Bubble Generation in MgO-C Crucible Charged with Slag and Metal in Relation to Local Corrosion

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ABSTRACT

The local corrosion of MgO-C crucible by molten slag (CaO-SiO_2-Al_2O_3-(Fe_tO)) and metal is greatly influenced by the bubbles generated at the crucible-slag-metal three-phase boundary and at the crucible-metal interface. Bubbles generated at the crucible-slag-metal three-phase boundary suppress the local corrosion, while bubbles generated at the crucible-metal interface enhance the local corrosion. Mechanism of the bubble generation was studied by *in-situ* X-ray observation and also by theoretical analysis. It is revealed that bubbles form mainly according to the reaction between (FeO) in the slag film between crucible and metal and $C_{(s)}$ in the crucible: $(FeO)+C_{(s)}=Fe_{(l)}+CO_{(g)}$. (FeO) in the slag film comes from the reaction: $2\underline{Fe}+(SiO_2)=2(FeO)+\underline{Si}$ for the FeO-free slag-electrolytic iron system.

KEY WORDS: MgO-C crucible; Molten slag; Molten iron; Local corrosion; Mechanism; Gas bubble generation.

1. Introduction

MgO-C refractory is widely used in various steelmaking processes. The local corrosion of the MgO-C refractory at the slag-metal interface (That is, refractory-slag-metal three-phase boundary) is considered as one of the important factors shortening the life of the refractory. It has been verified by *in-situ* X-ray observation at high temperature and investigation on cooled specimens after corrosion experiments[1~4]. It was also found that the local corrosion was caused by the cyclic dissolution reactions that MgO in the refractory dissoves into slag and graphite dissolves into the metal[2, 3]. Experiments also show that bubbles generated at the (MgO-C crucible)-slag-metal three-phase boundary and at the crucible-metal interface[1, 2].

In this study, effects of bubbles on the local corrosion rate and mechanism of gas bubble generation were studied by using the high temperature X-ray radiographic technique and analyzed theoretically.

2. Experimental

In-situ observation on the bubble generation in the MgO-C crucible charged with slag and metal was carried out in the $LaCrO_3$ heater furnace with the X-ray radiographic apparatus and recorded on the videotape under an atmosphere of high purity argon (>99.999%, O_2<0.2ppm, 200 ml/min) at 1873K[1]. MgO-C crucible (36mm I.D., 84mm depth) supplied by Kurosaki Corporation, Japan, $CaO-SiO_2-Al_2O_3$ -Fe_tO (C/S=1.0, Al_2O_3=10mass%, T.Fe=0 or 5mass%) slag, electrolytic iron ($\underline{O}$=60ppm), and Fe-C alloy containing 1.57mass% and 3.54mass%C, respectively, were used in the experiments. Chemical composition and physical properties of the MgO-C crucibles are given in Table 1. After experiment, the crucible was taken out from the furnace to cool rapidly. The rapidly cooled crucible was cut into two parts to analyze the situation of local corrosion. The corrosion depth was measured from the photos printed out from the videotape and also verified by the analysis of the cooled samples.

Rate of bubble generation in the C15 crucible charged with 60g $CaO-SiO_2-Al_2O_3$ (C/S=1.0, Al_2O_3=10mass%) slag and 200g electrolytic iron ($\underline{O}$=60ppm) was measured at the gas outlet of the furnace with a flowmeter during the experiments. Electrolytic iron was firstly melted in the C15 crucible for 25minutes, and then, slag was added on the surface of the molten metal and hold for 27minutes. Finally, 3.0g aluminum was inserted into the molten metal and observed for 40min. During the experiment, the rate of bubble generation was measured.

3. Results
3.1 Bubble generation

As shown in Table 2, gas bubble was not observed when only electrolytic iron was melted in MgO-C crucibles in an argon atmosphere at 1873K. When $CaO-SiO_2-Al_2O_3-(Fe_tO)$ (C/S=1.0, Al_2O_3=10mass%, T.Fe=0 or 5mass%) slag was added on the surface of the molten metal, generation of gas bubble was observed. For all the corrosion experiments of MgO-C crucible charged with slag and metal at 1873K, bubbles generate actively and continuously at the metal-crucible interface (Fig.1) and at the crucible-slag-metal three-phase boundary (Fig.2). Generation of gas bubbles stopped immediately after adding Al to the molten metal.

