Thermodynamic Analysis on Metastable Alumina Formation in Aluminum Deoxidized Iron Based on Ostwald’s Step Rule and Classical Homogeneous Nucleation Theories

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A mechanism for the formation of unstable alumina (δ, γ, and κ-alumina) in Al-deoxidized iron has been investigated on the basis of Ostwald’s Step Rule and two homogeneous nucleation theories. The two homogeneous nucleation theories include a simplified theory in widespread use and the other is a modified theory in which the Gibbs free energy change of the parent iron phase is taken into consideration. Comparison of the chemical potential of various aluminas from the standpoint of the Ostwald’s Step Rule showed that the unstable alumina could form from the liquid iron alloy supersaturated with oxygen. Moreover, the rule revealed that there is a possibility of liquid alumina formation. The two homogeneous nucleation theories also proved the possibility of the formation of unstable and liquid alumina. The latter nucleation theory indicated the easier nucleation of liquid and unstable aluminas than that for α-alumina from the liquid iron containing oxygen contents in excess of the critical value of nucleation at 1 873 K. In contrast, nucleation was rare for oxygen contents less than the critical point at 1 873 K. However, unstable alumina can be formed during cooling and solidification since the oxygen contents of the critical point decreases with temperature decrease. When iron solidifies whilst in the supercooled condition, the nucleation rates of unstable and liquid alumina can be accelerated as a result of the oxygen enrichment at the solidifying front. The authors propose a mechanism of the network-like or coral like inclusion formation by taking into consideration of the liquid alumina formation.

KEY WORDS: α-alumina; δ-alumina; γ-alumina; κ-alumina; liquid alumina; nucleation; Ostwald’s Step Rule; homogeneous nucleation theory; nucleation rate; network-like inclusion; coral-like inclusion.

1. Introduction

The δ, γ, κ, and θ phases of alumina and amorphous silica inclusions have been observed in aluminum-deoxidized iron.1–7) As was reported in the latest report,2) the δ and γ-alumina were observed as secondary inclusions formed during cooling of iron. However, the δ, γ, κ, and θ-alumina are not stable at steelmaking temperatures and are metastable at ordinary temperatures, whilst the α-alumina is stable. Also, cristobalite is the stable form of silica at the steelmaking temperatures. Therefore, it is not obvious why unstable alumina and amorphous silica are formed under these conditions.

Okubo et al.7) thought that enthalpy evolved due to the heat of formation when an alumina particle is formed in liquid iron could force it to melt and, as a consequence, the alumina melt would be supercooled resulting in the solidification of unstable alumina. In contrast, Kusakawa et al.8) reported that only 50 degrees centigrade temperature rise of steel would result from the heat of formation of alumina and thus there was no possibility of liquid alumina formation in the steel. However, Kiessling9) reported the presence of glassy and partly-molten alumina inclusions. He considered that local overheating with high local temperature peaks resulted from the reaction between liquid aluminum and oxygen in steel at the surface of the steel and thus caused the melting of alumina.

According to the Ostwald’s Step Rule,10,11) a supercooled liquid material, which shows polymorphism, solidifies first as an unstable (metastable) crystal and then gradually transforms into other polymorphs with lower chemical potentials in a step by step manner. Therefore, as Okubo et al. have stated, once liquid alumina has formed in the liquid iron, it could subsequently solidify as unstable aluminas. Certainly, liquid alumina could be formed immediately after aluminum addition due to the local overheating as Kiessling reported.9) However, it is unlikely that the alumina in bulk liquid iron would melt during the cooling process as a consequence of the heat of formation evolution due to the reaction between oxygen and aluminum; these oxygen and aluminum are already present as solutes in liquid iron, even if they are present in the supersaturated state. Furthermore, the temperature rise required for the melting of silica is also improbable although the amorphous silica can easily form from liquid silica and nothing other than the liquid silica formation could explain the presence of amorphous silica.
Oxygen levels in aluminum–deoxidized liquid iron often exceed over equilibrium levels for solid α-alumina for a considerable time after aluminum deoxidation. The excess oxygen would be transformed into an alumina inclusion during the solidification process because the aluminum which is insoluble to acid is detected in the solidified iron. The insoluble aluminum is also detected in the solidified iron in equilibrium with α-alumina. Therefore, the investigation of the excess oxygen is important in order to investigate the mechanism of alumina formation. Many researchers believe that the excess oxygen originates from supersaturated oxygen in the liquid iron. However, the present authors have doubts as to why the oxygen and aluminum remain separate and non-reactive in the liquid iron for a long time without forming a very stable alumina at 1 873 K, but then, react and form alumina inclusions at lower temperatures during cooling.

