1. Introduction

In recent years, investigations of inclusions in steel can be roughly divided into two trends. One of the trends is devoted to minimizing the inclusion amount, reducing the inclusion size and changing inclusions into those of harmless shapes and compositions for the purpose of manufacturing clean steel. The other trend, which began in the early 1990’s, is dedicated to utilizing fine oxide inclusion particles as the heterogeneous nucleation sites during the solidification and phase transformation for the microstructural control of steel. This method is firstly named “oxide metallurgy” by Mizoguchi et al. 1)

As early as 1970’s, Mori et al. 2) pointed out the possibility of deoxidation of molten steel with magnesium vapor. By means of vaporization of Mg metal, the magnesium vapor was blown into the molten steel with Ar carrier gas. The obtained solubility product is [Mg] · [O] / 1.0 \times 10^{-6} at 1873 K. In Si–Mn complex deoxidation of Fe–Ni alloy 3) and Al deoxidation of molten stainless steel 4) with CaO–SiO2–Al2O3–MgO slag, Nishi et al. found that the MgO content in inclusions gradually increased with time and the spinel (MgO · Al2O3) inclusion was formed because of reduction of MgO contained in slag by Si or Al.

With holding Al killed steel in an MgO crucible by use of CaO–Al2O3–MgO flux, Matsuno et al. 5) discovered that the MgO type inclusion in high carbon steel was generated not only from reduction of the flux but also from reduction of the MgO crucible. After industrial experiment studies of the impact of ladle age on the formation of inclusions in steel using the ladles with carbon bearing MgO lining, Du et al. 6,7) concluded that the ladle glaze was the major source of inclusions in the melt, and MgO inclusion could be formed in steel by slag-refractory lining reactions. In recent years, a number of equilibrium studies 8–12) on MgO formation were carried out. The phase stability regions of MgO, Al2O3 and MgO · Al2O3 in the Fe–Al–Mg–O system 9,11) were obtained by plotting Mg vs. Al concentrations. In addition, Najafabadi et al. 13) proposed a deoxidation method of molten steel with the immersion MgO–C porous tube, in which the magnesium vapor produced by the reaction between MgO and C was used for deoxidation of molten steel. Shan et al. 14–16) developed another deoxidation method of molten steel with magnesium vapor produced in situ by carbothermic or aluminothermic reduction of magnesium oxide.

On the other hand, a great deal of effort has endeavored to positively utilize the fine inclusion particles for the mi-
crostructural control of steel in recent years. On the basis of in-situ observation of inclusions on the molten steel surface with a confocal scanning laser microscope, the attractive force between a pair of MgO inclusions was found to be one-tenth of that between a pair of alumina inclusions so that MgO inclusions had a much weaker tendency to aggregate or to form clusters.\(^{17}\) The grain growth of Fe–10mass%Ni alloy was strongly inhibited by the primary inclusions of MgO particles, which were evenly distributed in the alloy after Mg deoxidation.\(^{18}\) With using Fe–10mass%Ni alloy, Suito \textit{et al.} systematically examined the dispersion of fine primary MgO inclusions,\(^{19}\) studied the characteristics of size distribution of MgO particles\(^{20}\) and the dispersion behavior of deoxidation particles of MgO during solidification,\(^{21}\) furthermore, clarified the effect of primary deoxidation products of MgO on precipitation of TiN\(^{22}\) and MnS\(^{23}\) in the alloy. The effect of size distribution of MgO particles on austenite grain growth in Fe–0.05mass%C alloy was also investigated.\(^{24}\)

The purpose of present work is to study the behavior of the primary inclusions in deoxidation process of molten steel with magnesium vapor produced in situ by aluminothermic reduction of magnesium oxide. The produced magnesium vapor was injected into the molten steel with argon carrier gas to react with oxygen dissolved in it. As the magnesium partial pressure is decreased by use of Ar carrier gas, deoxidation will mainly proceed on the Mg–Ar bubble surface. Therefore, it is possible for most of the formed MgO inclusions to be removed by floating up with the rising Ar–Mg bubbles. The remaining MgO inclusions should be fine in size and be evenly distributed in the molten steel. As a result, the harmful impact of the large deoxidation products on the mechanical properties of steel such as strength and toughness is minimized, while the remaining fine MgO inclusions can be used as the heterogeneous nucleation sites that is beneficial to grain refinement of steel. These fine MgO inclusions will also promisingly act as inoculants for the heterogenous nucleation of TiN and MnS.

