the composition gas mixture, indicating the absorption rate is controlled by the mass transfer in the bulk melt. At the later stage, the CO and CO₂ diffusion in the gas phase tends to control the absorption and desorption process.

2.2.3. Chemical Reaction

Fruehan *et al.*³³⁾ employed the isotope exchange technique to study the chemical kinetics of CO on liquid iron by using a double isotope of CO containing C¹³ and O¹⁸ (C¹³O¹⁸). The reaction is shown in Eq. (5). As seen in Fig. 7, at 1 600°C, the isotope exchange rate for C¹³O¹⁸ in normal CO on liquid iron was not a strong function of sulfur content up to 0.43 wt%, but a function of gas flow rate, implying that the rate is controlled by gas phase mass transfer. At low temperature (1 250°C) and S > 0.015 wt%, the reaction rate may be controlled by mixed controlling steps, *i.e.* gas phase mass transfer and chemical kinetics. Under this condition, the reaction rate constant is estimated to be 1.5×10^{-5} mol·cm^{−2}s^{−1}. However, Sasaki *et al.*⁵²⁾ re-examined the interfacial reaction of CO with liquid iron by using the isotope exchange technique as well. They concluded that the rate constant of the CO(g) → C(ads) + O(ads) reaction, as determined by Fruehan *et al.*,³³⁾ was too small (5.4×10^{-5} mol·cm^{−2}s^{−1} for iron containing 0.1 wt.% S) based on their theoretical calculations. They proposed that the small value was attributed to the fact that the melt surface was partially covered by sulfur in Fruehan *et al.*'s experiment, while the rate constant should be estimated according to a bare surface. The presence of sulfur blocked the CO adsorption sites, resulting in a lower CO desorption rate compared with the actual value, which was re-evaluated to be 1.3×10^{-3} mol·cm^{−2}s^{−1}.

Kim *et al.*⁴⁶⁾ studied the carburization of iron with CO gas by using isotope exchange method and observed the following mechanism.

Fig. 7. Rate of the CO isotope exchange reaction on Fe-S alloys at 1600°C.³³⁾ (Online version in color.)

For steel with low impurities (oxygen and sulfur activities are less than 0.02), the adsorbed molecules CO(ads) were found to be easily dissociated into adsorbed atoms, *i.e.* C(ads) and O(ads), as there were sufficient vacant sites around the adsorbed sites by CO (see Fig. 8). The carburization reaction was thus controlled by CO adsorption. However, for steel containing high impurities (sulfur activity is higher than 0.02), the carburization reaction tends to be controlled by the CO dissociation reaction (*i.e.* Eq. (10)), as there are fewer available sites to accommodate the dissociated carbon and oxygen atoms. Although the work on the effect of sulfur content on the $\underline{\text{C}} + \underline{\text{O}} \rightleftharpoons \text{CO}(\text{g})$ reaction rate is limited in the literature, a number of studies have been found in decarburization with CO₂ ($\underline{\text{C}} + \text{CO}_{2(\text{g})} \rightleftharpoons 2\text{CO}(\text{g})$). It has been observed by many researchers that sulfur can retard the decarburization rate.^{13,58–64)} Hayer *et al.*⁶⁰⁾ studied the decarburization with a CO–CO₂ (0.1 atm) gas mixture and reported a clear decelerating effect of sulfur on the decarburization rate at a sulfur content between 0 and 0.4 wt.%. As sulfur is a strong surfactant, the melt/gas interface sites are partially occupied by these sulfur atoms in the sulfur-containing melt, leaving less sites available for the gaseous molecules such as CO₂ or O₂. Thus, the decarburization rate is slowed down. Lee *et al.*⁶¹⁾ investigated the decarburization of an Fe–C melt with the levitation technique using a CO–CO₂ gas mixture at 1700°C. The results clearly indicate that increasing the sulfur content up to 0.05 wt.% significantly decreases the decarburization rate. At the sulfur content above 0.05 wt.%, the rate of decarburization is approximately 60% of the value obtained at 0 wt.% sulfur.