In an earlier report, the present authors proposed the presence of alumina-associated compounds in the liquid iron in equilibrium with solid α-alumina, and developed an associated solution model. The model showed that reasonable explanations could be obtained for both the thermodynamic properties and the inconsistencies in the measurements obtained in various studies of liquid iron. Almost all the oxygen is present as oxygen-containing associated compounds. Thus the model does not consider the free oxygen in the usual concentration ranges of oxygen and aluminum in liquid iron. In a previous report, the present authors applied this model to liquid iron containing excess oxygen. The results showed that the model could be applied to liquid iron with excess oxygen and the excess oxygen should originate, partly, from the suspension of fine alumina deoxidation products and partly, from the supersaturation of alumina-associated compounds. The suspended aluminas could coalesce during cooling and the solidification process to form secondary inclusions. Thus, the structure of the coalesced secondary alumina depends on the original suspended alumina, which is the primary deoxidation product. Also, the supersaturated-alumina-associated compounds should agglomerate or precipitate on the suspended alumina and solidify as an alumina secondary inclusion. Thus, if the secondary alumina inclusion originates from the suspended alumina and supersaturated-associated compounds and is not due to the free oxygen, then the heat of alumina formation reaction does not arise during cooling. Thus, another driving force to cause an alumina particle to melt to form liquid alumina must be sought or another reason for unstable, alumina formation is needed to explain this behaviour.

In the present study, the formation of unstable alumina will be discussed on the basis of the Ostwald’s Step Rule, and two homogeneous nucleation theories (namely, one in common use and a modified theory which follows the original equation of the homogeneous nucleation theory). In both homogeneous nucleation theories, the dependence of the interfacial free energy between liquid iron and alumina on oxygen concentration has been taken into account in different ways. In the latter theory, which was discussed in detail in a previous report, the Gibbs free energy change of parent iron phase has been considered.

2. Supersaturated State and Alumina Associated Compound

Generally, the supersaturated state of oxygen means the supersaturation of aluminum and oxygen in relation to the state in equilibrium with α-alumina. The state in equilibrium with solid α-alumina is hereafter referred to as the equilibrium state. The $\mu^{\text{s.s.}}$, which is the sum of the chemical potential of aluminum and oxygen in the supersaturated state ($\mu_{\text{Al}}^{\text{s.s.}}$ and $\mu_{\text{O}}^{\text{s.s.}}$), is expressed by both the supersaturation degree, $S$, and the chemical potential of solid α-alumina, $\mu_{0}^{\text{a.s.}}$.

$$\mu^{\text{s.s.}} = 2\mu_{\text{Al}}^{\text{s.s.}} + 3\mu_{\text{O}}^{\text{s.s.}} = RT\ln S + 2\mu_{\text{Al}}^{\text{a.s.}} + 3\mu_{\text{O}}^{\text{a.s.}} = RT\ln S + 2\mu_{0}^{\text{a.s.}}, \quad \text{..................................}(2-1)$$

$$S = (a_{\text{Al}}^{\text{s.s.}})^2/(a_{\text{Al}}^{\text{a.s.}})^2/(a_{\text{O}}^{\text{s.s.}})^3, \quad \text{..........................}(2-2)$$

where, $\mu_{\text{Al}}^{\text{a.s.}}$ and $\mu_{\text{O}}^{\text{a.s.}}$ are the chemical potentials of aluminum and oxygen in the equilibrium state, respectively. The $(a_{\text{Al}}^{\text{s.s.}})^2/(a_{\text{Al}}^{\text{a.s.}})^2$ and $(a_{\text{O}}^{\text{s.s.}})^3/(a_{\text{O}}^{\text{a.s.}})^3$ are the activity products of aluminum and oxygen in the supersaturated state, and in the equilibrium state, respectively. If the alumina-associated compound is present in liquid iron in the supersaturated state, its chemical potential, $\mu_{\text{Al}}^{\text{s.s.}}$, can be written in the same manner as Eq. (2-1) since the mass action law should hold even in the supersaturated state.

