1. Introduction

For the control of microstructure and properties of steel by finely dispersed particles of deoxidation products, it is of importance to first establish the method of controlling the number, size, chemical composition and dispersion of particles. In view of controlling the particle size distribution, the nucleation and growth behavior immediately after deoxidant addition and the subsequent particle coarsening behavior should be clarified under the condition of no fluid flow. When oxide particles are effectively utilized as heterogeneous nucleation sites for phase transformation and precipitation, it seems to be particularly important to recognize the role of fine particles below 1 μm whose number density is considerably large and volume fraction is small.

After nucleation of deoxidation product, the particles grow by the following steps such as the collision and subsequent coagulation, the diffusion of reactants to the oxide nuclei and Ostwald ripening. It was calculated by Turkdogan1) that if the particle growth by collision does not occur under no fluid flow and the number of nuclei per unit volume is greater than $10^8 \text{mm}^{-3}$, the diffusion-controlled deoxidation reaction would be expected to be complete within a fraction of a second. This implies that the equilibrium concentrations of M and O in liquid steel determined by the equilibrium, $xM + yO = M_O$, in which $M_O$ particles have the mean particle size, is obtained very rapidly.

Based on the diffusion model in Si deoxidation, Lindberg and Torssel2) reported that the time for attending the 90% of the equilibrium value of particle volume is 0.2 s. Miyashita3) studied the time dependence of total O and dissolved O contents in the Si deoxidation experiment using radio active Si (silicon-31). It was found that dissolved O content drops sharply with time compared with total oxygen content, thus indicating that the deoxidation equilibrium establishes in short time. Furthermore, it has been shown that the deoxidation equilibrium reaches in relatively short time from the measurement of oxygen activity by using a solid electrolyte.4)

On the basis of these previous results, it can be stated that particle growth after nucleation which is the initial stage of deoxidation is attributed solely to Ostwald ripening under the condition of no fluid flow. Kluken and Grong5) and Suzuki et al.6) studied the growth of deoxidation particles in low alloy steel weld and stainless steel (SUS304) during continuous casting, respectively, and concluded that the particle growth is explained by Ostwald ripening. In their experiments, however, the measured particle size is in the range of greater than a few μm and to the authors’ knowledge, there is little study focusing on the growth of the fine particles below 1 μm.

The influence of initial particle size distribution on coarsening of tungsten particles during liquid phase sintering has been experimentally investigated using a W–14%Ni–6%Fe alloy by Fang and Patterson.7) It was found that the particles with initially broader size distribution coarsened more rapidly than those with an initially narrow size distribution. There is no report dealing with the effect of particle size distribution on coarsening rate in deoxidation process.

In the previous article,8) the characteristics of the particle size distribution of deoxidation products have been reported in the experiments where an Fe–10mass%Ni alloy was deoxidized with Zr, Mg, Al, Ca and Mn/Si at $1873 \text{K}$ and held
for 60 to 1800 s, followed by rapid quenching. The present study was a continuation of previous investigations\(^{8)}\) and is concerned with basic studies of the particle growth mechanism, focusing on the effect of dissolved oxygen and size distribution on the coarsening rate in Ostwald ripening.

2. Experimental

Induction furnace (100 kHz) in which a graphite susceptor with 20 mm thickness was installed between induction coil and an alumina crucible was used in order to eliminate the melt stirring due to the induction current. An Fe–10mass%Ni alloy (70 g) containing 100 to 120 mass ppm oxygen was deoxidized at 1873 K with a Ni–10mass%Mg, Fe–10mass%Zr, Fe–10mass%Al, Ni–7mass%Ca or Fe–30mass%Si–60mass%Mn alloy (% and ppm represent mass% and mass ppm, respectively, hereinafter). After addition of deoxidant a melt was stirred for 10 s by an alumina rod to disperse particles homogeneously and held for 60, 180, 600 and 1800 s, followed by rapid quenching. Experimental procedure, the method of chemical analysis and the estimation of three-dimensional particle size and number are explained in detail elsewhere.\(^{9)}\)