The rate of bubble generation was measured as 0 when only electrolytic iron was melted in C15 crucible for 25minutes at 1873K. When $CaO-SiO_2-Al_2O_3$(C/S=1.0, Al_2O_3=10mass%) slag was added on the surface of the molten metal, the measured rate of bubble generation was shown in Fig.3. After adding Al to the molten metal, the rate of bubble generation was also measured as 0. Change of metal composition was also shown in Table 3.

Cross-section of the rapidly cooled samples shows that the slag film exists at the slag-metal-crucible three-phase boundary, the crucible-metal interface and also on the bottom of the molten metal.

3.2 Local corrosion rate

As shown in Fig.4, the local corrosion rate (variation of corrosion depth with time) of the MgO-C crucible increases with increasing graphite content of the crucible in the range from 0mass% to 15mass%, while a decrease in the local corrosion rate of the crucible with graphite content from 15mass% to 25mass% is found.

Fig.4(a) and Fig.4(b) indicate that the local corrosion rate with the Fe_tO-bearing slag is less than that with the Fe_tO-free slag. In the case of Fe_tO-free slag, the local corrosion rate with the metal containing 1.57mass% C is less than that with electrolytic iron (Fig.4(c)). In the case of the Fe_tO-bearing slag, changes in the local corrosion rate with carbon concentration in the metal are very little for both C15 and C5 crucibles (Fig.5).

4. Effects of bubble generation on the local corrosion rate of the crucible

As revealed by the authors in the previous researches[1~4], the mechanism of the local corrosion of MgO-C refractories by molten slag and metal can be explained as follows. During the corrosion experiments, the slag-metal interface was observed to move upwards and downwards along the crucible wall in an oscillating manner. That is, the metal phase creeps up along the crucible wall and the slag phase penetrates into the crucible wall-metal interface and forms slag film. According to the different wettability of MgO and graphite in the refractory with slag and metal phase, the process of the creeping up of metal along the crucible wall and the formation of slag film at the metal-crucible interface cycles, and the dissolution of graphite into metal and MgO into slag are promoted. This cyclic process results in the progress of the local corrosion of the MgO-C refractory. Increasing graphite content in the MgO-C crucible increases the contacting time of the metal phase with the refractory wall in the local corrosion zone, the frequency of the metal creeping up (i.e. the frequency of the slag film forming and disappearing), and the local corrosion depth. So the local corrosion rate increases with increasing the graphite content from 0mass% to 15mass%. But the other phenomena described in 3.2 can not be explained only with this mechanism, and should be explained in the point of effects of bubble generation on the local corrosion of the crucible.

4.1 Bubbles generated at the metal-crucible interface

As shown in Fig.1, bubbles at the metal-crucible interface mainly form at the corner of the crucible bottom. The bubbles creep up along the metal-crucible interface with growing up, and pass through the local corrosion zone, and are finally transferred into gas phase along the slag-crucible interface. When the bubble is passing through the local corrosion zone, the slag film in the local corrosion zone is pulled upwards together with the bubble, and the metal is also partially pulled upwards. Thus, the slag-metal interface is strongly disturbed and oscillates violently. The frequency of bubble generation at metal-crucible interface decreases with both increasing C concentration in the metal and graphite content in the crucible, and increases with increasing (FeO) concentration in the slag. Therefore, gas bubbles generated at the metal-crucible interface enhance the local corrosion by agitating the motion of the slag film and metal at the slag-metal interface. It accounts for the results that the local corrosion rate with the metal containing 1.57mass%C is less than that with electrolytic iron in the case of Fe_tO-free slag as shown in Fig.4.

4.2 Bubbles generated at the slag-metal-crucible three-phase boundary

Gas bubbles generate in a large number at the three-phase boundary. As shown in Fig.2(a), in the system of crucible (15mass% graphite)-slag (5mass%T.Fe)-Fe-C(1.5mass%) alloy, a gas curtain (gas film) forms between the crucible wall and slag above the three-phase boundary. In the case of the crucible containing 25mass% graphite, the gas curtain forms for both the Fe_tO-free slag in Fig.2(b) and the Fe_tO-bearing slag as shown in Fig.2(c).