In addition, effects of immersion tube material, initial oxygen concentration, carrier gas flow rate and addition method of MgO–Al pellets on deoxidation rate and the number of the formed inclusions are also studied. The size, composition and morphology of inclusions, and the characteristics of remaining inclusions in the ingot, are also discussed.

2. Experimental

2.1. Procedure

Figure 1 schematically shows the experimental apparatus. A high frequency induction furnace (15 kW, 100 kHz) was used to melt electrolytic iron of 350 g in the magnesia crucible of 40 mm i.d. and 100 mm in height. The electrolytic iron had the compositions of 18 ppm C, 6 ppm S, less than 10 ppm P, less than 5 ppm Si, 1 ppm Mn, 1 ppm Cu, 8 ppm N, 80 ppm O and remaining Fe. The crucible contained 98% MgO and 1% CaO. The inert atmosphere was maintained by blowing argon gas onto the melt surface at a gas flow rate of 1.33×10\(^{-3}\)Nm\(^3\)/s. As shown in Fig. 2, the employed dense Al\(_2\)O\(_3\) or porous MgO immersion tube was of 11 mm i.d. and 15 mm o.d. At their lower parts, there were 4 holes for the MgO porous tube or 4 ZrO\(_2\) nozzles with the inner diameter of 1.0 mm for the dense Al\(_2\)O\(_3\) tube. Through the holes and nozzles, the produced magnesium vapor together with the argon carrier gas was injected into the molten steel.

The pellets charged into the immersion tube were the mixture composed of magnesia powder (0.4 \(\mu\)m in average diameter and purity higher than 99.99%) and aluminum powder (75–150 \(\mu\)m in diameter and purity higher than 99.5%). With mixing the magnesium oxide and aluminum powders at a molar ratio of 2:1, the pellets were formed by use of a cold isostatic press (CIP) under the pressure of 150 MPa for one hour, approximately having a diameter of 3 mm and a length of 5 mm. After melting the electrolytic iron, predeoxidation was conducted by blowing 50vol%Ar–50vol%H\(_2\) mixture gas onto the melt surface at the total gas flow rate of 1.7×10\(^{-3}\)Nm\(^3\)/s for 30 min. The initial oxygen concentration in the melt was subsequently adjusted by blowing 98vol%Ar–2vol%O\(_2\) mixture gas onto the melt surface for a prescribed time. Finally the pellet was charged into the immersion tube that had been inserted into the iron melt in advance. The magnesium vapor produced in situ by aluminothermic reduction of magnesium oxide was injected directly into the molten steel together with the argon carrier gas, to react with oxygen dissolved in it.

2.2. Chemical Analysis and Microscopic Observation

The deoxidation processes were examined by taking
samples from the melt with quartz tubes of a inner diameter of 1.5 mm at the appropriate time intervals for analyzing oxygen, magnesium, aluminum and silicon contents. The oxygen in the sample was analyzed by non-scattered infrared ray detector after being extracted by the gas impulse melting method. The oxygen concentration was calibrated by two kinds of standard samples (46 ppm and 437 ppm). The magnesium, aluminum and silicon contents in the sample were determined by Induction Coupled Plasma Emission Spectroscopy (ICP) with the relative scattering less than 5%, after samples were completely dissolved in hydrochloric acid solvent.

The surface parallel to the axis of the cylindrical sample was polished with 180 grade emery paper, followed by intermediate polishing with the diamond suspension of 9 μm and 3 μm. Finally it is polished with Masterprep polishing suspension of 0.05 μm. The planar particle number and size distribution of particles on a polished cross section were observed in this study. The number of inclusions per unit area, \( N_p \), was the average value of about 50 locations, and each value was obtained from counting the number of inclusions for a given area by a SEM microphotograph. The microphotograph was taken at a magnification of 2000, corresponding to the area of 0.003810 mm\(^2\). In addition, the size distribution of inclusions was obtained by measuring about 100 particles selected in a random manner. The planar particle diameter, \( d_A \), was estimated as the diameter of a circle with the same area of a sectioned inclusion. Finally, the inclusion composition for each sample was the average value of about 20 particles and each value was obtained by analysis with an energy dispersive spectrometer (EDS).