2.1. Measurement of Particle Size Distribution

The particle size distribution was measured for the particles obtained as residue on a filter after the electrolytic extraction by the following method: The extraction of a metal sample was made by using a potentiometric electrolytic extraction technique (150 mV and 50 mA) so that the total amount of charge reached 150 coulomb. The amount of dissolved metal was about 0.05 g. The electrolyte solution was filtered by using polycarbonate membrane filter of an open pore size of 0.05 μm (10 mm in diameter). The oxide particles on some part of a film filter were measured by SEM at a magnification of 10000. The observed area was about 10\(^4\) μm\(^2\), which corresponds to the area of about 0.01% of a film filter. The size and number of particles were analyzed by using an image analyzer for the photomicrograph obtained by SEM, which was enlarged by 2 to 2.5 times. The chemical composition of particles was analyzed for the particles on a film filter by EPMA. Experimental procedure, the method of chemical analysis and the estimation of three-dimensional particle size and number are explained in detail elsewhere.\(^{9)}\)

3. Results and Discussion

3.1. Mechanism of Particle Growth

Under the condition of no melt stirring, the particle growth of deoxidation products in molten steel can be explained by the following four major processes: i) diffusion of reactants in the melt to the oxide nuclei, ii) coagulation of particles due to the difference in ascending velocity, iii) coagulation by Brownian motion and iv) coarsening by Ostwald ripening. The possibility of the processes i) to iii) under the present experimental condition is discussed in this section.

3.1.1. Growth by Diffusion

When particles grow by diffusion, the growth rate of a particle \(\Delta r/\Delta t\) can be expressed as

\[
\frac{\Delta r}{\Delta t} = D_0 \frac{(C_O - C_{eq})}{(C_p - C_{eq})} \quad \text{..........................(1)}
\]

where \(r\) is the particle radius (m), \(D_0\) is the diffusion coefficient of oxygen (m\(^2\)·s\(^{-1}\)), \(C_O\) is the dissolved oxygen concentration in liquid Fe (kg·m\(^{-3}\)), \(C_{eq}\) is the equilibrium oxygen concentration with oxide (kg·m\(^{-3}\)) and \(C_p\) is the oxygen concentration in oxide (kg·m\(^{-3}\))

The time, \(t_{90}\), until the particle volume becomes 90% of the equilibrium particle volume is derived by Wert and Zener\(^{10)}\) using Eq. (1) as follows:

\[
t_{90} = \frac{1.0}{D_0} \cdot \frac{(C_p - C_{eq})}{(C_i - C_{eq})} \cdot r_{i}^2 \quad \text{..........................(2)}
\]

where \(C_i\) is the dissolved oxygen concentration in liquid Fe before deoxidant addition (kg·m\(^{-3}\)) and \(r_i\) is the mean particle radius after growth by diffusion (m).

The deoxidation process in which the liquid Fe containing initial oxygen content of 100 ppm is deoxidized with Mg and the resulting equilibrium dissolved oxygen content is 1 ppm is considered. The relationship between \(r_i\) and \(t_{90}\) was obtained by substituting \(C_i = 0.7\) kg·m\(^{-3}\), \(C_p = 1.45 \times 10^{-3}\) kg·m\(^{-3}\), \(C_{eq} = 7 \times 10^{-3}\) kg·m\(^{-3}\) and \(D_0 = 3 \times 10^{-9}\) m\(^2\)·s\(^{-1}\)) into Eq. (2). The results are shown in Fig. 1, showing that \(t_{90}\) is 0.01 s at \(r_i = 0.1\) μm and 1 s at \(r_i = 1\) μm. These calculated results suggest that the particle growth by diffusion under the aforementioned condition occurs very rapidly and the particle growth of deoxidation product during the holding time of 60 to 1800 s at 1873 K is not explained by diffusion mechanism.

