Characteristics of Particle Size Distribution in Early Stage of Deoxidation

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The spread of the size distributions obtained by deoxidizing an Fe–10mass%Ni alloy with Zr, Mg, Al, Ca and Si/Mn has been discussed with particular emphasis on the particle size distribution soon after the nucleation of deoxidation product. The geometric standard deviation in size distribution was found to be related to the interfacial energy between oxide and liquid Fe, $\gamma_{\text{oxide-Fe(l)}}$. The nucleation rate decreases with an increase in $\gamma_{\text{oxide-Fe(l)}}$ based on the homogeneous nucleation theory. Thus, the geometric standard deviation decreases with increasing the nucleation rate in which $\gamma_{\text{oxide-Fe(l)}}$ is low such as the case of MnO–SiO₂ particles. The experiment in which an Fe–10mass%Ni alloy was first deoxidized with Ti followed by Mg was carried out and narrow size distribution was obtained by separating the nucleation and growth processes.

KEY WORDS: particle size distribution; Ostwald ripening; inclusion; interfacial energy; homogeneous nucleation theory; supersaturation.

1. Introduction

It has been found in the previous studies^{1,2)} that Ostwald ripening is the dominating inclusion growth mechanism in deoxidation process under no fluid flow. This indicates that deoxidation equilibrium establishes very rapidly. The particle growth rate can be reduced by lowering the dissolved oxygen content using a strong deoxidant, which results in the increase in the number of small size particles.

Particle size distributions are usually found to be well modeled as log-normal function with characteristic parameter, $\ln \sigma$, the geometric standard deviation which is a measure of the width of a size distribution. It was found in previous study²⁾ that the size distribution of initial deoxidation product was dependent on deoxidation power while the width of a size distribution was independent of deoxidation power.

The influence of initial size distribution on coarsening during liquid phase sintering has been experimentally investigated using a W–14%Ni–6%Fe alloy by Fang and Patterson.³⁾ They found that the coarsening rate was related to the width and shape of initial particle size distribution; that is, the particles with an initially broader size distribution coarsen more rapidly than those with an initially narrow size distribution. On the basis of these previous observations,³⁾ it can be seen that the control of particle growth rate is necessary for the control of particle size distribution in deoxidation.

For the control of size distribution of deoxidation particles the factor influencing the initial size distribution soon after nucleation of deoxidation product must be considered. This problem on initial precipitation has been solved by

LaMer and Dinegar⁴⁾ and Kampmann and Kahlweit⁵⁾ in the field of colloid chemistry and material science, respectively, by using the classical homogeneous nucleation theory. In their study the number and size of initial precipitates and their size distribution are theoretically derived based on the supersaturation degree of precipitation estimated from the interfacial energy between particle and matrix. The critical supersaturation degree of Al and Si deoxidations has been calculated by Turpin and Elliott⁶⁾ using the classical homogeneous nucleation theory and the results are compared with the experimental values. They demonstrate the good correlation between the critical supersaturation degree and the oxide–liquid interfacial energy, but they do not mention the inclusion characteristics such as size and number.

In this paper the significance of narrow size distribution of particles is first considered. Then, the spread of the size distributions previously obtained by deoxidizing an Fe–10mass%Ni alloy with Zr, Mg, Al, Ca and Si/Mn²⁾ is discussed based on the nucleation rate which depends on the interfacial energy between oxide and liquid Fe. Furthermore, the experiments in which an Fe–10mass%Ni alloy was deoxidized with Ti followed by Mg was carried out in order to obtain narrow size distribution.

2. Experimental Procedure and Measurement of Particle Size Distribution

2.1. Procedure

Induction furnace (100 kHz) was used for melting experiments. A graphite susceptor with 20 mm thickness was employed around the crucible to aid in melting and to eliminate the melt stirring. A mother alloy was prepared by mix-

ing high purity electrolytic iron (99.99 mass%: % represents mass%, hereinafter) and globular Ni (99.97%) to obtain an overall composition of Fe–10%Ni alloy. The Ni–10%Mg, Fe–10%Zr, Fe–10%Al, Ni–7%Ca and Fe–30%Si–60%Mn alloys prepared by an arc furnace were used as a deoxidant.

An Fe–10%Ni alloy (70 g) in an alumina crucible was first melted at 1873 K in order to control the initial oxygen content of 100 to 120 mass ppm (ppm represents mass ppm, hereinafter) by keeping the holding time for 30 min and the size of the electrolytic Fe constant. Then, a deoxidant was added by the amount of the initial deoxidant $[\%Mg]_i=0.1$, $[\%Zr]_i=0.05$, $[\%Al]_i=0.05$, $[\%Ca]_i=0.05$, $[\%Si]_i=0.5$ and $[\%Mn]_i=1$.