During gas bubble generation, the slag film is pushed away from the local corrosion zone, and the creeping up of the metal is also restrained. Therefore, gas bubbles generated at the three-phase boundary restrain the local corrosion. Experiments show that the size of the

bubble generated at the three-phase boundary decreases with increasing FeO concentration in the slag, C concentration in the metal and graphite content in the refractory, while the generation frequency increases. In the case of the Fe_tO-free slag, although gas bubbles generate actively at the three-phase boundary, the creeping up phenomenon of the metal can be observed, and the local corrosion can also be confirmed. So the local corrosion rate of C25 with Fe_tO-free slag is less than that of C15 as shown in Fig.4(a). In the case of Fe_tO-bearing slag, the restraint of the local corrosion by the gas bubbles generated at the three-phase boundary is superiority to the enhancement of the local corrosion by the gas bubbles generated at the metal-refractory interface. When the gas curtain is formed, the creeping up phenomenon of metal almost disappears, and the local corrosion can not be clearly confirmed. So, the influence of C concentration in the metal on the corrosion rate is also very little as shown in Fig.5.

Based on the proposed mechanism of the local corrosion of this system, the above mentioned experimental results are explained as follows. The gas curtain formed above the three-phase boundary prevents the slag film formation and the direct contact between graphite and metal, which suppresses the local corrosion.

5 Mechanism of gas bubble generation
5.1 Preferential conditions for gas bubble generation

The criterion for gas bubble generation is

$$P_{CO} \geqq P_{Ar} + P_0 + 2\sigma/r \qquad (1)$$

where P_{CO} is the pressure of CO gas bubble, P_{Ar} is the pressure of the argon atmosphere in the furnace, P_0 is the hydrostatic pressure caused by the molten metal and slag, σ is the surface tension of molten slag, and r is the radius of the gas bubble.

The position for the preferential generation of gas bubble is the gas-filled cavity or crevice on the surface of the crucible in contact with metal or slag phase. The preferential conditions for the nucleation and growth of gas bubbles are as follows: (1) the gas-filled cavity or crevice exists, (2) the hydrostatic pressure P_0 is relatively small, and (3) the bad wettability between slag phase and the graphite in the MgO-C crucible. The slag-metal-crucible three-phase boundary and the corner of the bottom of MgO-C crucible are the positions for the preferential formation of gas bubbles because of the existence of cavity or crevice and relatively small hydrostatic pressure. The location where slag contacts with graphite is advantageous to the growth of gas bubbles due to the bad wettability and lower surface tension of slag, while the place where metal contacts with graphite is disadvantageous to the growth of gas bubbles due to the good wettability and higher surface tension of metal.

5.2 Mechanism of gas bubble generation

The consideration in 5.1, the experimental results shown in Tables 2 and 3, and theoretical analysis support the mechanism that CO gas bubbles form mainly by the reaction between (FeO) in the slag film and $C_{(s)}$ in the crucible (reaction (2)). (FeO) in reaction (2) is supplied by different reactions in different cases described as follows and transferred from the slag-metal interface to the slag film-crucible interface. The slag-graphite interface is the prevailing position for the nucleation and growth of gas bubbles due to the bad wettability and lower surface tension of slag.

In the case of FeO-bearing slag or the molten metal containing high oxygen concentration, FeO in the bulk slag and the reaction (3) are the main sources of FeO.

$$(FeO) + C_{(s)} = Fe_{(l)} + CO_{(g)} \qquad (2)$$
$$\underline{O} + Fe_{(l)} = (FeO) \qquad (3)$$
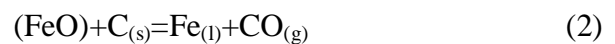
In the case of FeO-free slag and the molten metal containing low oxygen concentration, FeO concentration depends on the concentration of $\underline{C}$, $\underline{Si}$, $\underline{Al}$, etc., and can be analyzed by using the deoxidation equilibia in liquid iron alloys at 1873K[5].

If adding deoxidants such as Al, Si, etc. into the molten metal, the oxygen concentration is

controlled by $\underline{Al}$, $\underline{Si}$, etc. according to Eqs.(4) and (5). Bubble generation stopped immediately after adding Al into the molten metal in the both cases of FeO-bearing slag and FeO-free slag. Since the (FeO) concentration controlled by $\underline{Al}$ (reaction (4)) is lower than that in equilibrium with $C_{(s)}$, CO gas bubble can not form by the reaction (2).

$$2\underline{Al}+3\underline{O}=(Al_2O_3) \tag{4}$$

$$\underline{Si}+2\underline{O}=(SiO_2) \tag{5}$$

If the molten iron alloy contains high carbon concentration, such as Fe-C(1.57mass%) alloy and Fe-C(3.54mass%) alloy, (FeO) concentration is controlled by $\underline{C}$ concentration (reaction(6)). The rate of bubble generation decreases with increasing the $\underline{C}$ concentration in the metal. This result supports that CO gas bubble generates according to reaction (2), because the increase in $\underline{C}$ decreases $a_{(FeO)}$ of reaction (3) due to the decrease in $\underline{O}$ according to reaction (6) which results in the decrease in the rate of bubble generation.