A plot of the number of particles per unit volume, \(N_v\), versus \(t_{90}\) is also shown in Fig. 1. The \(N_v\) value was obtained by substituting \(r_i\) into Eq. (3) at \(f_i = 0.0004\) which corresponds to the volume fraction of MgO particles in the case that the initial oxygen of 100 ppm is deoxidized with Mg.

\[
f_i = (4\pi/3) r_i^3 N_v \quad \text{..........................(3)}
\]

In the case of Mg deoxidation mentioned above, the \(N_v\) value at \(t_{90} = 1\) s is \(10^4\) mm\(^{-2}\).
3.1.2. Coagulation of Particles Due to the Difference in Ascending Velocity

The ascending velocity of a particle depends on particle size, as is evident from Stokes's law. In the case of particles having a size distribution this leads to the collision of particles with particles caused by the difference in ascending velocity under the condition of no fluid flow.

This mechanism can be expressed by the following collision frequency function, \( W_s \):

\[
W_s(r_i,r_j) = 2\pi \left( \rho_n - \rho_p \right) \left( g/9 \eta \right) \left( r_i + r_j \right)^3 |r_i - r_j| \ldots (4)
\]

where \( r_i \) and \( r_j \) are the radius of \( i \) and that of \( j \), respectively. \( \rho_n \) and \( \rho_p \) are the density of liquid Fe and that of particles, respectively and \( \eta \) is the viscosity of liquid Fe.

The number of a particle with \( r \) per unit volume and unit time which collides with other particles can be given by the following collision rate equation:

\[
\frac{\Delta N_{V(t)}}{\Delta t} = \sum_{j=1}^{n} r_j \cdot N_{V(t)} W_s(r_i,r_j)
\ldots (5)
\]

The collision rate (\( \text{mm}^{-3} \cdot \text{s}^{-1} \)) was estimated as a function of particle radius from Eq. (5) using the size distribution of MgO, ZrO\(_2\) and Al\(_2\)O\(_3\) particles obtained at the holding time of 60 s at 1873 K. The results are shown in Fig. 2, in which the \( \Delta N_{V(t)}/\Delta t \) values increase with increasing the \( r_{V(t)} \) value, but in the range of \( r_{V(t)}>0.5\) \( \mu m \), the collision rate increases in the order of \( \text{ZrO}_2<\text{MgO}<\text{Al}_2\text{O}_3 \). The collision frequency function, \( W_s \), is affected by the density difference between liquid Fe and oxide, the particle size and the spread of a particle size distribution, as is obvious in Eq. (4). The collision rate is low in the case of \( \text{ZrO}_2 \) particles due to small density difference between liquid Fe and oxide, while the collision rate is high in the case of \( \text{Al}_2\text{O}_3 \) particles due to the broader spread of a particle size distribution. The collision rate is below 1 \( \text{mm}^{-3} \cdot \text{s}^{-1} \) at around particle radius of 0.1 \( \mu m \), as shown in Fig. 2. When the particles collision occurs at this rate during 1800 s, the decrease of particle number, \( \Delta N_{V(t)} \), is about \( 10^3 \text{mm}^{-3} \).

However, it was confirmed experimentally that the \( N_{V(t)} \) value for the MgO particles having the size of about 0.1 \( \mu m \) decreases from \( 10^6 \) to \( 10^3 \) during the holding time of 60 to 1800 s at 1873 K. On the basis of this finding it can be concluded that the observed collision rates are much higher than those predicted from Eq. (5). This is also true for the \( \text{ZrO}_2 \) and \( \text{Al}_2\text{O}_3 \) particles.

The coagulation of particles due to the difference in ascending velocity seldom occurs for the particle below 0.1 \( \mu m \). The \( \Delta N_{V(t)}/\Delta t \) value for the particles with about 1 \( \mu m \) is in the order of \( 10^2 \text{mm}^{-3} \cdot \text{s}^{-1} \), which is comparatively large. For the \( \text{Al}_2\text{O}_3 \) particles with 1 \( \mu m \), however, the decrease of \( \Delta N \) is estimated as about \( 10^3 \text{mm}^{-3} \cdot \text{s}^{-1} \) during the holding time of 1800 s at 1873 K. It was found experimentally that the \( N_{V(t)} \) value for the \( \text{Al}_2\text{O}_3 \) particles with about 1 \( \mu m \) decreases from \( 10^7 \) to \( 10^3 \text{mm}^{-3} \cdot \text{s}^{-1} \) during the holding time of 60 to 1800 s. In the case of \( \text{Al}_2\text{O}_3 \) particles, therefore, the value of \( 10^5 \text{mm}^{-3} \cdot \text{s}^{-1} \) predicted from Eq. (5) cannot be neglected compared with the observed value.