When deoxidant is added to molten steel by dropping, deoxidant content is instantaneously enriched around the deoxidant. Such a spatial and time-dependent heterogeneity for solute content cannot be experimentally estimated. In order to avoid this problem as much as possible the following experimental technique was used: The Fe–10%M (M=Zr and Al) and Ni–7~10%M (M=Mg and Ca) alloys were used instead of pure deoxidant metal and furthermore nearly the same size of alloy was dropped followed by immediately stirring by an alumina rod for 10 s in order to disperse the primary inclusion particles uniformly. Thereafter, a melt was held for 60, 180, 600 and 1800 s at 1873 K and then withdrawn from the furnace, followed by rapid quenching in water. In addition to these experiments the experiments with the initial addition of deoxidants of $[\%Mg]_i=0.05$, $[\%Zr]_i=0.1$ and $[\%Al]_i=0.1$ were also carried out.

2.2. 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 10 000. The observed area was about $10^4 \mu\text{m}^2$, 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.⁷⁾

The secondary deoxidation product can be neglected in the present experiments except for the Si/Mn deoxidation in which the dissolved oxygen content is not negligibly small. In the Si/Mn deoxidation the bi-modal size distribution was observed and the particles with about 100 nm diameter which correspond to the smaller peak in the size distribution are not taken into consideration for the present discussion. In the present deoxidation experiments with strong deoxidant, the amount of particles precipitated during solidifi-

cation and subsequent cooling is negligibly small compared with that of the primary deoxidation particles, because the dissolved oxygen content in melt is considerably small.

3. Significance of Narrow Size Distribution

It was found in the previous study²⁾ that the particle size distribution of deoxidation product is dependent on the coarsening of particles by Ostward ripening under no melt stirring. The $\ln \sigma$ value which describes the spread of the distribution was found to decrease in the order of $\text{Al}_2\text{O}_3 > \text{ZrO}_2 > \text{MgO} > \text{CaO}-\text{Al}_2\text{O}_3 > \text{MnO}-\text{SiO}_2$ particles. The reason that the $\ln \sigma$ value is affected by deoxidant is explained in Chap. 3. In this chapter emphasis is placed on the significance of the spread of size distribution; namely, $\ln \sigma$, which strongly affects the number of particles per unit volume, N_V .

The volume fraction of spherical particles, f_V , is expressed as

$$f_V = (\pi/6) \cdot \bar{d}_V^3 \cdot N_V \dots\dots\dots (1)$$

where $\bar{d}_V$ is the arithmetic mean diameter of a particle in three dimensions.

When an Fe–10mass%Ni alloy containing initially 100 mass ppm oxygen is completely deoxidized with Mg, the volume fraction of MgO particles is calculated to be 0.0004 by using the density values for Fe ($7.8 \times 10^3 \text{ kg/m}^3$) and MgO ($3.65 \times 10^3 \text{ kg/m}^3$). On substituting $f_V=0.0004$ into Eq. (1), the relationship between N_V and $\bar{d}_V$ is plotted by the solid line in Fig. 1. An Fe–10mass%Ni alloy containing initially 100 to 120 mass ppm oxygen was deoxidized with Mg, Zr, Al, Ca and Mn/Si at 1873 K for 60 to 1800 s, followed by rapid quenching. (% and ppm represent mass% and mass ppm, respectively, hereinafter.) The details of the experimental procedure is given elsewhere.⁷⁾ The experimental results are also shown in Fig. 1, in which the N_V value for a given $\bar{d}_V$ is roughly one order of magnitude lower than that estimated from Eq. (1). Based on these results it is important to realize that the relationship given in Eq. (1) cannot be applied to the particles with a broad size distribution under a constant f_V ; namely, strictly speak-

Fig. 1. Experimental and calculated relationship between N_V and $\bar{d}_V$.

Fig. 2. Calculated size distribution as a function of $\ln \sigma$ (upper diagram) and experimental and calculated relationship between β and $\ln \sigma$ (lower diagram).

ing, Eq. (1) is valid only in the case of mono-disperse particles.