$$\underline{C}+\underline{O}=CO_{(g)} \tag{6}$$

Finally, in the FeO-free slag-electrolytic iron system, (FeO) comes from reaction (7), that is, the (FeO) concentration is controlled by $\underline{Si}$ concentration and (SiO$_2$) concentration. Mechanism of bubble generation in this system is shown in Fig.6. In the experiment for measuring the rate of bubble generation, the slag of 45mass%(49mol%)CaO-45mass%(45mol%)SiO$_2$-10mass%(6mol%)Al$_2$O$_3$ is used. The activity of (SiO$_2$), a_{SiO_2}, is 0.10 obtained from the activity of the CaO-SiO$_2$-Al$_2$O$_3$ system[5] with the standard state of pure solid SiO$_2$. From the deoxidation equilibria in liquid iron alloys at 1873K[6], $\underline{O}$ concentration in equilibrium with 0.75mass%$\underline{C}$ and 1atm CO is 0.0030mass%, while $\underline{O}$ concentration in equilibrium with 0.32mass%$\underline{Si}$ and a_{SiO_2}=0.1 is 0.0025mass%. It indicates that although $\underline{C}$ concentration increases with the progress of the local corrosion due to the dissolution of C(s) in the refractory into the metal, the oxygen concentration is still controlled by the $\underline{Si}$ concentration and (SiO$_2$) concentration.

$$(SiO_2)+2Fe_{(l)}=\underline{Si}+2(FeO) \tag{7}$$

Thermodynamically, CO gas bubbles can also generate according to the reaction (8). However, reaction (8) can hardly explain the phenomenon that bubble generation stops immediately after adding Al to the metal during the experiments (Table 2).

$$(SiO_2)+2\underline{C}(orC_{(s)})=\underline{Si}+2CO_{(g)} \tag{8}$$

$$\Delta G_8^o = 604505 - 399.4T \qquad K_8 = \frac{a_{Si} \cdot P_{CO}^2}{a_C^2 \cdot a_{SiO_2}}$$

where ΔG_8^o is calculated by using the reported data[7]. The standard state is selected as: C(s), SiO$_2$(s)-pure solid；(FeO)-pure liquid; $\underline{C}$, $\underline{Si}$-Fe melt containing 1mass% C or Si.

After adding 3g Al to the molten metal in the experiment for measuring the rate of bubble generation, the slag compositions are predicted to change into 45mass%(46mol%)CaO-36mass%(34mol%)SiO$_2$-19mass% (20mol%)Al$_2$O$_3$ by assuming that the 3g Al is completely used to reduce the SiO$_2$ in the slag. a_{SiO_2} in this slag equals to 0.07 from the activity of the CaO-SiO$_2$-Al$_2$O$_3$ system[5]. By assuming a_C=1 and P_{CO}=1atm, $a_{Si} = 707$. Without considering the influence of $\underline{C}$ on the a_{Si} and using the data $e_{Si}^{Si} = 0.11$, it can be obtained that [Si mass%] = 15 by reaction (8). It means that CO gas will continuously generate until $\underline{Si}$ equals to 15mass%. But experiments show that bubble generation was not observed.

Gas bubble may also form according to the reaction (9) between $\underline{O}$ in the metal and $C_{(s)}$ in contact with $\underline{O}$.

$$\underline{O}+C_{(s)}=CO_{(g)} \tag{9}$$

But experiments show that gas bubbles were not observed when only the metal phase was melted in MgO-C crucible in the argon atmosphere. Even in the case of MgO-C crucible-slag-metal system, the time for $\underline{O}$ in the metal directly contacting with C(s) in the refractory is very

short due to the existence of slag film at the metal-refractory interface. Gas bubble generation according to the reaction (6) is possible if the solubility product $[\%\underline{C}]\_[\%\underline{O}]$ is much larger than that equilibrated with $P_{CO}=1$atm. However, reaction (6) can not explain the phenomenon that the gas bubbles generate continuously in the MgO-C crucible-metal-slag system during the progress of the local corrosion.

We can summarize that continuous generation of gas bubbles during the progress of the corrosion of MgO-C crucible by molten slag and metal is mainly caused by the reaction between $C_{(s)}$ in the crucible and oxygen. The oxygen mainly comes from (FeO) in the slag. For the Fe_tO-free slag-electrolytic iron system, (FeO) in the slag is supplied by the reaction between (SiO_2) in the slag and Fe.