3. Principle of Deoxidation with Magnesium Vapor Produced in Situ by Aluminothermic Reduction of Magnesium Oxide

3.1. Principle of Aluminothermic Reduction of Magnesium Oxide

The reduction of magnesium oxide by aluminum takes place in two stages:\(^{25}\) At the first stage, the magnesium oxide is reduced to produce magnesium vapor and MgO·Al\(_2\)O\(_3\) spinel.

\[
4\text{MgO (s)} + 2\text{Al (l)} = 3\text{Mg (g)} + \text{MgO·Al}_2\text{O}_3 (s) \quad \text{...(1)}
\]

At the second stage, the spinel is further reduced by aluminum.

\[
3(\text{MgO·Al}_2\text{O}_3) (s) + 2\text{Al (l)} = 3\text{Mg (g)} + 4\text{Al}_2\text{O}_3 (s) \quad \text{...(2)}
\]

The reduction efficiency of magnesium oxide, \( \eta_{R,\text{MgO}} \), is introduced, which is defined as the ratio of the reduced magnesium mass, \( W_{\text{Mg,R}} (g) \), to the initial mass of magnesium in the pellet, \( W_{\text{Mg,O}} (g) \).

\[
\eta_{R,\text{MgO}} = \frac{W_{\text{Mg,R}}}{W_{\text{Mg,O}}} \times 100 (\%) \quad \text{...(3)}
\]

At the temperature of 1873 K, the carrier gas flow rate of 1.67×10\(^{-6}\) Nm\(^3\)/s, and with the pellets composed of MgO and Al at the molar ratio of 2:1, the reduction efficiency of magnesium oxide was measured and shown in Fig. 3. In the first 10 min, the reduction rate was very fast and the regression equation of \( \eta_{R,\text{MgO}} \) as a function of time is given by

\[
\eta_{R,\text{MgO}} = 69.1 \times [1 - \exp(-t/105)] (\%) \quad (t<600 \text{ s}) \quad \text{...(4)}
\]

After 10 min, the reduction rate became slow, the change in \( \eta_{R,\text{MgO}} \) with time can be described as

\[
\eta_{R,\text{MgO}} = 68.4 + 0.000831t (\%) \quad (t \geq 600 \text{ s}) \quad \text{...(5)}
\]

Then the number of moles of magnesium produced during the time from \( t \) to \( t + \Delta t \), \( \Delta n_{\text{Mg}}(t) \), can be described by

\[
\Delta n_{\text{Mg}}(t) = \frac{W_{\text{Mg,0}}}{M_{\text{Mg}}} \times [\eta_{R}(t + \Delta t) - \eta_{R}(t)]/100 (\text{mol}) \quad \text{...(6)}
\]

where \( M_{\text{Mg}} \) is the molecular mass of Mg (g/mol), \( t \) is the time (s), \( \Delta t \) is the time increment for calculating \( \Delta n_{\text{Mg}}(t) \), which is taken as 6 s in the calculation.

Therefore the initial magnesium partial pressure in the bubble injected into the melt, \( P_{\text{Mg}}(t) \), can be expressed as

\[
P_{\text{Mg}}(t) = \frac{P_1 \cdot \Delta n_{\text{Mg}}(t) / \Delta t}{Q_{\text{Ar}} / (R \cdot T)} (\text{atm}) \quad \text{...(7)}
\]

where \( Q_{\text{Ar}} \) is the argon carrier gas flow rate (Nm\(^3\)/s), \( R \) is the gas constant (atm · m\(^3\) · mol\(^{-1}\) · K\(^{-1}\)), \( T \) is the room temperature (K) being taken as 298 K here, \( P_1 \) and \( P_t \) are the pressure of the Ar carrier gas and the total pressure in the bubble injected into the melt (atm), respectively, and both are taken as 1.0 atm here.

Figure 3 also shows the calculated results of \( P_{\text{Mg}}(t) \) at the carrier gas flow rate of 5.0×10\(^{-7}\) Nm\(^3\)/s and 1.67×10\(^{-6}\) Nm\(^3\)/s. It is seen that the values of \( P_{\text{Mg}}(t) \) decrease rapidly at the initial stage of the experiments being the constant values of 0.012 and 0.0037 atm after 10 min for the carrier gas flow rate of 5.0×10\(^{-7}\) Nm\(^3\)/s and 1.67×10\(^{-6}\) Nm\(^3\)/s, respectively.