The observed values of N_V are about one order of magnitude lower than that predicted from Eq. (1). This discrepancy is considered quantitatively in the following. The particle size distributions are approximated by log-normal function and shown in the upper diagram of Fig. 2 as a function of $\ln \sigma = 0.2$ to 1.0 under the conditions of $\bar{d}_{(\text{art.})} = 0.2 \mu\text{m}$, $\Delta d/d = 0.1$ and $f_V = 0.0004$, where $\bar{d}_{(\text{art.})}$ is the arithmetic mean particle diameter and Δd is the magnitude of size interval in the particle distribution. The total number of particles for a given $\ln \sigma$ is defined by $N_{V(\ln \sigma)}$. The $N_{V(\ln \sigma)}$ value is the total number of monodispersed particles ($\ln \sigma = 0$). It is to be noted that the β value is almost independent of the values Δd and $\bar{d}_{(\text{art.})}$. The ratio of the number of particles per unit volume at a given $\ln \sigma$ to that at mono-disperse particles ($\ln \sigma = 0$) which is represented by $\beta = N_{V(\ln \sigma)} / N_{V(\ln \sigma = 0)}$ is plotted against $\ln \sigma$ in the lower diagram of Fig. 2 by the solid line, along with the experimental results for different oxides. The experimental data fall on the calculated line, although the data scatter to a considerable degree. The β values decrease with increasing $\ln \sigma$ and in particular the N_V value for Al₂O₃ particles with $\ln \sigma = 0.8$ to 1.0 represented by the triangles is about one order of magnitude lower than that estimated from Eq. (1) by using $\bar{d}_V$ for Al₂O₃ particles.

A plot of N_V versus $\ln \sigma$ is shown as a function of the arithmetic mean radius, $\bar{d}_{(\text{art.})} = 0.2$ to 0.8 in Fig. 3, together with the experimental results. It is to be noted that the decrease in N_V value with increasing $\ln \sigma$ is independent of the arithmetic mean radius. Thus, it may be concluded from the above mentioned results that for the purpose of obtaining a large number of particle for a given f_V , the particle size distribution should be controlled by approaching the mono-disperse particles as much as possible. This is true to the inhibition of grain growth by pinning.

The limiting mean grain diameter in three dimensions, $\bar{D}_V$, can be written as

Fig. 3. Experimental and calculated relationship between N_V and $\ln \sigma$ as a function of arithmetic mean radius.

Fig. 4. Effect of holding time at 1873 K on the geometric standard deviation for different deoxidation particles.

$$\bar{D}_V = \alpha \cdot \frac{1}{\bar{d}_V^{3n-1} \cdot N_V} \dots \dots \dots (2)$$

where α is a constant and $n=1$ (Zener⁸), $1/2$ (Doherty *et al.*⁹) and $2/3$ (Nishizawa *et al.*¹⁰).

When the grain size is controlled by pinning using the particles with size distribution, the limiting mean grain diameter estimated from Eq. (2) becomes considerably larger due to the decrease in N_V compared with that predicted from the respective models by using $\bar{d}_V$ and N_V values.

4. Spread of Particle Size Distribution and Interfacial Energy, $\gamma_{\text{oxide-Fe(l)}}$

The geometric standard deviation, $\ln \sigma$, for the size distribution of deoxidation particles is plotted as a function of holding time at 1873 K in Fig. 4. On the basis of the $\ln \sigma$ values obtained by extrapolating the respective lines to zero holding time, it is clear that the $\ln \sigma$ values soon after the

Fig. 5. Relationship between extrapolated $\ln \sigma$ and interfacial energy between oxide and liquid iron, γ_{PL} ,⁸⁻¹⁵ for various deoxidation particles.

Table 1. Experimental and calculated critical supersaturation degree for precipitation of oxides.

Oxide	V_O [cm ³ ·mol ⁻¹]	γ_{PL} [erg·cm ⁻²]	S_O^* (exp.)	S_O^* (cal.)	S_O
MgO	11.0	1800 ^(11,14,15)	(8.4)	280	$3.6 \sim 7.2 \times 10^4$
ZrO ₂	10.1	1630 ^(12,14,15)	4.5	85	48 ~ 68
Al ₂ O ₃	8.6	2290 ^(13,14,16)	14.7	529	37 ~ 60
CaO	16.5	1170 ⁽¹⁷⁾	(3.4)	83	—
CaO-Al ₂ O ₃	14.7	1300 ⁽¹⁸⁾	(3.6)	92	8.5×10^4
SiO ₂	11.3	1240 ⁽¹⁷⁾	1	27	—
MnO-SiO ₂	13.6	1000 ⁽¹⁸⁾	(1.7)	18	1.5

() : The values estimated from the line in Fig. 6.

nucleation of deoxidation products decrease in the order of $Al_2O_3 > ZrO_2 > MgO > CaO-Al_2O_3 > MnO-SiO_2$ particles.