6.Conclusions

The local corrosion of MgO-C crucible by molten slag $(CaO-SiO_2-Al_2O_3-(FeO))$ and metal is greatly influenced by the bubbles generated at the crucible-slag-metal three-phase boundary and at the crucible-metal interface. Bubbles generated at the crucible-metal-slag three-phase boundary suppress the local corrosion, while bubbles generated at the crucible-metal interface enhance the local corrosion.

Gas bubbles form mainly according to the reaction between (FeO) in slag film and $C_{(s)}$ in the crucible: $(FeO)+C_{(s)}=Fe_{(l)}+CO_{(g)}$.

In the case of FeO-free slag-electrolytic iron system, (FeO) in the slag film comes from the reaction: $2\underline{Fe}+(SiO_2)=2(FeO)+\underline{Si}$.

REFERENCES

1) Z. Li, K.Mukai and Z. Tao: Reactions between MgO-C refractory, molten slag and metal. ISIJ International. Vol40(2000), Supplement, S101~105.
2) Z. Tao, K. Mukai et al. *Texture evaluation and relation to properties for refractories,* ed. by the iron and steel institute of Japan, (1999), 126.
3) K.Mukai, J.M.Toguri, and J.Yoshitomi: Corrosion of alumina-graphite refractories at the slag-metal interface. *Can. Metal. Q.*, 25(4)(1986), 265~275.
4) K.Mukai: Marangoni flows and corrosion of refractory walls. *Phil. Trans. R. Soc. Lond. A*, 356 (1998), 1015~1026.
5) The committee for fundamental metallurgy: Slag atlas, Verlag Stanleisen m.b.H., (1981) P120.
6) E. T. Turkdogan: Physical chemistry of high temperature technology. Academic press, New York, 1980, P380.
7) I. Barin and O. Knacke: Thermochemical properties of inorganic substances. Verlag Stanleisen m.b.H., Dusseldorf. 1973.
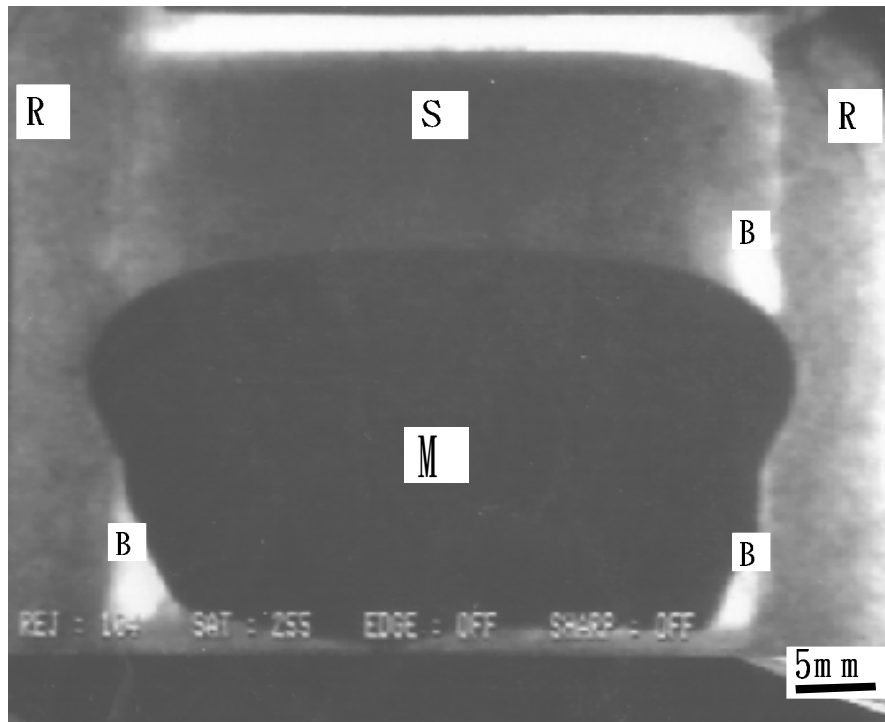
Fig.1 Bubble generated at the metal-refractory interface and it
passed just the slag-metal-refractory boundary at 1873K.
S: Slag; M: Metal; R: Refractory.
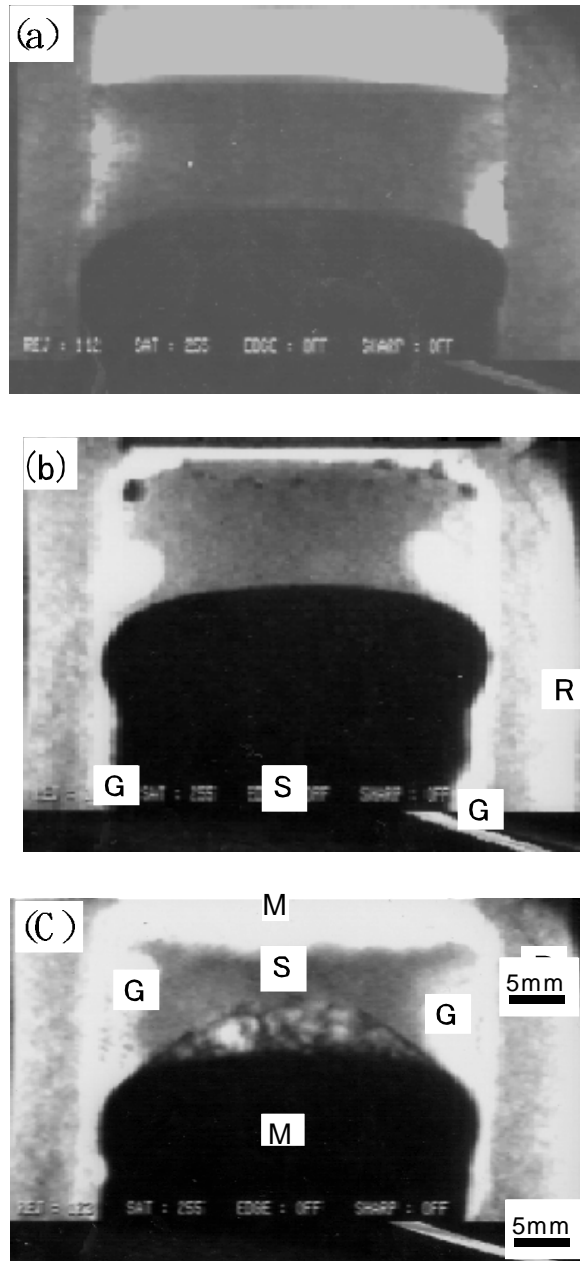R: C15; S: T.Fe=0mass%; M: Electrolytic iron.