2.2.4. CO Nucleation

Rathke and Tarby⁴⁷⁾ studied the influence of reduced CO pressure on the $\underline{\text{C}}-\underline{\text{O}}$ reaction in an Fe - 0.21 wt% $\underline{\text{C}}$ melt in a precision casting system (induction melting). As seen in Fig. 9, the efficiency of carbon deoxidation was not significantly increased by vacuum degassing at a chamber pressure below 100 torr (0.13 atm). The bubble

Fig. 8. Change of rate-determining step from (a) CO adsorption to (b) CO dissociation with increasing the activities of oxygen and sulfur in the bulk phase at 1550°C.⁴⁶⁾

Fig. 9. Average final oxygen content of initially 0.21 wt% carbon steel melts as a function of the partial pressure of CO over the bath.⁴⁷⁾ (Online version in color.)

nucleation mechanism was considered to be the rate-limiting step for vacuum desorption of CO. Similarly, the work of Swisher and Turkdogan,^{65,66)} and the study by Jamieson and Masson⁶⁷⁾ also confirm that the nucleation phenomenon plays an important role in the decarburization process.

There are a few studies focusing on the melt-slag reaction, involving also $\underline{\text{C}} + \underline{\text{O}} \rightleftharpoons \text{CO}(\text{g})$ reaction.^{68–72)} However, this is beyond the scope of this paper, which focuses on melt-gas interactions.

3. Summary and Discussion

The summary of the reviewed papers is listed in Table 1. The kinetics of the CO absorption and desorption are influenced by various parameters, such as carbon and oxygen content in liquid steel/iron, impurity level (*e.g.* sulfur content), gas composition (CO partial pressure) and flow

Table 1. Summary of the previous investigations.