3.2. Principle of Deoxidation with Magnesium Vapor

If the magnesium vapor produced by the above reductions is injected directly into the molten steel, the deoxidation proceeds as

\[
\text{Mg (g) + O}_2 = \text{MgO (s)} \quad \text{...(8)}
\]
If the dissolved magnesium in the melt reacts with the dissolved oxygen, it can be written as

$$\text{Mg} + \text{O} \rightarrow \text{MgO} \quad \text{(s)} \quad \Delta G^\circ_{\text{f}} = -89.98 - 0.08194T \text{(kJ/mol)}$$

$$\quad \text{(11)}$$

4. Experimental Results and Discussion

4.1. Inclusions Formed by Use of the Dense Al$_2$O$_3$ Immersion Tube

Figure 4 shows the variations of the total oxygen concentration and the inclusion number per unit area with time. The dense alumina immersion tube was used, the temperature was 1873 K, the argon carrier gas flow rate was $5.0 \times 10^{-2}$ Nm$^3$/s, and all of the pellets with the mass of 1.8 g were charged by one time. In the figures hereinafter, $W_i$ is the pellet mass charged at each time and $W_T$ is the total pellet mass. Because the experiment was started the moment pellets were charged into the tube, the oxygen concentration decreased quickly at first due to the fast initial reduction rate of magnesium oxide. After 5 min, the oxygen concentration maintained almost a constant value because of quite a slow reduction rate of magnesium oxide. The inclusion number per unit area increased rapidly at first, reached a peak at 5 min, and then decreased gradually.

When the magnesium partial pressure is high at the initial stage of experiment, deoxidation with magnesium vapor should take place both on the bubble surface and in the melt because some produced magnesium vapor dissolves into the melt. Deoxidation in the melt should result in the increase in the inclusion number per unit area. When some MgO particles formed during deoxidation on the bubble surface drop out of the rising bubbles, this also leads to the increase in the inclusion number. Therefore the inclusion number per unit area increases at the initial stage of the experiment.

However, with the decrease in reduction rate of magnesium oxide after 5 min, the formation rate of inclusions by deoxidation with magnesium vapor turns to be slower than the removal rate by floating up with rising bubbles, the inclusion number per unit area thus decreases.

The final oxygen concentration of about 80 ppm is relatively high in the present case. One of the reasons is that the magnesium addition amount is relatively little, being 0.23 mass% of the melt mass. Thus deoxidation by magnesium does not proceed to the ultra low oxygen concentration in the present case. In addition, because the magnesium concentration is rather low at the later stage of deoxidation, the disintegration of MgO crucible is liable to take place, which results in the increase in oxygen concentration in the melt. Furthermore, the remaining inclusions are so fine in size that it is difficult for them to be removed from the melt. In fact, the final inclusion number per unit area of 280 nm$^{-2}$ is relatively high.

The SEM images of inclusions at 0, 5, 45 min are presented in Fig. 5. Before the experiment, the inclusions usually have the size of about 2 μm with the main composition of iron oxide as shown in the upper diagram of Fig. 5. Although molten steel has quite a large oxygen solubility of 0.23% in equilibrium with FeO at 1873 K, the solid iron, such as γ-Fe, has the oxygen solubility of only 0.003%. Therefore, the dissolved oxygen in molten steel is liable to precipitate in the form of FeO during the solidification process.

After charging pellets into the immersion tube, most of inclusions formed during magnesium deoxidation are very small in size and of spherical shape. They usually have a diameter of about 1 μm and tend not to aggregate as shown in the middle diagram of Fig. 5. Since the focal spot size of the electron beam is about 1 μm and the strength of the
beam is of a Gaussian distribution, elemental Fe in the matrix is inevitably detected by EDS. From the analysis results of EDS, it is therefore reasonable to justify that the inclusion contains mainly MgO and SiO$_2$ at 5 and 45 min after pellet charging. It should be noted that in contrast to the dispersion of MgO inclusions, the alumina inclusions formed during deoxidation with aluminum is liable to form cluster aggregation. These results can be explained from the in-situ observations of alumina and magnesia inclusions on the surface of molten steel with a confocal scanning laser microscope by Kimura et al. They found that the attractive force between a pair of MgO inclusions is one-tenth of that between a pair of alumina inclusions so that MgO inclusions have a much weaker tendency to aggregate. At 45 min after pellet charging, the remaining inclusions are further small in size, but usually have a higher content of SiO$_2$. During the observation of inclusions in steel after aluminum deoxidation with an alumina crucible, Wasai et al. also observed some amorphous SiO$_2$ inclusions and suggested that they were originated from impurities in the alumina crucible.

A line analysis result of an inclusion at 5 min is given in Fig. 6. Near the edge of the inclusion, since elemental Fe in the matrix is more detected, the contents of Mg, Al, Si and O simultaneously decrease. Form the line analysis results, one can identify that the whole inclusion almost contains Mg, Al, Si and O uniformly.