Fig.2 Bubbles generated at the slag-metal-refractory three-phase
boundary at 1873K.
R: Refractory; S: Slag; M: metal; G: gas 5mm in.
(a) R:C15; S: T.Fe=5mass%; M: Fe-C(1.5mass%) alloy;
(b) R:C25; S: T.Fe=0mass%; M: Electrolytic iron;
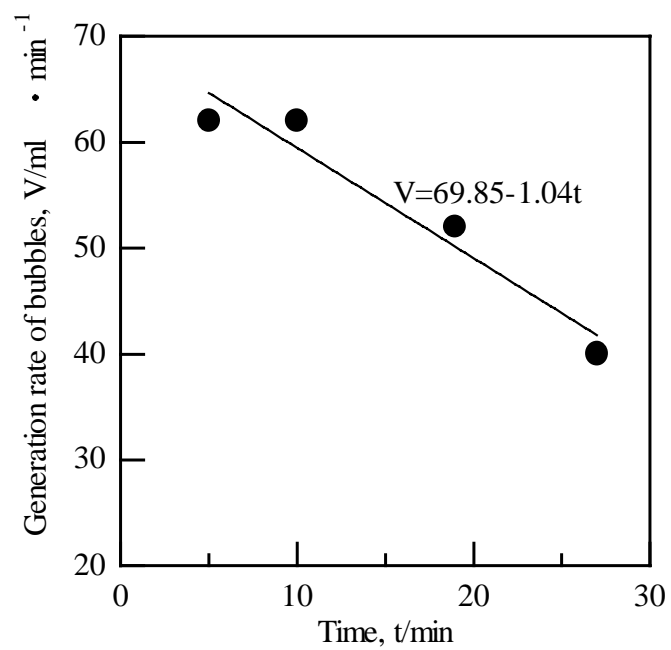(c) R:C25; S: T.Fe=5mass%; M: Electrolytic iron.