Figure 5 shows a plot of the extrapolated value of $\ln \sigma$ versus interfacial energy between oxide and liquid Fe, γ_{PL} , which is summarized in **Table 1**. It follows from Fig. 5 that the $\ln \sigma$ values observed immediately after the nucleation of deoxidation products are low for the liquid CaO- Al_2O_3 and MnO-SiO₂ oxides whose values of γ_{PL} are also low, while those are high for solid MgO, ZrO and Al_2O_3 oxides whose values of γ_{PL} are also high. The reason that the spread of the particle size distribution after the nucleation of particles is in a good correspondence to the γ_{PL} value is discussed in the next chapter.

5. Factors Affecting Nucleation Rate in Deoxidation

The free-energy change, ΔG (erg per unit volume) during the nucleation of a spherical nucleus with radius, r , is expressed from the classical nucleation theory as follows:

$$\Delta G = 4\pi r^2 \gamma_{PL} - (4/3)\pi r^3 \cdot \Delta G_V \dots \dots \dots (3)$$

ΔG_V (erg) is defined by

$$\Delta G_V = -RT \ln S_O / V_O \dots \dots \dots (4)$$

Table 2. Equilibrium constants used in the present study.

Reaction	$\log K_{eq.}$	Reference
at 1873 K		
$Al_2O_3(s) = 2 \underline{Al} + 3 \underline{O}$	-13.34 (= 11.80 - 62,790/T)	19, 20
$ZrO_2(s) = \underline{Zr} + 2 \underline{O}$	-8.67 (= 21.76 - 57,000/T)	21
$MgO(s) = \underline{Mg} + \underline{O}$	-7.86 (= 12.45 - 38,050/T)	19, 22, 23
$SiO_2(s) = \underline{Si} + 2 \underline{O}$	-4.64 (= 11.58 - 30,400/T)	19, 20
$MnO(s) = \underline{Mn} + \underline{O}$	-1.33 (= 6.70 - 15,050/T)	24
$CaO(s) = \underline{Ca} + \underline{O}$	-10.23 (= 7.77 - 33,700/T)	19, 22

where V_O (cm³·mol⁻¹) is the molar volume of oxide given in Table 1 and S_O is the supersaturation degree expressed by $K_{MO}/K_{eq.(O)}$ per one mole of oxygen. K_{MO} is the solubility product per one mole of oxygen ($= [\%M]^{1/X} \cdot [\%O]$; X in MO_X) and $K_{eq.(O)}$ is the equilibrium constant per one mole of oxygen ($= K_{eq.}/X$) which is given in **Table 2**.

The critical size of nuclei, r_C , can be obtained $\delta \Delta G / \delta r = 0$ as

$$r_C = -\frac{2\gamma_{PL}}{\Delta G_V} = \frac{2\gamma_{PL} \cdot V_O}{RT \ln S_O} \dots \dots \dots (5)$$

On substituting Eq. (5) into Eq. (3), the free energy change necessary for the nucleation, ΔG^* , is obtained by

$$\Delta G^* = \frac{16\pi\gamma_{PL}^3}{3\Delta G_V^2} = \frac{16\pi\gamma_{PL}^3 V_O^2}{3(RT \ln S_O)^2} \dots \dots \dots (6)$$

The rate of formation of nuclei per cm³ of metal per second, I , is given by using Eq. (6) as

$$I = A \exp\left(-\frac{\Delta G}{k_B T}\right) = A \exp\left[-\frac{16\pi\gamma_{PL}^3 V_O^2}{3k_B R^2 T^3 (\ln S_O)^2}\right] \dots \dots (7)$$

where k_B is the Boltzman constant (1.38×10^{-16} erg·K⁻¹) and A is the frequency factor (cm⁻³·s⁻¹).

The S_O value at $I=1$ (cm⁻³·s⁻¹) is defined by the critical supersaturation degree, S_O^* . On substituting I (cm⁻³·s⁻¹)=1 and $S_O=S_O^*$ into Eq. (7), the following relationship is derived.

$$S_O^* = \exp\left(\frac{V_O}{RT} \sqrt{\frac{16\pi\gamma_{PL}^3}{3k_B T \ln A}}\right) \dots \dots \dots (8)$$

The S_O^* value obtained by substituting the values for γ_{PL} , V_O and $A=10^{26}$ cm⁻³·s⁻¹ into Eq. (8) is defined by $S_{O(cal)}^*$ which is given in Table 1.