Figure 7 presents the change in inclusion compositions with time. In the SEM-EDS analyses, five elements of Fe, O, Mg, Al and Si were detected. Fe is considered to be from the surrounding Fe matrix because it has a much weaker affinity to oxygen than Mg, Al and Si. Therefore the compositions of inclusions can be evaluated by converting the total mole fraction of MgO, Al$_2$O$_3$ and SiO$_2$ into 100%. The MgO content in the inclusions decreased from 58% at 5 min to 16% at 45 min. The SiO$_2$ content increased from 30% at 5 min to 82% at 45 min. The Al$_2$O$_3$ content ranged from 2 to 20%.

To explain why the inclusion compositions changed in this way, analyses of Mg, Al and Si concentrations in the melt were carried out and the results are shown in Fig. 8.

The Mg concentration increased rapidly at first, reached a peak value at 5 min, and then decreased gradually. Rapid increase in Mg concentration at the initial stage of experiment is due to the fast initial reduction rate of magnesium oxide, while the subsequent decrease in Mg concentration is attributed to vaporization of the dissolved magnesium from the melt and bubble surface. Therefore the main reason of the decrease in the MgO content in inclusions is the decrease in the magnesium concentration in the melt. In addition, most of the MgO inclusions are formed on the bubble surface and are easily removed from the melt by floating up with the rising bubbles. This also leads to the decrease in the MgO content in inclusions.

At the initial stage of experiment, the increase in Al concentration in the melt is caused by the reaction of the dissolved magnesium with Al$_2$O$_3$ in the refractory materials, such as the dense Al$_2$O$_3$ immersion tube and the Al$_2$O$_3$ impurity in magnesia crucible. Similarly, the increase in Si concentration in the melt is due to the reaction of dissolved magnesium with the quartz sample tube and the SiO$_2$ impurity in magnesia crucible. These reactions can be expressed as following:

$$\text{Al}_2\text{O}_3 + 3\text{Mg} = 3\text{MgO} + 2\text{Al}$$

or

$$4\text{Al}_2\text{O}_3 + 3\text{Mg} = 3(\text{MgO} \cdot \text{Al}_2\text{O}_3) + 2\text{Al}$$
At the later stage of experiment, with the decrease in Mg concentration, the dissolved Si and Al in the melt can reversely react with O to form SiO$_2$ and Al$_2$O$_3$ as follows:

\[
\begin{align*}
\text{Si} + 2\text{O} &\rightarrow \text{SiO}_2, \\
2\text{Al} + 3\text{O} &\rightarrow \text{Al}_2\text{O}_3.
\end{align*}
\]

This results in the decrease in the Si and Al concentrations in the melt. It can be seen that the changes in the SiO$_2$, Al$_2$O$_3$ contents in inclusions are in close relation with the Si, Al concentrations in the melt.

The evenly distributed fine MgO inclusions can be used as the heterogeneous nucleation sites for grain refinement of steel. In order to maintain the inclusions having the main composition of MgO, it will be effective to divide pellet charging into several portions so that the magnesium concentration in the melt can maintain a higher value during the whole period of deoxidation. On the other hand, it is possible to prevent the formation of SiO$_2$ inclusion by aborting sampling with the quartz tube.

The two dimensional diameter distribution of inclusions at a certain time is obtained by measuring about 100 inclusion particles selected in a random manner. The inclusions are observed by a SEM at a magnification of 2000, so that the inclusions above 0.25 μm can be estimated by this method. The total inclusion diameter range of 0–4 μm is sectioned into 16 zones, each of which has an interval of 0.25 μm. Then the frequency of the inclusion diameter appearing in a certain zone is calculated by

\[
\text{Frequency} (\%) = \frac{\text{Inclusion number in a certain zone}}{\text{Total number of inclusions}}.
\]

Figure 9 gives the diameter distribution of inclusions at the different experimental time. It is seen that the diameters of almost all the inclusions are smaller than 4 μm, and most of them are smaller than 2 μm. It is obvious that the inclusions formed during the magnesium deoxidation process is rather small in size. From the change in the diameter distribution with time, the inclusion diameter decreases with the progress of experiment. At 45 min, almost all of the observed inclusions have a size smaller than 2 μm. This is because the larger inclusions are easily removed from the melt by floating up with rising bubbles.