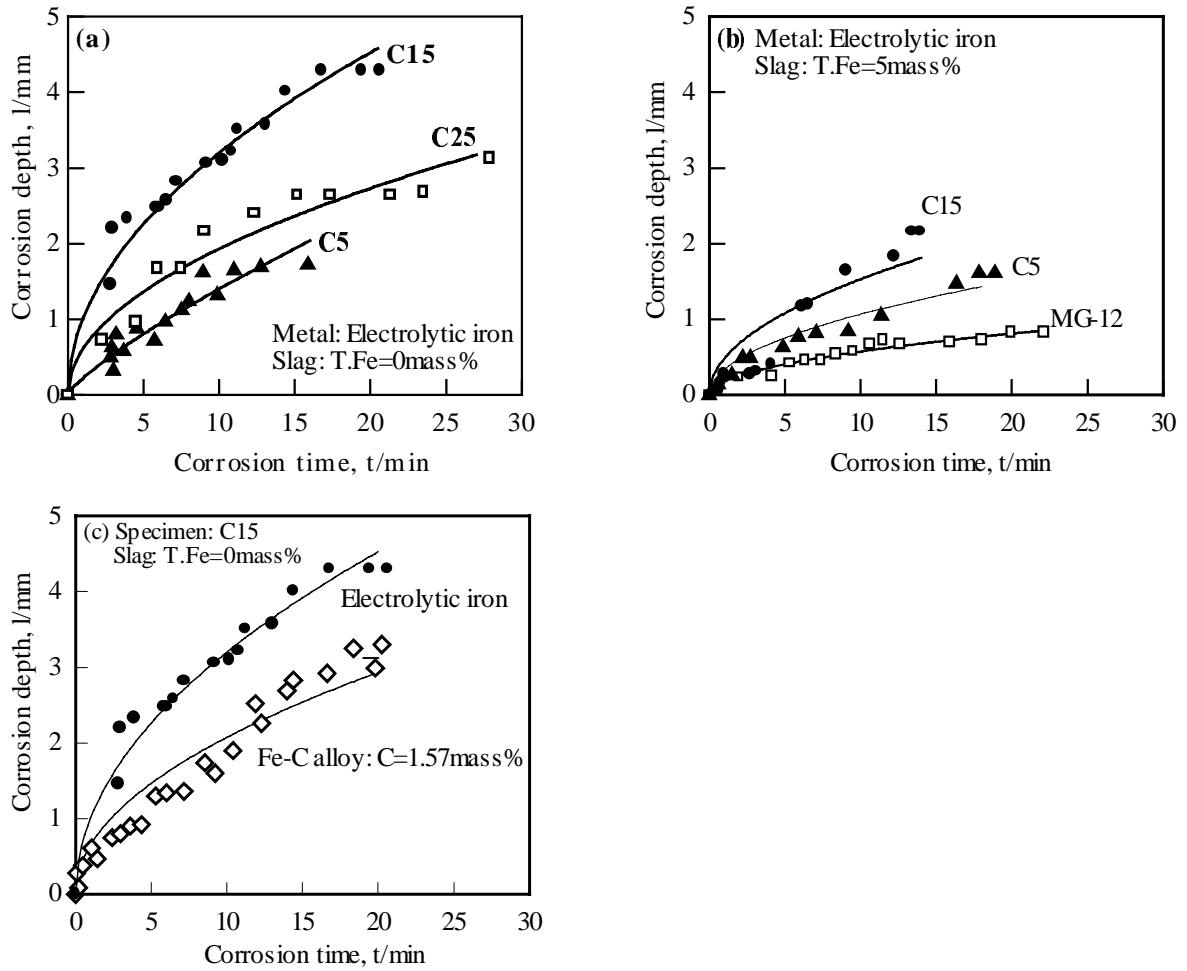Fig.3 Change of the rate of bubble generation with time.