Li and Suito²⁵⁾ experimentally determined the S_O^* values for Al_2O_3 , ZrO_2 and SiO_2 and these values of the critical supersaturation degree per one mole of oxygen, $S_{O(exp.)}^*$, are plotted against the $S_{O(cal)}^*$ values in **Fig. 6** by the open circles. It can be seen that the experimental values are consid-

Fig. 6. Relationship between experimental critical supersaturation degree and calculated one for various deoxidation particles.

erably smaller than the calculated values, but the data for Al_2O_3 , ZrO_2 and SiO_2 lie on the straight line. The line in Fig. 6 is obtained by using the method of least squares. The disagreement between experimental and theoretical values shown in Fig. 6 may arise from the aforementioned fact and/or the disregard of the effect of curvature-dependent interfacial energy on nucleation for deoxidation. The S_O^* values for MgO , $\text{CaO-Al}_2\text{O}_3$ and MnO-SiO_2 were estimated from this line, as indicated by the arrow and summarized in Table 1.

The substitution of $I (\text{cm}^{-3} \cdot \text{s}^{-1}) = 1$ and $S_O = S_O^*$ into Eq. (7) leads to the estimation of A in Eq. (7) which is rewritten as

$$A = \exp \left[\frac{16\pi\gamma_{\text{PL}}^3 V_O^2}{3k_B R^2 T^3 (\ln S_O^*)^2} \right] \dots\dots\dots (9)$$

The nucleation rate, $I (\text{cm}^{-3} \cdot \text{s}^{-1})$, is expressed by substituting Eq. (9) into Eq. (7) as

$$\ln I = \frac{16\pi\gamma_{\text{PL}}^3 V_O^2}{3k_B R^2 T^3} \left\{ \frac{1}{(\ln S_O^*)^2} - \frac{1}{(\ln S_O)^2} \right\} \dots\dots\dots (10)$$

In the present investigation, the initial amounts of Mg, Zr and Al are 0.1, 0.05 and 0.05 %, respectively, and those of Si and Mn are 0.5 and 1 %, respectively and the initial amount of oxygen is 100 ppm. The supersaturation degree, S_O , per one mole of oxygen ($=K_{\text{MO}}/K_{\text{eq.(O)}}$) was obtained from K_{MO} which was estimated from the initial amount of deoxidant and that of oxygen and $K_{\text{eq.(O)}}$ which was estimated from $K_{\text{eq.}}$ given in Table 2. The S_O values for deoxidation products are listed in Table 1. The $\ln I$ value was calculated by substituting the values for $S_{O(\text{exp})}^*$ and S_O and the respective parameters into Eq. (10) and this value is plotted against the S_O/S_O^* ratio in Fig. 7. The number given in figure refers to the initial amount of deoxidant [%M]_i. It seems apparent that $\ln I$ increases with the S_O/S_O^* ratio in the range of the S_O/S_O^* ratio between 1 and 10 and tends to be leveled off except for the case of SiO_2 . These results indicate that

Fig. 7. Effect of S_O/S_O^* ratio on nucleation rate for various deoxidation products.

Fig. 8. Relationship between nucleation frequency and interfacial energy between oxide and liquid iron.⁸⁻¹⁵⁾

$\ln I$ depends strongly on the kind of deoxidant, not on the S_O/S_O^* ratio.

The dependence of the nucleation rate, $\ln I$, on interfacial energy, γ_{PL} , is shown in Fig. 8, indicating that the nucleation rate is strongly dependent on the interfacial energy. The $\ln I$ values in Fig. 8 are used from the data points shown by the filled circles indicated in Fig. 7. The $\ln I$ value for MnO-SiO_2 particles whose γ_{PL} is about one-half of that of Al_2O_3 is about ten times greater than that for Al_2O_3 particles.

By coupling the relation between $\ln \sigma$ and γ_{PL} shown in Fig. 5 with the relation between $\ln I$ and γ_{PL} shown in Fig. 8, the relation between extrapolated $\ln \sigma$ and $\ln I$ can be obtained, as shown in Fig. 9. It is seen that with an increase in $\ln I$, the $\ln \sigma$ value decreases, which means that the particle size distribution becomes narrower. The reason for this is explained in the next chapter.

6. Separation of Nucleation and Growth

The nucleation and growth in the early stage of deoxida-

Fig. 9. Relationship between extrapolated $\ln \sigma$ and nucleation rate for various deoxidation particles.