3.1.3. Coagulation by Brownian Motion

Variation of particle number with time due to the particle coagulation by the Brownian motion can be expressed as:

\[
N_{V(t)} = N_{V(0)} \left( 1 + \frac{8k_BT N_{V(0)}}{3\eta} \right)^t \ldots (6)
\]

where \( k_B \) is the Boltzmann constant (1.39 \( \times 10^{-23} \text{J} \cdot \text{K}^{-1} \)), \( N_{V(0)} \) is the initial particle number, \( \eta \) is the viscosity of liquid (0.043 \( \text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1} \) at 1873 K) and \( T \) is the absolute temperature (K).

Combination of Eq. (3) and Eq. (6) yields

\[
\bar{r}_V^3 = 2/(\pi \cdot \eta \cdot k_B \cdot T) f_V \cdot t \ldots (7)
\]

It is said from Eq. (7) that \( \bar{r}_V^3 \) is proportional to \( t \) at a constant \( f_V \) and the \( \bar{r}_V \) value for a given time \( t \) is independent of the kind of particle; namely, the chemical composition of oxide. In practice, however, the values for \( \bar{r}_V \) for a given time are observed to be strongly affected by the composition of oxide, as explained in Sec. 3.2.

The relationship given by Eq. (6) is shown as a function of \( N_{V(0)} \) in Fig. 3, in which this relation remains unchanged in the case of \( N_{V(0)} > 10^4 \text{mm}^{-3} \). The experimental results included in Fig. 3 indicate that the data for \( \text{Al}_2\text{O}_3 \) and MnO–SiO\(_2\) particles approximately follow the line of \( N_{V(0)} > 10^5 \text{mm}^{-3} \), but those for MgO, ZrO\(_2\), and CaO–Al\(_2\)O\(_3\) particles are one order of magnitude higher than the line of \( N_{V(0)} > 10^5 \text{mm}^{-3} \) for a given holding time.

On the basis of the above observations it appears that the coagulation by the Brownian motion cannot be completely eliminated for the growth of \( \text{Al}_2\text{O}_3 \) and MnO–SiO\(_2\) particles. As explained in next section, the number of particle per unit volume for MgO, ZrO\(_2\), and CaO–Al\(_2\)O\(_3\) particles is one or two order of magnitude higher than that for \( \text{Al}_2\text{O}_3 \) and MnO–SiO\(_2\) particles. This observed phenomena cannot be explained by the above mentioned mechanism. It can thus be concluded that the particle growth for deoxidation products observed during holding at 1873 K cannot be explained by the growth processes (i) to (iii).
3.2. Growth by Ostwald Ripening

Based on the LSW (Lifshitz, Slyozov\textsuperscript{14} and Wagner\textsuperscript{15}) theory, the particle growth by Ostwald ripening can be given by

\[ \bar{r}^3 - \bar{r}_0^3 = \alpha \cdot k_d \cdot t \] \hspace{1cm} (8)

With \( k_d \) as

\[ k_d = \frac{2\gamma D_0 V_o C_O}{RT(C_p - C_O)} \] \hspace{1cm} (9)

where \( \bar{r} \) is the mean particle radius at time \( t \) (cm), \( \bar{r}_0 \) is the mean particle radius at the start of Ostwald growth (cm), \( \alpha \) is the coarsening coefficient (= 4/9 for the LSW theory), \( \gamma \) is the interfacial energy between oxide and liquid Fe (J · m\textsuperscript{-2}), \( D_0 \) is the diffusion constant of oxygen (2.91 \times 10\textsuperscript{-9} m\textsuperscript{2} · s\textsuperscript{-1}), \( C_O \) is the dissolved oxygen concentration expressed by weight per unit volume (kg · m\textsuperscript{-3}), \( C_p \) is the oxygen concentration in oxide expressed by weight per unit volume (kg · m\textsuperscript{-3}), \( V_O \) is the molar volume oxide per 1 atom of oxygen (m\textsuperscript{3} · atom\textsuperscript{-1}) \( [=M_O/C_P] \) where \( M_O \) is the atomic weight of oxygen. \( R \) is the gas constant (J · mol\textsuperscript{-1} · K) and \( T \) is the absolute temperature (K).