$$\mu_{\text{Al}}^{\text{s.s.}} = 2\mu_{\text{Al}}^{\text{a.s.}} + 3\mu_{\text{O}}^{\text{a.s.}}, \quad \text{..........................}(2-3)$$

Therefore, $\mu_{\text{Al}}^{\text{s.s.}}$ equals to $\mu^{\text{s.s.}}$. The $\mu_{\text{Al}}^{\text{s.s.}}$ can be also written as follows.

$$\mu_{\text{Al}}^{\text{s.s.}} = \mu_{\text{Al}}^{\text{a.s.}} + RT\ln a_{\text{Al}}^{\text{s.s.}}\quad \text{..........................}(2-4)$$

where, $S_{\text{a.s.}} = (a_{\text{Al}}^{\text{a.s.}}/a_{\text{Al}}^{\text{s.s.}})$, $a_{\text{Al}}^{\text{s.s.}}$, $a_{\text{Al}}^{\text{a.s.}}$ and $\mu_{\text{Al}}^{\text{s.s.}}$ expresses the supersaturation degree, activity in the supersaturated state, activity in the equilibrium state, and chemical potential in the equilibrium state, respectively, of alumina-associated compound. The subscript a.s. means alumina-associated compound. The $\mu_{\text{Al}}^{\text{a.s.}}$ equals to $\mu_{0}^{\text{a.s.}}$ because, in the equilibrium state, the alumina-associated compound is in equilibrium with solid α-alumina. Thus, the two supersaturation degrees, $S$ and $S_{\text{a.s.}}$, are also equal. This can also be deduced from the next equation.

$$S_{\text{s.s.}} = a_{\text{Al}}^{\text{s.s.}}/a_{\text{Al}}^{\text{a.s.}} = (K_{\text{s.s.}}(a_{\text{Al}}^{\text{s.s.}})^2/(a_{\text{Al}}^{\text{a.s.}})^2)/(K_{\text{s.s.}}(a_{\text{O}}^{\text{s.s.}})^3/(a_{\text{O}}^{\text{a.s.}})^3)$$

$$= K_{\text{s.s.}}, \quad \text{..........................}(2-5)$$

where, $K_{\text{s.s.}}$ is the equilibrium constant for the formation reaction of alumina-associated compound.
3. Results and Discussion Based on Various Rule and Theories

3.1. Ostwald's Step Rule

In Fig. 1, the chemical potential differences ($\mu_a^{\circ} - \mu_o^{\circ}$) between unstable aluminas (â, g and k-aluminas; $\mu_o^{\circ}$) and $\alpha$-alumina ($\mu_a^{\circ}$) are shown as functions of temperature. In Fig. 1, the $\mu_a^{\circ} - \mu_o^{\circ}$ (m: chemical potential of liquid alumina) is also plotted. The value of $\mu_a^{\circ} - \mu_o^{\circ}$ from the melting point to 1700 K indicates the value of supercooled liquid alumina. All the chemical potentials are cited from the JANAF Thermochemical Tables.14) Apparently, the $\mu_a^{\circ}$ is larger than any other chemical potentials, $\mu_o^{\circ}$'s. Judging from Fig. 1 and Ostwald’s Step Rule, one can estimate that the supercooled liquid alumina solidifies into $\delta$, $\gamma$ or $\alpha$-alumina since their chemical potentials are larger than that of $\alpha$-alumina.