Fig. 10. Crystallization process of deoxidation particles^{24,25}: (a) variation of supersaturation degree with time and (b) variation of crystallized particle size, r_c , and critical radius with time, r .

tion are affected by the supersaturation degree, S , the interfacial energy between oxide and liquid Fe and the equilibrium deoxidation constant under no coagulation of deoxidation particles by collision. The variation of the supersaturation degree with time in the crystallization process after deoxidant addition is schematically shown in Fig. 10(a). The solubility product of deoxidant and oxygen contents which corresponds to S for a given deoxidant increases rapidly after the addition of deoxidant. Further increase of solubility product to the critical supersaturation degree, S_0^* , at t' leads to the initiation of nucleation. The critical radius of nuclei $r_c (= 2\gamma_{PL} \cdot V_m / (RT \ln S))$ where V_m is the molar volume of particle MO_x is shown in the lower diagram. The S value decreases because of the lowering of dissolved deoxidant and oxygen consumed for the nucleation and growth. When S reaches S^* at t'' , the nucleation ends.

The time at which the Ostwald growth starts is not certain. When the melt is in equilibrium with MO_x particles

Fig. 11. Variation of supersaturation degree : (a) separation of nucleation and growth and (b) coexistence of nucleation and growth.

having the mean radius r which corresponds to the point c, the particle growth by diffusion ends, but the Ostwald growth continues to occur. After the growth path curve of a particle crosses the r_c curve, this particle dissolves and vanishes due to Ostwald ripening, as shown schematically in Fig. 10(b). The schematic illustration shown in Fig. 10 has been used by LaMer and Dinegar⁴) and Kampmann and Kahlweit⁵) for the explanation of the precipitation phenomena.

In the case of low nucleation rate, i.e., low S and high γ_{PL} , the time between a and b shown in Fig. 10(a) becomes longer, the particle size distribution becomes broader. For the narrow size distribution, therefore, it is necessary to reduce the driving force for particle growth by rapidly finishing the nucleation event. It should be noted that if the size distribution becomes narrower, the particle growth by Ostwald ripening can be restrained. This principle of producing fine particles having a narrow size distribution in a large amount is of essential importance. In the case of actual deoxidation process, however, it is extremely difficult to control the supersaturation curve; namely, the separation of nucleation and growth. This is because the supersaturation reaches the point c in a very short time.

The curve shown in Fig. 10(a) is determined by the nucleation rate and the growth rate. The curve I shown in Fig. 11(a) corresponds to the case that nucleation ceases rapidly and the equilibrium represented by the point c attains in a short time because of high supersaturation degree and high nucleation rate.

Similarly, the curve II shown in Fig. 11(b) corresponds to the case that the nucleation and growth by diffusion occur simultaneously and the equilibrium attains in a long time because of low supersaturation degree and low nucleation rate. The curve I corresponds to the Si/Mn deoxidation in which the nucleation rate is high due to low interfacial energy between MnO-SiO₂ oxide and liquid Fe, thus leading to a narrow size distribution. The curve II corresponds to the Al deoxidation in which the nucleation rate is low due to high interfacial energy between Al₂O₃ and liquid Fe, thus leading to a broad size distribution.

The number of crystallized particles per unit volume, N_V ,

Fig. 12. Number of crystallized particles per unit volume, N_V , and mean particle radius, $\bar{d}_V$, plotted against holding time.

and the mean particle diameter, $\bar{d}_V$, for the curves I and II shown in Fig. 11 are schematically illustrated in **Fig. 12**. As shown in the upper diagram the N_V value for the case of high supersaturation degree (curve I) increases rapidly at first (Region a or a') and the particle growth rate by Ostwald ripening cannot increase because of a narrow size distribution. The behavior of N_V versus time for the curve II is an opposite case. After the N_V value reaches the maximum, it decreases with time according to the relation²⁾: $N_V \propto t^{-1}$ which is the characteristics of Ostwald ripening (Region c or c'). As explained elsewhere,²⁾ if f_V is small and constant, a size distribution is narrow and a particle is controlled by Ostwald ripening (Region c or c') i.e., $\bar{d}_V \propto t^{1/3}$, the product of $N_V \cdot t$ becomes constant based on Eq. (1).

The $\bar{d}_V$ value increases with time by the relation: $\bar{d}_V \propto t^{1/2}$, due to the particle growth by diffusion mechanism (Region a or a'). The time at which the Ostwald growth (Region c or c') starts is late for the curve II in comparison with that for the curve I. It should be pointed out that the time scale shown in Figs. 10 to 12 cannot be determined experimentally in the case of deoxidation. This is because the nucleation rate as well as the growth rate is very fast compared with those of the precipitation of particles in solid state such as carbide precipitation.