From the two dimensional diameter of inclusions, Fullman derived the three dimensional diameter of inclusions as following:

\[
Z = \left( \sum \frac{1}{d_{A_j}} \right) / n, \\
r_v = \pi/4Z.
\]

where $d_{A_j}$ and $n$ are the diameter and the number of inclusions on the cross sectional plane, respectively. $Z$ is the reciprocal of the harmonic mean two dimensional diameter of inclusions, $r_v$ is the arithmetic mean three dimensional radius of inclusions. Then the relationship of the number of inclusions between per unit volume, $N_v$, and per unit area, $N_A$, can be given as

\[
N_v = (2/\pi) \cdot N_A \cdot Z.
\]

Figure 10 are the plots of $r_v$ and $N_v$ against time. The arithmetic mean three dimensional radius of inclusions, $r_v$, is 0.608 μm at 5 min, and decreases to 0.533 μm at 45 min. The inclusion size decreases with the progress of experiment. The number of inclusions per unit volume, $N_v$, decreases at first, but does not change very much at the later stage of experiment. The variations of $r_v$ and $N_v$ with time indicate that the larger inclusions tends to be removed during the experiment, but the smaller inclusions is liable to remain in the melt.
The oxygen content that originates from the various kinds of inclusions in the melt can be obtained by

$$[\text{ppmO}]_{\text{MgO}} = \frac{4}{3} \pi r_i^3 N_V \frac{M_{\text{O}} \rho_{\text{MgO}} [\% \text{MgO}]}{M_{\text{MgO}} \rho_{\text{Fe}}} \times 10^4$$

(21)

$$[\text{ppmO}]_{\text{Al}_2\text{O}_3} = \frac{4}{3} \pi r_i^3 N_V \frac{3M_{\text{O}} \rho_{\text{Al}_2\text{O}_3} [\% \text{Al}_2\text{O}_3]}{M_{\text{Al}_2\text{O}_3} \rho_{\text{Fe}}} \times 10^4$$

(22)

$$[\text{ppmO}]_{\text{SiO}_2} = \frac{4}{3} \pi r_i^3 N_V \frac{2M_{\text{O}} \rho_{\text{SiO}_2} [\% \text{SiO}_2]}{M_{\text{SiO}_2} \rho_{\text{Fe}}} \times 10^4$$

(23)

where $[\text{ppmO}]_{\text{MgO}}$, $[\text{ppmO}]_{\text{Al}_2\text{O}_3}$, and $[\text{ppmO}]_{\text{SiO}_2}$ are the oxygen contents in the melt originated from the inclusions of MgO, Al$_2$O$_3$ and SiO$_2$, respectively. $M_{\text{O}}$, $M_{\text{MgO}}$, and $M_{\text{SiO}_2}$ are the molecular mass of O, MgO, Al$_2$O$_3$ and SiO$_2$, respectively. $[\% \text{MgO}]$, $[\% \text{Al}_2\text{O}_3]$ and $[\% \text{SiO}_2]$ are the mass percent content of MgO, Al$_2$O$_3$ and SiO$_2$ in inclusions, respectively. $\rho_{\text{Fe}}$, $\rho_{\text{MgO}}$, $\rho_{\text{Al}_2\text{O}_3}$ and $\rho_{\text{SiO}_2}$ are the densities of Fe, MgO, Al$_2$O$_3$ and SiO$_2$, being 7.870, 3.580, 3.970 and 2.200 kg/m$^3$, respectively. Therefore the oxygen concentration originated from all kinds of inclusions, $[\text{ppmO}]_{\text{ins}}$, is given as

$$[\text{ppmO}]_{\text{ins}} = [\text{ppmO}]_{\text{MgO}} + [\text{ppmO}]_{\text{Al}_2\text{O}_3} + [\text{ppmO}]_{\text{SiO}_2}$$

(24)

**Figure 11** is the comparison between the experimental analysis results ($[\text{ppmO}]_{\text{exp}}$) and the oxygen concentration originated from all kinds of inclusions ($[\text{ppmO}]_{\text{ins}}$). The oxygen concentration originated from all kinds of inclusions decreases from 109 ppm at 5 min to 26 ppm at 45 min, indicating that the inclusions are removed during the experiment. Since oxygen in samples was extracted by the gas impulse melting method and was analyzed by the non-scattered infrared ray detector, $[\text{ppmO}]_{\text{exp}}$ is the total oxygen concentration in the melt including both the dissolved oxygen and the oxygen from inclusions. The oxygen concentrations originated from all kinds of inclusions are roughly equal to the analysis ones at the initial stage of experiment. This is because the magnesium concentration is relatively high at this moment so that almost all of the oxygen is originated from inclusions due to the very low dissolved oxygen concentration. But at the later stage of experiment, the analysis oxygen concentration is higher than that from inclusions. At this stage, since the magnesium concentration in the melt decreases to quite a low level, the disintegration of magnesia crucible possibly results in an increase in the dissolved oxygen in the melt, which should be responsible for the different between the analysis oxygen concentration and that from inclusions. However, since magnesium easily vaporizes from the melt and bubble surface at such a high temperature, the magnesium concentration does not increase along with the disintegration of magnesia crucible as shown in Fig. 8.