Ostwald also pointed out that the supersaturated state created unstable or metastable states.10) Thus, the Step Rule should be applied for the supersaturated state. The $\mu_h^{\circ} - \mu_o^{\circ}$ values at $S$=100, 50, 10 and 5 are plotted in Fig. 1. All the $\mu_h^{\circ}$ values are larger than the chemical potentials of various aluminas. Therefore, it can be deduced that, not only the $\delta$, $\gamma$ and $\alpha$-aluminas but also the liquid alumina could be formed from the supersaturated state. The liquid alumina formed will solidify as $\delta$, $\gamma$, $\kappa$ or $\alpha$-alumina. The supersaturated state will arise not only at the final stage after deoxidation but also at the stage of initial deoxidation process. Thus, above results show the possibility of forming unstable and liquid alumina in both stages without involving the process of temperature rise. However, the Ostwald’s Step Rule is an empirical one, and is not necessarily valid. Therefore, more inspection on the basis of nucleation theory is necessary.

3.2. Classical Homogeneous Nucleation Theory

The nucleation rate can be calculated from the following equations based on the classical, simplified homogeneous nucleation theory15,16) which is often used when considering the nucleation of inclusions.

$$I=A \exp \left\{ -(\Delta g^* + \Delta g_{D})/kT \right\}, \quad \text{...........(3-1)}$$

$$\Delta g^* = 16\pi \sigma_\text{Fe}^2 M^2/(3\rho_i^2 (\mu_a^{\circ} - \mu_o^{\circ})^2), \quad \text{...........(3-2)}$$

$$A=n_i^*(\sigma_\text{Fe}/kT)^1/2(2\sqrt{\pi})^{1/2}n(kT/h), \quad \text{...........(3-3)}$$

where $\Delta g_{D}$ is the Gibbs free energy of activation for transporting a molecule across the interface and is neglected in calculation because this term is unknown and is thought to be very small in comparison with $\Delta g^*$. The $\Delta g^*$ is the Gibbs free energy change for the formation of a critical nucleus in which the Gibbs free energy term of parent iron phase is ignored. In Eq. (3-2), $\rho_i$, $\mu_i^{\circ}$ and $M$ are the density of critical nucleus of various aluminas, $i$ (i: $\alpha$, $\delta$, $\gamma$ or liquid-alumina), the standard chemical potential of $i$, and the atomic weight of alumina, respectively. In Eq. (3-3), $n_i^*$, $v_i$ and $n$ are the number of molecules on the surface of the $i$’s critical nucleus, the volume per molecule of $i$’s critical nucleus, and the number of molecules per mole of parent phase, respectively. The $n_i^*$, $n$, and $v_i$ values are written as follows:

$$n_i^* = 4\pi (\rho_i)^{1/2} (M/(\rho_i N))^{2/3}, \quad \text{...........(3-4)}$$

$$n = (6 \cdot 10^{-7} M_{\text{Fe}}/3M_{\text{Al}})SN, \quad \text{...........(3-5)}$$

$$v_i = (M/\rho_i)N, \quad \text{...........(3-6)}$$

where, $n$ is assumed to be one third of the total number of oxygen atoms in the iron, because an alumina molecule is constituted of three oxygen atoms. As the oxygen content in the equilibrium state is around 0.0006 mass%, the value of $n$ is expressed by Eq. (3-5). The $M_{\text{Fe}}, M_{\text{Al}}$ and $N$ are the atomic weights of iron and oxygen and the Advagodoro’s Constant, respectively. The density of liquid alumina can be expressed as a function of temperature ($\rho_l = 5.34 - 1.15 \cdot 10^{-3} T$ ($g \cdot m^{-3}$), where $T$ is in K), which was derived from a figure in the data book.17) The densities of $\alpha$, $\delta$ or $\gamma$-alumina phases ($\rho_o$, $\rho_\delta$, $\rho_\gamma$) derived from the ASTM card were used here but the density of $\kappa$-alumina could not be found.