7. Experimental Confirmation of Refinement of Particles

It was found that to narrow the initial particle size distribution as well as to lower the dissolved oxygen content are indispensable for obtaining fine deoxidation particles. For this purpose deoxidant with low interfacial energy between liquid Fe and oxide, and strong deoxidant with which dissolved oxygen can be lowered must be chosen. As given in Tables 1 and 2, deoxidants which satisfy the above-mentioned two conditions are difficult to find in practice, thus resulting in the use of complex deoxidation. In this study, the Ti deoxidation whose interfacial energy between TiO_x and liquid Fe is low ($\gamma_{\text{Ti}_2\text{O}_3/\text{Fe(l)}} = 1200$ and $\gamma_{\text{TiO}_2/\text{Fe(l)}} = 510 \text{ erg} \cdot \text{cm}^{-2}$) is first carried out, followed by the Mg

Fig. 13. Particle size distributions obtained by Mg (○), Al followed by Mg (△) and Ti followed by Mg deoxidations (◇).

deoxidation in which the dissolved oxygen content is very low.

7.1. Complex Deoxidation Experiments

An Fe–10%Ni alloy was melted at 1873 K for 30 min in an alumina crucible under flowing atmosphere and then an Fe–10%Ti and Ni–10%Mg alloys were added in the following four experiments, in which the initial oxygen content was 100 ppm.

i) Ti ($[\% \text{Ti}]_i = 0.1$) was added followed by stirring for 10 s and then Mg ($[\% \text{Mg}]_i = 0.1$) was added. After stirring for 10 s, the melt was held for 3 and 10 min at 1873 K, followed by rapid quenching.

ii) Ti ($[\% \text{Ti}]_i = 0.1$) was added followed by stirring every 5 min for 10 s for total 30 min in order to eliminate deoxidation particles of TiO_x by flotation and then Mg ($[\% \text{Mg}]_i = 0.1$) was added followed by stirring for 10 s. The melt was held for 3, 10 and 30 min at 1873 K, followed by rapid quenching.

iii) Mg ($[\% \text{Mg}]_i = 0.1$) was added followed by stirring for 10 s and then the melt was held for 1, 3, 10 and 30 min at 1873 K followed by rapid quenching.

iv) Al ($[\% \text{Al}]_i = 0.1$) was added followed by stirring for 10 s and then Mg ($[\% \text{Mg}]_i = 0.1$) was added followed by stirring for 10 s. The melt was held for 3 min at 1873 K, followed by rapid quenching. The experiment with the reverse addition with respect to Al and Mg was also carried out.

The total oxygen contents were 69–83 ppm for the experiment numbers (i), (iii), and (iv) and 24–33 ppm for the experiment number (ii). The number and size of particles were estimated by the method described in detail elsewhere.⁷⁾ The aforementioned experiments i) to iv) denote Ti/Mg, Ti(30 min)/Mg, Mg and Mg/Al or Al/Mg, respectively, hereinafter.

7.2. Effect of Ti Addition on Refinement of Particles

Size distribution observed in the Ti/Mg deoxidation ex-

Fig. 14. Number of particles per unit volume and geometric standard deviation plotted against mean particle diameter obtained in different deoxidation experiments.

periment held for 3 min at 1873 K is shown in **Fig. 13**, in which the results obtained in the Mg and Al/Mg deoxidation experiments are also included for comparison. It is clear that the number of fine particles with the radius of $0.04 \mu\text{m}$ in the Ti/Mg deoxidation is much greater than that in the Mg deoxidation. Furthermore, it is seen that the number of fine particles in the Al/Mg deoxidation is significantly small. These results suggest that the interfacial energy between oxide and liquid Fe is importance for the refinement of deoxidation particles.

The number of particles and the geometric standard deviation in the experiments held for 3 min at 1873 K are plotted against the mean particle diameter in the upper and lower diagrams of **Fig. 14**, respectively. It is seen from the upper diagram that the number of particles increase and the particle size decrease in the order of $\text{Al/Mg} < \text{Mg}$, $\text{Mg/Al} < \text{Ti/Mg}$. From the results indicated in the lower diagram it follows that the particle size becomes smaller with a decrease in the $\ln \sigma$ value. The number of particles obtained in the Ti(30 min)/Mg deoxidation represented by the half-filled diamond is smaller than that observed in the Ti/Mg deoxidation due to the lower volume fraction of particles in the former experiment. However, the particle size and $\ln \sigma$ values observed in the Ti(30 min)/Mg deoxidation are almost the same as those in Ti/Mg deoxidation.