The arithmetic mean radius, \( \bar{r}_{\text{art.}} \) and number of oxides per unit volume, \( N_V \) which are obtained in our previous deoxidation experiments\textsuperscript{8} are plotted as a function of holding time at 1 873 K in Figs. 4 and 5, respectively. In the case of MnO–SiO\textsubscript{2} particles the bi-modal size distribution was observed. Therefore, smaller particles due to the crystallization and/or precipitation during cooling and solidification were not taken into consideration for the evaluation of \( \bar{r}_{\text{art.}} \) and \( N_V \) values. It can be seen from Fig. 4 that the mean radius for a given holding time increases in the order of MgO<CaO–Al\textsubscript{2}O\textsubscript{3}<ZrO\textsubscript{2}<Al\textsubscript{2}O\textsubscript{3}<MnO–SiO\textsubscript{2} and furthermore, increases with holding time with the slope of 1/3 on both logarithmic scales. The \( N_V \) value decreases with time with the slope of −1 on both logarithmic scales, although the datum point at 1 800 s for Al\textsubscript{2}O\textsubscript{3} particles deviates to a considerable degree.

Inserting the observed relationship that three power of the mean particle radius is proportional to the holding time at 1 873 K into Eq. (3), we obtain the following relation under a constant \( f_V \) :

\[ N_V \cdot t = \text{constant} \] \hspace{1cm} (10)

The slope of minus unity in a plot of \( N_V \) versus \( t \) is explained by this relationship. Thus it can be concluded that if the particle growth is dominated by Ostwald ripening, the mean particle radius increases with time with the slope of 1/3 and the number of particle per unit volume decreases with the slope of 1 on both logarithmic scales under a constant volume fraction of particles. On substituting the values for \( C_O = 1 \) ppm (7 \times 10\textsuperscript{-3} kg · m\textsuperscript{-3}), \( C_p = 1.45 \times 10\textsuperscript{9} \text{ kg · m}^\text{-3} \text{ (for MgO)}, D_0 = 2.91 \times 10\textsuperscript{-9} \text{ m}^\text{2} \text{ · s}^\text{-1}, V_O = 1.10 \times 10\textsuperscript{-5} \text{ m}^\text{3} \text{ · atom}^\text{-1} \text{ (for MgO)}, \alpha = 0.44 \) (4/9 for the LSW theory) into Eqs. (8) and (9), the relationships between \( \bar{r} \) and \( t \) are calculated as a function of the initial particle size of \( r_0 \) which corresponds to the size at the start of Ostwald growth. The results are shown in Fig. 6.
the hatched area corresponds to the present holding time at 1873 K of 60 to 1800 s. It is clear that in the case of $r_0/H_{1005}$, the particle radius, $r$, increases linearly with time on both logarithmic scales in the range of more than one second.

The theoretical lines by Ostwald ripening (LSW theory) were obtained by substituting the respective values for oxides listed in Table 1 into Eqs. (8) and (9) and the results are shown in Fig. 7 together with the experimental data. The experimental data are negatively deviated from the theoretical lines except for those of Al$_2$O$_3$ particles. The fact that the rate of particle growth depends on the chemical composition of oxide can be reasonably explained by Ostwald growth mechanism, but not by the coagulation due to the Brownian motion, as explained in Section 3.1.3. On the basis of these findings it can be concluded that the particle growth of deoxidation products is predominant by Ostwald ripening under the present experimental condition.