Authors	Composition of liquid iron ($\underline{C}$, $\underline{O}$, $\underline{S}$, $\underline{Al}$)/wt%	Reaction type	Experimental technique and conditions	Rate-limiting step	Important conclusions and remarks	Year of published paper
Rathke <i>et al.</i> ⁴⁷⁾	$\underline{C}$: 0.21	CO degassing under vacuum (desorption: $\underline{C} + \underline{O} \rightarrow \text{CO}$)	Induction vacuum melting and sampling	CO bubble nucleation control in metal bulk	$\underline{C}$ - $\underline{O}$ reaction was not significantly increased by vacuum degassing at chamber pressure below 100 torr (0.13 atm)	1969
Suzuki <i>et al.</i> ³⁴⁾	$\underline{C}$: 0.01–0.1; $\underline{O}$: 0.01–0.09	CO desorption ($\underline{C} + \underline{O} \rightarrow \text{CO}$)	Induction melting with sampling	$\underline{O}$ mass transfer control for $\underline{C} > 0.03$ wt% ($k_a = 3.5 \times 10^{-2}$ cm/s); $\underline{C}$ mass transfer control for $\underline{O} > 0.06$ wt% ($k_c = 5.1 \times 10^{-2}$ cm/s).	The change-over from oxygen mass transfer control to carbon mass transfer control occurs at a ratio of $C_c/C_o = 0.69$ (C_c , C_o : concentration of $\underline{C}$ and $\underline{O}$ in mol/cm ³)	1977
Wang <i>et al.</i> ³⁵⁾	$\underline{C}$: 0.257–3.47 $\underline{Cr}$: 10.3–15.5	CO desorption ($\underline{C} + \underline{O} \rightarrow \text{CO}$)	Crucible melting, gas blowing into the melt	The decarburization is controlled by the mass transfer in the liquid iron.	With blowing CO ₂ , the utilization of the available oxygen for decarburization was higher as compared to O ₂ injection in the case of melts containing higher carbon levels (>1 wt.%).	2009
Kim <i>et al.</i> ⁷³⁾		CO absorption and desorption ($\underline{C} + \underline{O} \rightleftharpoons \text{CO}$)	Crucible melting, based on the data from Dancy ⁵⁵⁾ and Lloyd <i>et al.</i> ⁵⁶⁾	Forward reaction rate constant, $k = 1.33 \times 10^8 \exp(-250\,000/\text{RT})$, mol/(m ² s) backward reaction rate constant, $k = 2.40 \times 10^{11} \exp(-277\,000/\text{RT})$, mol/(m ² s)		2010
Parlee <i>et al.</i> ³⁶⁾	$\underline{C}$: 0.15–4.4	CO absorption and desorption ($\underline{C} + \underline{O} \rightleftharpoons \text{CO}$)	Sieverts type (at constant pressure), inductively stirred melts	$\underline{O}$ mass transfer control in metal, $k_o = 2\text{--}3 \times 10^{-3}$ cm/s (for $\underline{C} = 0.15\text{--}0.95$ wt%); $k_o = 1\text{--}2 \times 10^{-2}$ cm/s for $\underline{C} < 0.1$ wt%	a) For high $\underline{C}$ content, crucible reaction occurs; b) the direction of the reaction (<i>i.e.</i> absorption or desorption) did not influence the kinetics of the process	1958
King <i>et al.</i> ³⁷⁾	$\underline{C}$: ~4.5	CO absorption and desorption ($\underline{C} + \underline{O} \rightleftharpoons \text{CO}$)	Sieverts type, naturally-convecting melts	$\underline{O}$ mass transfer control for absorption in all $\underline{C}$ content and desorption in $\underline{C} > 0.2$ wt%	For low $\underline{C}$ steel (~0.05 wt% $\underline{C}$) desorption rate was anomalously slow due to sites limited in availability by strong adsorption of oxygen	1970
Solar <i>et al.</i> ²⁹⁾	$\underline{C}$: ~0.008; $\underline{O}$: ~0.008	CO absorption ($\text{CO} \rightarrow \underline{C} + \underline{O}$)	Sieverts type (at constant volume), stagnant iron	Simultaneous mass transfer control of $\underline{C}$ and $\underline{O}$; $D_{co} = 9.8 \times 10^{-5}$ cm ² /s ('apparent diffusion coefficient' of CO)	The 'apparent diffusion coefficient' of CO, D_{co} , essentially took into account both carbon and oxygen diffusivity.	1972
Schenck <i>et al.</i> ²⁸⁾		CO desorption ($\underline{C} + \underline{O} \rightarrow \text{CO}$)	Sieverts type (at constant pressure)	Mass transfer control in liquid phase ($\underline{C}$ and $\underline{O}$); $D_o = 22 \times 10^{-5}$ cm ² s ⁻¹ (1 600°C)	In low $\underline{C}$, desorption rate increase with $\underline{C}$, in high $\underline{C}$, however, with the reciprocal value of $\underline{C}$ content.	1971, 1973
Baker <i>et al.</i> ³⁹⁾	$\underline{C}$: 0–5.5	Decarburization by blowing gas mixture containing O ₂ ($\underline{C} + \text{O}_2 \rightarrow \text{CO}$)	Levitated droplet experiments	O ₂ mass transfer control in gas phase for high $\underline{C}$ steel; $\underline{C}$ mass transfer control for low $\underline{C}$ steel	An equation was derived to predict the rate of oxygen diffusion to the droplet through the gas boundary layer	1967
Distin <i>et al.</i> ³⁰⁾	$\underline{C}$: ~4.0	Decarburization by blowing O ₂ , CO ₂ , O ₂ + H ₂ O and O ₂ + Ar ($\underline{C} + \text{O}_2 \rightarrow \text{CO}$)	Levitated droplet experiments	O ₂ mass transfer control in gas phase; $k_o = 2\text{--}3 \times 10^{-3}$ cm/s $k_c = 3.2 \times 10^{-2}$ cm/s	Oxygen absorption to the liquid droplet during the tests is very slow.	1968
Ito <i>et al.</i> ^{31,40,41)}	$\underline{C}$: 0.028–0.095; $\underline{O}$: 0.03–0.09	CO desorption ($\underline{C} + \underline{O} \rightarrow \text{CO}$)	Both levitation and crucible melting	Desorption controlled jointly by mass transfer of $\underline{C}$ or $\underline{O}$ in metal and that of CO in gas phase $k_o = 4.1\text{--}5.0 \times 10^{-2}$ cm/s $k_c = 4.5\text{--}5.6 \times 10^{-2}$ cm/s	a. For levitation melting the CO desorption proceeds stoichiometrically obeying to $\underline{C} + \underline{O} = \text{CO}$ until carbon or oxygen is depleted; b. Crucible corrosion leads to an increase in $\underline{O}$ in the liquid iron.	1975, 1977, 1984
Brabic ⁵¹⁾	$\underline{C}$: 0.004 $\underline{Al}$: 0.02–0.4	CO absorption by Al-killed steel ($2\underline{Al} + 3\text{CO} \rightarrow \text{Al}_2\text{O}_3 + \underline{C}$)	Levitation droplet method	N.A.	CO absorption by Al-killed steel occurs in two stages: a first stage of rapid absorption, and the second stage of slow absorption in the presence of an alumina film covering the droplet.	1998