Figure 15 shows the size distributions represented by particle frequency which are obtained in the Mg, Al/Mg, Ti/Mg and Ti(30 min)/Mg deoxidations. Although the number of particles in the Ti(30 min)/Mg deoxidation is smaller than that in the Ti/Mg deoxidation, the spread of size distribution in both deoxidations is narrower than those in the Mg and Al/Mg deoxidations. On the basis of these results it can be concluded that the Ti addition influences the refinement of particles due to the fact that initial narrow size distribution arising from lower interfacial energy between oxide and liquid Fe reduces the coarsening rate of particle growth.

Fig. 15. Size distributions of different deoxidation products expressed in frequency.

Fig. 16. Variation of number of particles with holding time at 1873 K in Mg ($\circ$), Ti followed by Mg ($\diamond$), and after 30 min of Ti addition Mg deoxidations ($\blacklozenge$).

7.3. Effect of Ti Addition on Growth Rate

The number and size of particles for the Mg, Ti/Mg and Ti(30 min)/Mg deoxidations are plotted against the holding time at 1873 K in **Figs. 16** and **17**, respectively. The holding time at 1873 K for the Ti(30 min)/Mg deoxidation corresponds to the time for the Mg addition after 30 min. The decreasing rate of particle number in the Mg deoxidation is faster than the Ti/Mg and Ti(30 min)/Mg deoxidations. Although the volume fraction of particles in the Ti(30 min)/Mg deoxidation is much smaller than that in the Mg deoxidation, the number of particles observed in the Ti(30 min)/Mg deoxidation is higher than that in the Mg deoxidation.

It follows from the results in **Fig. 17** that the difference between the two lines corresponds to the $\alpha \cdot k_d$ value in Eq. (11) which is the expression of particle growth by the Ostwald ripening.

Fig. 17. Variation of mean particle diameter with holding time at 1873 K in Mg (○), Ti followed by Mg (◇), and after 30 min of Ti addition Mg deoxidations (◆).

$$\bar{r}_3 - \bar{r}_0^3 = \alpha \cdot k_d \cdot t \quad (11)$$

with k_d as

$$k_d = \frac{2\gamma D_O V_O C_O}{RT(C_P - C_O)} \quad (12)$$

where $\bar{r}$ is the mean particle radius at time t , $\bar{r}_0$ is the mean particle radius at the start of Ostwald growth, α is the coarsening coefficient, γ is the interfacial energy, D_O is the diffusion coefficient of oxygen, V_O is the molar volume of diffusing oxygen, C_P is the oxygen content in inclusion and C_O is the oxygen content in metal.

Inserting the observed relationship that three power of the mean particle radius is proportional to the holding time at 1873 K into Eq. (11), we obtain the following relation under a constant $\bar{r}_V$:

$$\bar{r}_V \cdot t = \text{constant} \quad (13)$$

The slope of minus unity in a plot of $\bar{r}_V$ 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.

If the composition of particles in the Mg and Ti/Mg deoxidations is MgO, this difference corresponds to the coarsening coefficient, which was found to be well correlated with $\ln \sigma$.²⁾ It can thus be concluded from these observations that the spread of the size distribution becomes narrower with the addition of Ti by the reason explained in Figs. 8 and 11, thus leading to the reduction of coarsening rate.

8. Conclusion

The spread of the particle size distribution which is rep-

resented by the geometric standard deviation, $\ln \sigma$, has been discussed with particular emphasis on the particle size distribution soon after the nucleation of deoxidation product. The results obtained are summarized as follows:

(1) The geometric standard deviation increases with an increase in the interfacial energy between oxide and liquid Fe.

(2) Based on the discussion on homogeneous nucleation theory, the nucleation rate decreases with an increase in the interfacial energy between oxide and liquid Fe, $\gamma_{\text{oxide-Fe(l)}}$. It was found that the geometric standard deviation decreases with increasing the nucleation rate. Therefore, to obtain a narrow size distribution, high nucleation rate in which $\gamma_{\text{oxide-Fe(l)}}$ is low such as the case of MnO-SiO₂ particles is needed before the initiation of the Ostwald growth.

(3) The Ti deoxidation, whose interfacial energy between oxide and liquid Fe is low, is first carried out, followed by the Mg deoxidation in which the dissolved oxygen content is very low. It can be concluded that the geometric standard deviation decreases by the initial Ti addition and the refinement of particles is confirmed due to the fact that initial narrow size distribution arising from lower interfacial energy between oxide and liquid Fe reduces the coarsening rate of particle growth.

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