### 3.3. Effect of Dissolved Oxygen on Ostwald Growth

The $k_d$ values given in Eq. (9) which were calculated by using the respective parameters listed in Table 1 are plotted against dissolved oxygen content in Fig. 8. The experimentally determined dissolved oxygen contents are indicated by the arrows. These values are determined by the amount of deoxidant; namely, dissolved deoxidant content and the corresponding equilibrium constant which is a measure of deoxidation potency. It can be seen that the $k_d$ values for a given dissolved oxygen content are not strongly affected by the chemical composition of oxide; that is, the kind of deoxidant, but are dependent on the contents of dissolved oxygen which are determined by the kind of deoxidant and its amount. Since the values for $\gamma$, $V_O$ and $C_p$ are not strongly dependent on deoxidant, it is considered from Eqs. (8) and (9) that the particle size, $r$, is proportional to 1/3

![Fig. 6. Effect of initial particle size, $r_0$, at the beginning of Ostwald growth on the relationship between $r$ and holding time.](image1)

![Fig. 7. Change of theoretical and experimental mean particle radius during holding time at 1873 K.](image2)

![Fig. 8. Relationship between $k_d$ and oxygen contents for MgO, ZrO$_2$ and Al$_2$O$_3$ (upper diagram) and that for CaO–Al$_2$O$_3$ and MnO–SiO$_2$ particles (lower diagram).](image3)
power of Co (= [% O]sol. 1/3) under the condition of a given \( \alpha \) and \( t \), and \( r > > r_0 \).

When the particle growth is controlled by Ostwald ripening, to lower the dissolved oxygen content with a strong deoxidant is of crucial importance in order to reduce the coarsening rate of oxide particles, as shown in Fig. 8. The coarsening rate constant \( k_s (= \dot{r}/t) \), which can be obtained from the intercept in a plot of \( r \) versus \( t \) on both logarithmic scales, is plotted against the experimentally determined dissolved oxygen content in Fig. 9. As shown in Fig. 8, \( k_s \) is not strongly dependent on the chemical composition of deoxidation products for a given dissolved oxygen content. It follows from Eq. (9), therefore, that \( k_s \) is proportional to \( C_0 \) if \( \alpha \) is constant. It is obvious from Fig. (9) that the \( k_s \) values for MgO, ZrO2, CaO–Al2O3, and MnO–SiO2 particles approximately fall on the line. The reason that the \( k_s \) values for Al2O3 particles are above the line determined by other oxides is considered to be due to the effect of the spread of the particle size distribution, which is discussed in the next section.

### 3.4. Effect of Size Distribution on Ostwald Growth

Fang and Patterson7) studied the growth of solid tungsten particles during the liquid sintering in a W–14%Ni–6%Fe alloy and found in a plot of \( r \) versus \( t \) on both logarithmic scales, is plotted against the experimentally determined dissolved oxygen content in Fig. 9. As shown in Fig. 8, \( k_s \) is not strongly dependent on the chemical composition of deoxidation products for a given dissolved oxygen content. It follows from Eq. (9), therefore, that \( k_s \) is proportional to \( C_0 \) if \( \alpha \) is constant. It is obvious from Fig. (9) that the \( k_s \) values for MgO, ZrO2, CaO–Al2O3, and MnO–SiO2 particles approximately fall on the line. The reason that the \( k_s \) values for Al2O3 particles are above the line determined by other oxides is considered to be due to the effect of the spread of the particle size distribution, which is discussed in the next section.

The \( k_s \) values for solid Al2O3, ZrO2, and MgO particles decrease with holding time, while the \( k_s \) values for liquid CaO–Al2O3 and MnO–SiO2 particles which are lower than those for the solid particles are independent of holding time. The \( k_s \) values for the theoretical size distribution obtained by the LSW theory is 0.47,24) Therefore, the \( k_s \) values for all particles tend to approach the \( k_s \) values of 0.47 estimated from the LSW theory, although in the case of Al2O3 and ZrO2 particles it seems to take much longer time.