Before the ICP analysis, the samples were dissolved in the hydrochloric acid. Since SiO$_2$ and Al$_2$O$_3$ are insoluble in hydrochloric acid, the Si and Al concentrations shown in Fig. 8 are the dissolved concentrations in the melt. And since MgO is partly soluble in hydrochloric acid, the dissolved Mg concentration in the melt is hardly obtained. As shown in Fig. 8, the dissolved Si and Al concentrations decrease with the progress of experiment. In addition, the dissolved Mg should decrease due to vaporization from the melt and bubble surface. Therefore, in equilibrium with the dissolved Si, Al and Mg in the melt, the dissolved oxygen should also increase at the later stage of experiment.

Furthermore, after experiment, the ingot in crucible was cut off through its perpendicular axis for observation of the floated up inclusions near the ingot surface. **Figure 12** gives the SEM observation result together with the EDS analysis result. Near the melt surface, an inclusion layer was formed. Near the melt surface, many aggregated inclusions were observed. Both of them had the main composition of MgO. It is therefore confirmed that in the present magnesium deoxidation process, many formed MgO inclusions are removed from the melt by floating up with the rising Ar bubbles, although some small MgO inclusions remain in the melt.

**4.2. Inclusions Formed by Use of the Porous MgO Immersion Tube**

Under the experimental conditions of using the porous MgO immersion tube, the temperature of 1873 K, the pellet mass of 1.8 g and the argon carrier gas flow rate of 5.0×$10^{-7}$ Nm$^3$/s, the deoxidation rate and the number of inclusions per unit area are shown in **Fig. 13**. The oxygen origin.
concentration decreased gradually from the initial oxygen concentration of 460 to 90 ppm at 60 min. In contrast to using the dense Al\textsubscript{2}O\textsubscript{3} immersion tube, the oxygen concentration with using the porous MgO immersion tube decreased slowly at the initial stage, but steadily decreased even at the later stage of experiment. This behavior has been confirmed in the repeated experiment and is also consistent with the result of desulfurization with the same kind of method, which was reported in our previous paper.\textsuperscript{38)} The produced Mg vapor seems to be absorbed by the porous MgO tube at the initial stage of experiment when the Mg partial pressure is relatively high, and to be released at the later stage of experiment when the Mg partial pressure is relatively low.

The number of inclusions per unit area increased at first and decreased after 6 min. The increase at the initial stage is due to the fast produced rate of magnesium vapor, and the decrease at the later stage results from most of the produced MgO inclusions removed from the melt by floating up with rising bubbles. In contrast to the results shown in Fig. 4, the value of the number of inclusions per unit area is much larger in this case. One of the possible reasons is the higher initial oxygen concentration. But such a high inclusion number seems to be related to the use of the porous MgO immersion tube, it should be further studied in the future.

4.3. Effect of Initial Oxygen Concentration on Inclusion Formation

Figure 14 shows the effect of the initial oxygen concentration on the deoxidation rate and the number of inclusions per unit area. The temperature was 1 873 K, the argon carrier gas flow rate was 1.67 \times 10\textsuperscript{-6} Nm\textsuperscript{3}/s, and the dense Al\textsubscript{2}O\textsubscript{3} immersion tube was used. The pellets of the mass of 1.8 g were evenly divided into three portions to be charged into the immersion tube at 0, 3 and 6 min. It is seen that the deoxidation rate increased with increasing the initial oxygen concentration. This indicates that the mass transfer of oxygen in the melt is one of the rate controlling steps in magnesium deoxidation process. In both cases, the number of inclusions per unit area increased at first, reached a peak value and then decreased. When the initial oxygen concentration was higher, the peak value was larger because of more inclusions formed in the melt and on the bubble surface.