Simento <i>et al.</i> ^{42–44)}	<u>C</u> : 3–4 <u>S</u> : < 0.27	CO desorption (<u>C</u> + <u>O</u> → CO)	Levitation droplet method	The decarburization rate with (1) O ₂ : limited by the transport of oxygen in the bulk gas, (2) CO ₂ : jointly controlled by gas phase mass transport and dissociative chemisorption of carbon dioxide, (3) O ₂ + CO ₂ : limited by O ₂ and CO ₂ transport in the gas phase and the interfacial reaction kinetics of CO ₂ , (4) O ₂ + H ₂ O: similar to that of O ₂ + CO ₂ , but the reaction between O ₂ and CO to produce CO ₂ occurs in the vicinity of the interface, lowering the decarburization rate.		1998, 1999
Widlund <i>et al.</i> ⁴⁵⁾	<u>C</u> : 4.0 <u>Si</u> : 0.37–0.71	CO desorption (<u>C</u> + <u>O</u> → CO)	Levitation droplet method	Mass transfer in gas phase	The decarburization rate increases from 0.11 to 0.17% when the oxygen partial pressure increases from 10 to 20% in the He–O ₂ mixture, indicating a gas mass transfer-controlled mechanism	2006
Fruehan <i>et al.</i> ³³⁾	<u>C</u> : 0.01–4.5; <u>S</u> : 0.008–0.43	C ¹³ O ¹⁸ dissociation (C ¹³ O ¹⁸ → C ¹³ + C ¹⁸)	Isotope exchange technique	Mixed control by chemical reaction and gas phase mass transfer for low temperature and <u>S</u> > 0.15% wt; rate constant $k = 1.5 \times 10^{-5} \text{ mol}\cdot\text{cm}^{-2}\text{s}^{-1}$.	Chemical rate is one order of magnitude larger than previously measured when the rate was controlled by liquid phase mass transfer.	1987
Sasaki <i>et al.</i> ⁵²⁾	<u>O</u> : 0.04; <u>C</u> : 0.02; <u>Al</u> : 0.007; <u>S</u> : 0.005.	CO(ads) → C(ads) + O(ads)	Isotope exchange technique	Re-evaluated reaction rate constant as $1.3 \times 10^{-3} \text{ mol}\cdot\text{cm}^{-2}\text{s}^{-1}$.	Re-examined the reaction constant measured by Fruehan <i>et al.</i>	2004
Kim <i>et al.</i> ⁴⁶⁾	<u>C</u> : 0.0019–3.3100 <u>O</u> : 0.0020–0.6170 <u>S</u> : 0.0026–0.018 <u>N</u> : 0.003–0.0821	2CO(g) + Fe(l) → C in Fe + CO ₂	Isotope exchange technique	Interfacial reaction at gas-metal surface can be converted from adsorption limited control to dissociation limited reaction, as the impurity concentrations of oxygen and sulfur increase.	In particular, it was found that sulfur has a greater influence on the conversion of the rate-limiting step of the carburization reaction of molten iron	2013
Fan ⁵³⁾	<u>C</u> : 1–4	CO desorption (<u>C</u> + <u>O</u> → CO)	Isotope tracing technique	N.A.	Their results indicate that the utilization rate of CO ₂ exceeds 97%, whereas approximately 52% of oxygen reacted with C in the melt and form CO and 17% form CO ₂ . The rest of oxygen was reacted during post combustion.	2019

$D_{\text{O}}, D_{\text{C}}$: diffusion coefficient of oxygen and carbon respectively.