The coarsening rate of particles is mainly dominated by the dissolved oxygen and the coarsening coefficient, as is clear from Eqs. (8) and (9). Therefore, the coarsening rate increases with an increase of the coarsening coefficient under a given dissolved oxygen. It was found by Fang and Patterson7) that the coarsening rate is strongly influenced by the width of the particle size distribution. This was confirmed by the following experiment. The variation of coarsening coefficient, \( \alpha \), with holding time is shown in Fig. 11. The \( \alpha \) values are obtained by dividing the measured \( k_s \) values by the \( k_s \) values given in Eq. (9) which are evaluated from the parameters given in Table 1. The \( \alpha \) values for solid Al2O3, ZrO2, and MgO particles decrease with
The reason that the spread of size distribution for Al$_2$O$_3$ and MnO–SiO$_2$ particles remain constant with holding time. The wider initial particle size distributions are observed for the MgO, ZrO$_2$ and Al$_2$O$_3$ particles in which the ln $s$ values are high, as shown in Fig. 10. This results in the higher coarsening growth rate, namely, the higher coarsening coefficient. It can be seen from the results shown in Figs. 10 and 11 that the width of size distribution (i.e. ln $s$) becomes narrower and the coarsening coefficients become smaller with holding time at 1 873 K. The coarsening rates for the liquid MnO–SiO$_2$ and CaO–Al$_2$O$_3$ particles are not significantly dependent on the holding time. This is due to the fact that the initial ln $s$ values for these oxides are smaller and independent of holding time in comparison with the results for the solid MgO, ZrO$_2$ and Al$_2$O$_3$ particles. The $\alpha$ values can be estimated from the studies on computer simulation in which the mean solute concentration in liquid phase is based on the solute diffusion similar to the case of the LSW theory. On the other hand, DeHoff$^{23}$ proposed the communicating neighbour (CN) model in which the solute diffusion along the metal side of the neighbouring particles is considered. As a result, DeHoff$^{23}$ derived the relation: $\alpha_{\text{CN}}=0.745 f_0^{1/3}$ from the CN model and the $\alpha_{\text{CN}}$ value in the present study is calculated as 0.0549 at $f_0=0.0004$ which is considerably smaller than the $\alpha_{\text{LSW}}$ value (0.444). These values are shown by the arrows in Fig. 11, indicating that the present $\alpha$ values are between $\alpha_{\text{LSW}}$ and $\alpha_{\text{CN}}$. Further research is necessary to clarify the reason for this.

The relationship between $\alpha$ and ln $\sigma$ is shown in Fig. 12, in which the $\alpha$ value tends to increase with increasing ln $\sigma$ except for the data obtained in MnO–SiO$_2$ particles. The reason for MnO–SiO$_2$ particles to deviate from the trend is probably due to the error in the estimation of the particle size distribution in which bi-modal distribution was observed.$^{31}$ The reason that the $k_s$ values for Al$_2$O$_3$ particles is higher than the predicted value from other oxide, as shown in Fig. 9, is explained by a high $\alpha$ value which is caused by a high ln $\sigma$ value for Al$_2$O$_3$ particles, as shown in Fig. 10. The reason that the spread of size distribution for Al$_2$O$_3$ particles is broader is explained in a separate publication.

All results mentioned above are discussed based on the Ostwald growth of oxygen diffusion, since dissolved oxygen content is a few order of magnitude smaller than dissolved deoxidant content under the conventional deoxidation. In the case of using strong deoxidant such as Ca or Mg, however, the content of dissolved oxygen and that of deoxidant are nearly the same order of magnitude. This leads to the possibility of the diffusion of Ca or Mg in stead of oxygen diffusion for the growth by Ostwald ripening.

The Ostwald growth by Mg diffusion is considered first in the following: The coarsening rate constant, $k_{\text{d,Mg}}$, can be written in a similar form of Eq. (9) with respect to dissolved oxygen as follows:

$$k_{\text{d,Mg}} = \frac{2\gamma D_{\text{Mg}} V_{\text{Mg}} C_{\text{Mg}}}{RT C_{\text{Mg}} C_{\text{O}}^2} \quad \text{(12)}$$

The notations used in Eq. (12) are similar meanings explained in Eq. (9) with respect to oxygen. The condition that Mg diffusion is the rate determining step is estimated from Mg diffusion and the oxygen diffusion which satisfy Eq. (14) are determined from the values given in Table 1. In this calculation, it is assumed due to the lack of available data for $D_{\text{Mg}}$ that the $D_{\text{Mg}}$ value is equal to the $D_{\text{O}}$ value because the solute diffusivities in liquid Fe is considered to be the same order of magnitude. The results are shown in Fig. 13 on a mass ppm basis where the region above the solid line is the rate determining step of Mg diffusion, and the region below the solid line is that of oxygen diffusion. The observed relationships between oxygen and magnesium shown by the open circles suggests that the coarsening of MgO particles is controlled by oxygen diffusion.