The interfacial free energy values between various aluminas and liquid iron, $\sigma_{\text{Fe-o}}$, are needed for the calculation of nucleation rate. The present authors have already proposed...
a correlation between the interfacial free energies of various metals and oxides, and the molar enthalpy values of oxides (Fig. 2). The interfacial free energies between various metals and oxides, $\sigma_{\text{metals-oxide}}$, can be expressed by linear regression analysis,13)

$$\sigma_{\text{metals-oxide}} = \sigma_{\text{metals-oxide}}^N N^{-\frac{1}{3}} V_{\text{oxide}}^{-\frac{2}{3}}.$$ \hspace{1em} (3-7)

$$\sigma_{\text{metals-oxide}} = -6215 + 0.1210 (H_{\text{oxide}}^0) \text{ (J/mol)},$$ \hspace{1em} (3-8)

$$H_{\text{oxide}}^0 = \Delta H_{\text{oxide}}^i + \int_{298}^{T} C_P_{\text{oxide}} dT.$$ \hspace{1em} (3-9)

The $V_{\text{oxide}}$ is the molar volume of oxide and $N$ is Avogadro’s number. The $H_{\text{oxide}}^0$, $\Delta H_{\text{oxide}}^i$ at 298 K and $C_P_{\text{oxide}}$ represent the molar enthalpy value of oxide at temperature, $T$, the molar enthalpy of formation of oxide at 298 K, and the molar heat capacity of oxide at constant pressure, respectively. Further details regarding Eqs. (3-7)–(3-9) have been given in a previous report.13) Thus, the interfacial free energies between liquid iron and various aluminas, $\sigma_{\text{Fe-oxide}}$, can be expressed as follows,

$$\sigma_{\text{Fe-oxide}} = \sigma_{\text{Fe-oxide}}^N N^{-\frac{1}{3}} V_{\text{oxide}}^{-\frac{2}{3}},$$ \hspace{1em} (3-10)

$$\sigma_{\text{Fe-oxide}}^i = -6215 + 0.1210 (H_{\text{oxide}}^0) \text{ (J/mol)},$$ \hspace{1em} (3-11)

$$H_{\text{oxide}}^0 = \Delta H_{\text{oxide}}^i + \int_{298}^{T} C_P_{\text{oxide}} dT,$$ \hspace{1em} (3-12)

where subscript $i$ means each alumina. The $\sigma_{\text{Fe-oxide}}^i$ calculated from the molar enthalpies of aluminas, $H_{\text{oxide}}^i$, using Eqs. (3-10)–(3-12) are shown as functions of temperature in Fig. 3. However, the values of $\sigma_{\text{Fe-oxide}}^i$ in Fig. 3 refer to those for alumina having zero curvature and oxygen-free iron. The interfacial free energy should change according to the change of nuclear curvature (or nuclear radius) and oxygen content in liquid iron. In the present calculation, it was assumed that all the interfacial free energies had similar dependencies on nuclear radius and oxygen content. This assumption means that the difference itself between $\sigma_{\text{Fe-oxide}}^i$ and $\sigma_{\text{Fe-oxide}}^j$ at a certain temperature, which is derived from Fig. 3, is constant and does not change according to the nuclear radius and oxygen content. In other words, each $\sigma_{\text{Fe-oxide}}^i$ can be determined at any value of the $\sigma_{\text{Fe-oxide}}^i$, even though $\sigma_{\text{Fe-oxide}}^i$ and $\sigma_{\text{Fe-oxide}}^j$ change according to the nuclear radius and oxygen content. Thus, $\sigma_{\text{Fe-oxide}}^i$ can be represented as a function of $\sigma_{\text{Fe-oxide}}^j$ and $\sigma_{\text{Fe-oxide}}^i$. The calculated nucleation rates from the supersaturated state ($S=50$) at 1873 K are shown in Fig. 4 as functions of $\sigma_{\text{Fe-oxide}}^i$.

Figure 4 shows that the nucleation rates of liquid, $\delta$ and $\gamma$-alumina are larger than that of $\alpha$-alumina. For a value of $\sigma_{\text{Fe-oxide}}^i = 0.8 \text{ N/m}$, the nucleation rates of liquid, $\delta$ and $\gamma$-alumina are $10^{15}$, $10^7$ and $10^3$, respectively, greater than that for $\alpha$-alumina.