$k_{\text{O}}, k_{\text{C}}$: mass transfer coefficient of oxygen and carbon respectively.

rate, temperature, and even refractory materials (Al_2O_3 and MgO). However, as seen from Table 1, particularly in the work of Suzuki *et al.*,³⁴⁾ Parlee *et al.*,³⁶⁾ Distin *et al.*,³⁰⁾ and Ito *et al.*,^{31,40,41)} although the experimental conditions (temperature, steel/iron composition, *etc.*) were different, the measured mass transfer coefficient of oxygen is always smaller than that of carbon in liquid iron/steel. This indicates that at the same concentration gradient (from liquid bulk to gas-liquid interface), oxygen transfer in the liquid phase is more likely to be the rate-controlling step compared with carbon. However, at either low carbon concentration or high oxygen content, the $\underline{C} + \underline{O} \rightarrow \text{CO}$ reaction rate is controlled by the mass transfer of carbon in liquid steel, as confirmed by Baker ($\underline{C} < 1 \text{ wt.}\%$) and Suzuki ($\underline{O} > 0.06 \text{ wt.}\%$). The gas phase diffusion was omitted in the discussion of CO desorption/absorption by many researchers, such as Rathke *et al.*,⁴⁷⁾ Suzuki *et al.*,³⁴⁾ Parlee *et al.*,³⁶⁾ King *et al.*,³⁷⁾ Solar *et al.*²⁹⁾ and Schenck *et al.*²⁸⁾ Nevertheless, it was found to be the rate-limiting step for the CO absorption or desorption in the work of Baker *et al.*,³⁹⁾ Distin *et al.*,³⁰⁾ and Ito *et al.*^{31,40,41)} This contradiction is mainly attributed

to the characteristics of the distinct experimental set-ups. In the experiment with furnace melting, the gas flow rate was optimized until the reaction rate was independent of the flow rate (*e.g.* 1 500 mL/min in Suzuki *et al.*'s work³⁴⁾ and 2 000 mL/min in Ito *et al.*'s study³¹⁾). Hence, the gas phase mass transfer was eliminated in the rate-limiting step discussion, with the research mainly focusing on the liquid phase diffusion. On the contrary, in the levitated droplet experiment, one of the important purposes is to study the effect of gas flow rate (varying in a wide range such as 270–3 000 mL/min in Ito *et al.*'s study^{31,40)}) on the reaction rate. The gas flow rate was controlled to be in a wide range, so that gas phase mass transfer could become the rate-limiting step for the reaction in the lower gas flow rate conditions/regions. To provide a comprehensive picture of the CO - liquid iron/steel reaction under a wider range of experimental conditions (temperature, gas/melt composition, gas flow rate, *etc.*), it is of paramount importance to examine the experimental result by taking the corresponding technique into consideration. Alternatively, a novel experimental set-up is requested, which enables the investigation of mass transfer

in both the gas and the liquid phase, while also allowing the measurement of the interfacial reaction rate.