In a manner similar to Mg diffusion, the region that Ca diffusion is the rate determining step is estimated from...
The observed arithmetic mean radii are scattered between arithmetic mean radii observed experimentally in theories by using Eqs. (8) and (9) are plotted against the points obtained by assuming the oxygen diffusion. Al$_2$O$_3$, ZrO$_2$ and MgO particles fall, rather than the data cated on the extrapolated line on which the results for Fig. 12 by the half-filled diamonds. These data are well lo-

ing is controlled by the Ca diffusion, not by the oxygen 
diffusion.

Fig. 13. Regions of diffusion of dissolved M (=Mg and Ca) and diffusion of oxygen.

The particle radii estimated from the LSW and the CN theories plotted against observed arithmetic mean radius.

Fig. 14. Calculated mean radius from LSW and CN theories plotted against observed arithmetic mean radius.

the values for $V_{Ca}$. $C_{P(Ca)}$ and $C_{Ca}$ in CaO–Al$_2$O$_3$ particles which are given in Table 1, assuming $D_{Ca} = D_{Ca}$. The result is indicated by the dash dotted-broken line and the observed dissolved oxygen and Ca are indicated by the diamonds in Fig 13. It can be seen that the experimental data are above the dash dotted-broken line, thus suggesting that the coarsening is controlled by the Ca diffusion, not by the oxygen diffusion.

The $\alpha$ values in the CaO–Al$_2$O$_3$ particles estimated from the assumption of Ca diffusion are plotted against ln $\sigma$ in Fig. 12 by the half-filled diamonds. These data are well located on the extrapolated line on which the results for Al$_2$O$_3$, ZrO$_2$ and MgO particles fall, rather than the data points obtained by assuming the oxygen diffusion.

The particle radii estimated from the LSW and the CN theories by using Eqs. (8) and (9) are plotted against the arithmetic mean radii observed experimentally in Fig. 14. The observed arithmetic mean radii are scattered between the two theories except for the coarsening of Al$_2$O$_3$ particles whose ln $\sigma$ is considerably higher than those of other particles.

4. Conclusion

The growth mechanism for deoxidation products of MgO, ZrO$_2$, Al$_2$O$_3$, CaO–Al$_2$O$_3$ and MnO–SiO$_2$ particles in an Fe–10%Ni alloy has been studied under the condition of no fluid flow by considering the effects of dissolved oxygen and size distribution on Ostwald growth. The results obtained are summarized as follows:

(1) The particle growth mechanism has been discussed based on the diffusion growth, the coagulation due to the difference in ascending velocity, the coagulation due to the Brownian motion and the coarsening by Ostwald ripening. As a result, the Ostwald growth is a predominate mechanism under the condition of no fluid flow.

(2) The coarsening rate of particles is largely dependent on the dissolved oxygen content, but the growth rate of Al$_2$O$_3$ particles is much faster than that predicted based on the dissolved oxygen content.

(3) The spread of particle size distribution decreases in the order of Al$_2$O$_3$ > ZrO$_2$ > MgO > CaO–Al$_2$O$_3$ > MnO–SiO$_2$ particles and that of solid Al$_2$O$_3$, ZrO$_2$ and MgO particles becomes narrower with holding time. The coarsening rate is also affected by the spread of size distribution curve and this is the reason that the coarsening rate of Al$_2$O$_3$ particles is higher than that predicted from dissolved oxygen content.

REFERENCES


3) Y. Miyashita: Tetsu-to-Hagané, 52 (1966), 1049.