The above-mentioned results depend largely on the estimated values of interfacial free energies of aluminas. Still, the estimated interfacial free energies shown in Fig. 3 should be appropriate. The present authors were unable to find any other methods for the reliable estimation of interfacial free energies. However, the homogeneous nucleation theory used in the above calculation does not include a term for the Gibbs free energy change of parent iron phase. Thus, the dependence of nucleation rate on oxygen and aluminum contents cannot be discussed.

3.3. Modified Classical Homogeneous Nucleation Theory13)

The original homogeneous nucleation theory includes a term for the Gibbs free energy of the parent phase. In this section, the influence of the Gibbs free energy change of the liquid iron phase is considered in the calculation of nucleation rates. Furthermore, the dependence of interfacial free energy on both the curvature and oxygen content is introduced.

The Gibbs free energy change of the 1 mol system can be expressed by the following equation.

$$\Delta G = \Delta G_\delta + \Delta G_\gamma + \Delta G_\alpha = n_i \theta,$$ \hspace{1em} (3-13)

where $n_i$ is the total number of nuclei in a 1 mol system and $\theta$ is the Gibbs free energy change for the formation of a nucleus. The first term, $\Delta G_\delta$, which arises from the newly formed interface between alumina and liquid iron, is expressed as follows.

$$\Delta G_\delta = n_i 4 \pi r^2 \sigma_{\text{Fe-oxide}}^i.$$ \hspace{1em} (3-14)
The $\Delta G_A$ represents the Gibbs free energy change of alumina nuclei's formation expressed as follows,

$$
\Delta G_A = -n_g m R T \ln \left( \frac{(a_{Al}^{4/3})(a_{O}^{1/3})}{(a_{Al}^{1/3})(a_{O}^{4/3})} \right) = -n_g m R T \ln S. \quad \text{..................................(3-16)}
$$

The term $\Delta G_B$ is the Gibbs free energy change of the parent liquid iron phase excluding the aluminum and oxygen consumed during nucleation. This term is expressed by the activities of aluminum, oxygen and iron before and after nucleation.

$$
\Delta G_B = RT \left( x_{Al} - 2n_g m \right) \ln a_{Al}^{(2)} + x_{O} \ln a_{O}^{(1)} - RT \left( x_{Al} - 2n_g m \right) \ln a_{Al}^{(1)} + x_{O} \ln a_{O}^{(2)} + \Delta G_0
$$

The superscripts (1) and (2) represent the phases before nucleation and after nucleation respectively, and $x_{Al}$, $x_{O}$ and $x_{Fe}$ are the mole fractions of aluminum, oxygen and iron, respectively. The value of $n$ in Eq. (3-3) is assumed to be one third of the total number of oxygen atoms in liquid iron since an alumina molecule contains three oxygen atoms. Thus,

$$
n = N x_{O}/3. \quad \text{..................................(3-18)}
$$

In order to calculate $\Delta G$, the interfacial free energy, which depends on oxygen content and curvature of alumina nucleus, should be evaluated. The dependence of interfacial free energy between liquid iron and $\alpha$-alumina on oxygen content was estimated in a previous report and can be written as follows.$^{13)}$

$$
\sigma_{Fe-\alpha} N m^{-1} = 2.328 - 43.18 \text{[mass%O]} - 70.6 \text{[mass%O]}^2. \quad \text{..........................(3-19)}
$$

Value for liquid, $\delta$ and $\gamma$-alumina were estimated by assuming the same dependence on oxygen content as that of $\alpha$-alumina. It is shown in the next equation.

$$
\sigma_{Fe-\delta} = 2.328 + D - 43.18 \text{[mass%O]} - 70.6 \text{[mass%O]}^2, \quad \text{..........................(3-20)}
$$

where, $D$ is the interfacial free energy difference between $\alpha$-alumina and other alumina polymorphs at 1 873 K in Fig. 3. The dependence of the interfacial free energy on the curvature of alumina of small nucleus, $\sigma_{Fe-s}$, can be assumed from the next equation.$^{12,18)}$

$$
\sigma_{Fe-s} = (1/V)\sqrt{(2\Gamma r)} \sqrt{(1/V)}, \quad \text{.............(3-21)}
$$

where $\Gamma$ is the surface excess and is assumed to be $\Gamma = N^{-1/3} V^{-2/3}$. From Eqs. (3-19)–(3-21), the $\sigma_{Fe-s}$, which depend on oxygen content and curvature of alumina nucleus, can be calculated.