4.4. Effect of Carrier Gas Flow Rate on Inclusion Formation

Effect of the carrier gas flow rate on inclusion formation is shown in Fig. 15 under the experimental conditions of the temperature of 1 873 K, the total pellet mass of 1.8 g and using the dense Al\textsubscript{2}O\textsubscript{3} immersion tube. The charge of pellet into immersion tube was divided into three portions at the carrier gas flow rate of 1.67 \times 10\textsuperscript{-6} Nm\textsuperscript{3}/s, but six portions at the carrier gas flow rate of 5.0 \times 10\textsuperscript{-7} Nm\textsuperscript{3}/s. It is seen that there is no great difference in the deoxidation rates and the peak values of the number of inclusions per unit area for the two cases. The lagged appearance of the peak for the carrier gas flow rate of 5.0 \times 10\textsuperscript{-7} Nm\textsuperscript{3}/s results from the lagged charge of pellets. The distinct difference between these two cases is the value of the number of inclusions per unit area at the later stage of deoxidation. Because the pellets were added at the initial stage of deoxidation, the
value of the number of inclusions per unit area at the later stage of deoxidation should not be obviously affected by the different pellet charging methods, thus it should result from the different carrier gas flow rates. It is larger when the carrier gas flow rate is larger. Since the melt is strongly agitated when the carrier gas flow rate is larger, the inclusions are more likely to be involved from the melt surface into the melt. This leads to the increase in the inclusion number at the later stage. In addition, despite the difference in the value of the number of inclusions per unit area, the oxygen concentrations almost have the same value for the two cases at the later stage of deoxidation. Since the detected compositions of inclusions did not change very much under the present experimental conditions, this is perhaps attributed to the different size distributions of inclusions or the different dissolved oxygen concentrations. However, the reason should be further studied in the future.

4.5. Effect of Pellet Charging Method on Inclusion Formation

Figure 16 presents the effect of pellet charging method on the deoxidation rate and the number of inclusions per unit area. The temperature was 1873 K, the argon carrier gas flow rate was $5.0 \times 10^{-7}$ Nm$^3$/s and the dense Al$_2$O$_3$ immersion tube was used. One of the experiments was conducted with all of the pellets charged at the beginning of experiment. The other was performed with dividing pellet charging into six portions. With dividing pellet charging, the deoxidation rate was slow at first, but deoxidation continued for a longer time. The deoxidation efficiency was somewhat increased.

For the both cases, the number of inclusions per unit area increased at first, reached a peak, and then decreased gradually. However, the peak value for dividing pellet charging into six portions was much higher than that with all pellet charged at the beginning. With all pellet charged at the beginning, since a great deal of magnesium vapor was produced at the initial stage of experiment, some of them should leave the metal surface without reacting with oxygen in the melt, so that the deoxidation efficiency of magnesium decreased. This resulted in less MgO inclusions formed. In addition, more magnesium vapor produced at the initial stage of deoxidation will also promote the removal of inclusions by rising bubbles.

5. Conclusions

Deoxidation of molten steel is carried out with magnesium vapor produced in situ by aluminothermic reduction of magnesium oxide. The behavior of primary inclusions formed during the deoxidation process are studied. Effects of the various operating parameters, such as materials of immersion tube, initial oxygen concentration, carrier gas flow rate and pellet charging method, on the deoxidation rate and the number of inclusions per unit area are investigated. The following conclusions can be drawn:

- Most of the inclusions formed in the deoxidation process are small in size and of spherical shape. They tend not to aggregate and form cluster. The inclusions usually contain Mg, Al, Si and O uniformly. The MgO content in the inclusions decreases, while the SiO$_2$ content increases with the progress of experiment. Larger inclusions are removed from the melt by floating up with the rising bubbles more easily and the fine inclusions tend to remain in the melt. The diameter of inclusions decreases with progress of experiment. The oxygen concentrations originated from inclusions can be reasonably explained from the experimental analysis results.

Deoxidation using porous MgO immersion tube proceeds slowly at the initial stage by comparison with that using dense Al$_2$O$_3$ immersion tube. But the deoxidation continues until the later stage of the experiment. The number of formed inclusions using the MgO immersion tube has a much higher value than that using the dense Al$_2$O$_3$ immersion tube. Increasing the initial oxygen concentration enhances the deoxidation efficiency of magnesium and increases the number of inclusions. In the case of the high carrier gas flow rate, the number of inclusions is large at the latter stage of experiment due to the strong involvement of inclusions from the melt surface into the melt. Dividing pellet charging into several portions increases the deoxidation efficiency, and increases the number of inclusions as well.

The behavior of the primary inclusions formed during the deoxidation with magnesium vapor produced in situ by aluminothermic reduction of magnesium oxide shows that the larger inclusions formed in the process are rapidly removed by the rising bubbles, which is beneficial to produce the high cleanness steel; and the remaining inclusions are very small in size, which is helpful for the grain refinement of steel during the solidification and phase transformation process.

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