Moreover, it is noticed that the gas-liquid interfacial reaction (for CO absorption and desorption) is measured to be much faster than the mass transfer in the liquid or gas phase. The reaction rate constant measured by Fruehan *et al.*³³⁾ is $5.4 \times 10^{-5} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ at 1250°C for steel containing 0.1 wt.% S. This is an order of magnitude larger than the previously measured reaction rate constant of the CO-liquid steel reaction when the process was controlled by liquid phase mass transfer. Therefore, the measured reaction rate in Fruehan *et al.*'s experiment,³³⁾ in which there is no liquid phase mass transfer limitation, is considerably more rapid than the situation where the mass transfer limitation is taken into account. Sasaki *et al.*⁵²⁾ re-measured the chemical rate constant; they obtained a value of $1.3 \times 10^{-3} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, which was even two orders of magnitude higher than the value estimated by Fruehan *et al.*³³⁾ However, in King *et al.*'s work³⁷⁾ for low C steel (~0.05 wt% C), the CO desorption rate was anomalously slower than the CO absorption rate. This was considered to be caused by the slow interfacial reaction, as there are limited available sites at the gas-melt interface due to the strong adsorption of oxygen. Kim *et al.*⁴⁶⁾ investigated the kinetics of CO absorption into molten iron and found that sulfur has a larger impact on the interfacial chemical reaction with respect to oxygen. In liquid iron containing high impurities (S activity > 0.02 wt%), it is observed that the absorbed CO molecules at the gas/liquid interface are difficult to dissociate into atoms due to fewer vacant sites around them (the sites are occupied by sulfur atoms). Hence, the impurity level can significantly reduce the reaction rate during CO absorption. However, in the CO desorption, in addition to the quantity of available sites at the gas-melt interface (determined by sulfur and oxygen content), the CO nucleation, as observed by many researchers,^{65,66)} may also play a critical role in determining the overall gas-melt reaction rate. For this reason, the CO absorption and desorption rate in molten iron/steel may significantly vary. Further experimental work on the kinetics of CO absorption and desorption with thoroughly controlled parameters, such as steel composition and interface area, are suggested. Moreover, an in-depth study on the interfacial reaction is required.

4. Conclusions

In the present work, the previous research on the CO absorption and desorption was reviewed. The experimental techniques were summarized and compared with each other. The C–O reaction mechanism was analyzed and discussed. Future work is suggested in order to clarify the CO absorption and desorption mechanism in liquid steel/iron. The conclusions are drawn as follows:

(1) A number of factors affect the kinetics of CO absorption and/or desorption by liquid steel/iron. These factors include temperature, steel composition (O, C, S, Al), CO partial pressure in the gas phase, stirring condition of the liquid phase, gas flow rate, and even the employed crucible materials.

(2) The overall reaction of CO absorption (and/or desorption) by liquid Fe–C–O alloys can be broken down

into several steps, *i.e.* 1) transport of the dissolved carbon and oxygen in the metal phase, 2) chemical reaction at the gas/metal interface ($\text{C} + \text{O} \rightleftharpoons \text{CO}$) and 3) transport of CO in a boundary layer of gas phase. In most studies, the rate-limiting step was determined to be 1) the mass transfer of C and O in the metal phase or 3) the transport of CO in gas phase, while 2) the chemical reaction rate at the interface was measured to be at least one order of magnitude larger than the mass transfer rate in the melt phase.

(3) When gas phase mass transfer is eliminated in the experiment, it can be generally concluded that the overall reaction is controlled by O mass transfer for high C steel ($\text{C} > 0.2 \text{ wt}\%$) and jointly by mass transfer of C and O for low C steel ($\text{C} < 0.03 \text{ wt}\%$). The mass transfer coefficients of oxygen and carbon were estimated to be, respectively, $k_o \approx 0.2 \times 10^{-2} - 5.0 \times 10^{-2} \text{ cm/s}$ and $k_c \approx 3.2 \times 10^{-2} - 5.6 \times 10^{-2} \text{ cm/s}$, *i.e.* varying with carbon and oxygen content.

(4) For the decarburization reaction of steel by blowing a gas mixture containing O₂ ($\text{C} + \text{O}_2 \rightarrow \text{CO}$), the rate-limiting step was found to be, respectively, O₂ mass transfer in gas phase for high C steel ($\text{C} > 0.2 \text{ wt}\%$) and C mass transfer in the metal phase for low C steel ($\text{C} < 0.1 \text{ wt}\%$).

(5) The interfacial reaction at the CO-liquid steel surface can be converted from CO adsorption-limited control to dissociation-limited reaction as the impurity concentrations of oxygen and sulfur increase (*e.g.* sulfur activity > 0.02). Further studies with special attention to the interfacial reaction are suggested.

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