Fig.4 Relationship between the corrosion depth at the slag-metal interface and corrosion time for MgO-C crucible at 1873K.
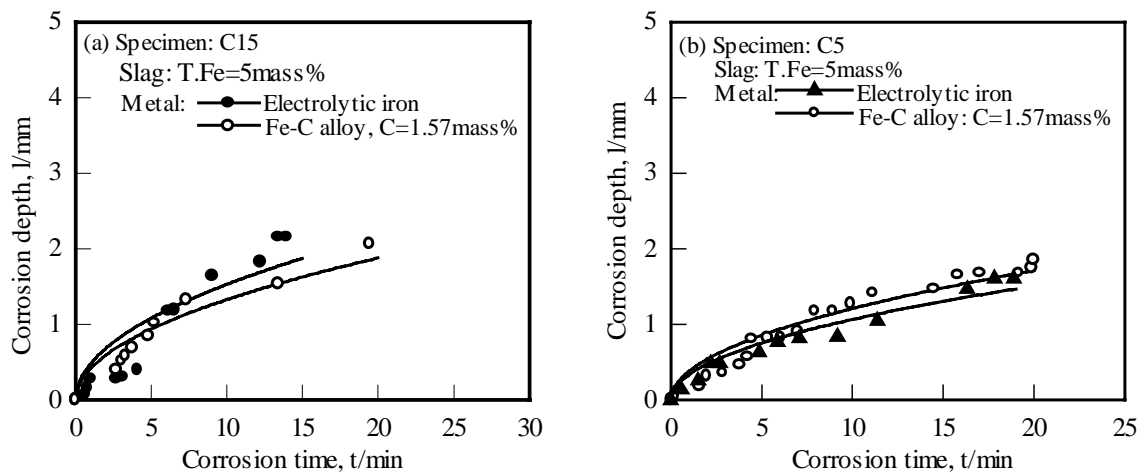

Fig.5 Relationship between the corrosion depth at the slag-metal interface and corrosion time for MgO-C crucible at 1873K.

C(s)+(FeO)=
CO(g)+Fe(l)

Bubble

$(SiO_2)+Fe(l)=$
$\underline{Si}+(FeO)$

(FeO)

MgO

Bubble

Graphite

Crucible wall
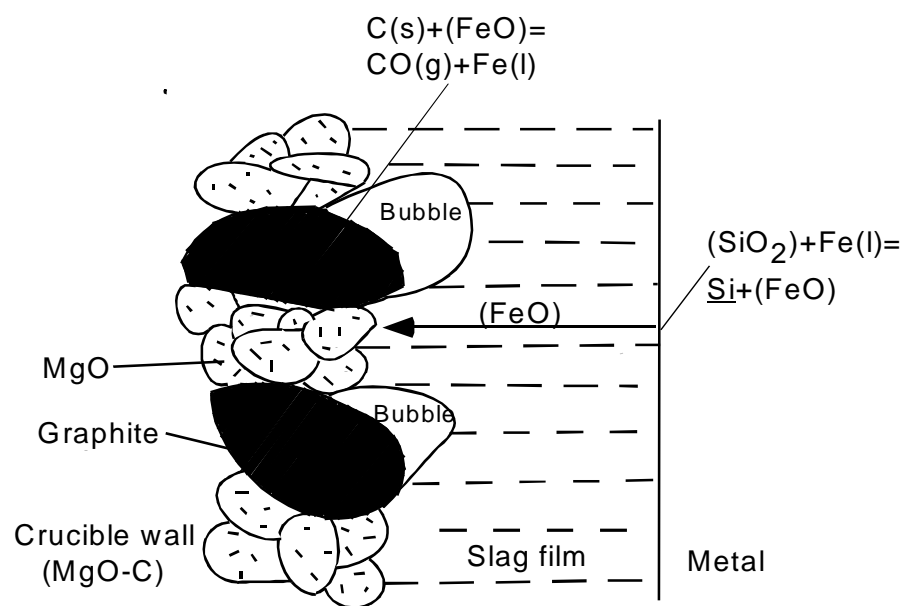(MgO-C)

Slag film

Metal

Fig.6 Mechanism of bubble generation in (MgO-C crucible)
-(FeO-free slag)-electrolytic iron system.

Table 1. Chemical composition and physical properties of MgO-C crucibles.

Specimen	C5	C15	C25	MG-12
MgO(mass%)	95	85	75	98
C(mass%)	5	15	25	--
Apparent porosity(%)	6.0	2.9	2.8	--
Bulk density(Mg · m^{-3})	3.04	2.92	2.79	--
Cold crushing strength(MPa)	66.5	45.1	38.9	--

Table 2. Bubble generation in the systems of MgO-C crucible-metal and MgO-C crucible-slag-metal observed directly by using the X-ray radiographic apparatus.

Position*	Only metal	Adding slag (T.Fe=0 or 5mass%) on the surface of metal	Adding Al to metal
Upper	No		No
Middle	No	Bubble generation; Extension of the position to the bottom	No
Bottom	No		No

*Upper: slag-metal-crucible 3-phase boundary;
Middle: metal-crucible interface;
Bottom: bottom of metal phase.

Table 3 Change of metal composition in the C15 crucible charged with slag.

	C	Si	O
Electrolytic iron	30massppm	<3massppm	60massppm
Only metal for 25min	0.080mass%	60massppm	
Adding slag for 27min	0.75mass%	0.32mass%	