The activities of the constituents were calculated on the basis of the associated solution model.$^{12,13)}$

The calculated values of $\Delta G$ are shown in Fig. 5 for nucleation in liquid iron containing initial contents of 0.1 mass% $\text{Al}$ and 0.0200 mass% $\text{O}$ at 1 873 K for the case where $n_g = 10^{16}$. Figure 6 shows $\sigma_{Fe-s}^{\text{Fe-\alpha}}$, $\sigma_{Fe-s}^{\text{Fe-\delta}}$, $\sigma_{Fe-s}^{\text{Fe-\gamma}}$, and $\sigma_{Fe-s}^{\text{Fe-\tau}}$ values change according to the growth of the nuclei and the accompanying decrease of oxygen content. The changes in oxygen content for the process and the $\sigma_{Fe-s}$ calculated from the oxygen content are also shown in Fig. 6. As the $\Delta G$ is the $n_0$ times of $\Delta g$, the maximum values of $\Delta G$ represents the $n_0$ times of $\Delta g^*$. As pointed out in the previous report,$^{13)}$ $\alpha$-alumina can nucleate from the liquid iron containing 0.1 mass% $\text{Al}$ and 0.0200 mass% $\text{O}$. From Fig. 6, it is clear that the maximum values of $\Delta G$ of $\alpha$, $\delta$, $\gamma$, and liquid-aluminas all display similar values and all the aluminas have a chance of nucleating. The value for $\delta$-alumina is the smallest, which indicates that $\delta$-alumina is the easiest to nucleate. In Fig. 7, the $\Delta G$ calculated for the liquid iron with initial contents of 0.1 mass% $\text{Al}$ and 0.0200 mass% $\text{O}$ are shown. The result indicates that the maximum value associated with liquid alumina is the smallest.

The nucleation rates calculated on the basis of Eqs. (3-1)–(3-4), (3-6), and (3-13)–(3-21) are shown in Table 1. Table 1 shows that $\alpha$, $\gamma$ and liquid-alumina all nucleate at a
similar rate and the rate of δ-alumina is the largest in the case of liquid iron with initial contents of 0.1 mass% Al and 0.0220 mass% O. In case of 0.1 mass% Al and 0.0220 mass% O initial content, the situation is entirely different and the nucleation rate of liquid-alumina has the largest value and that of α-alumina has the smallest value. The content of 0.0200 mass% O in liquid iron is located just above the critical point of supersaturation at 0.1 mass% Al (about 0.0150 mass% O at 1873 K). Therefore, the liquid and unstable alumina can nucleate easily from the iron with composition beyond the critical point and the liquid alumina-associated compound will finally solidify as an unstable or liquid alumina. In practice, the nucleation following the aluminum addition in liquid steel would proceed in the same manner as the above nucleation process from the liquid iron which exceeded the critical point. Therefore, many of the primary inclusions were found to be composed of the unstable alumina.

From the results of the previous calculation, the nucleation of α-alumina is scarce at any oxygen content below the critical point. The nucleation, with respect to the liquid and the unstable aluminas, will be more difficult below the critical point. However, any temperature decrease will bring about an oxygen decrease of the critical point. In Table 1, the nucleation rates at 1800 K and 1700 K of various aluminas with 0.0150 mass% O are shown. The table shows that δ and α-alumina can be formed at 1800 K and 1700 K, due to the decrease of oxygen of the critical point, but there would be difficulties in the formation of liquid and γ-alumina. Moreover, the oxygen solubility in δ-iron at 1720 K is about 0.0150 mass% O and it decreases to 0.0082 mass% O at 1663 K. Furthermore, in γ-iron, the oxygen solubility is less than 0.0001 mass% O according to O. Kubaschewski. Therefore, for supercooling conditions, the oxygen (or supersaturated-alumina-associated compound) in liquid iron at the solidification front will increase owing to the decrease of oxygen content in solid iron. The liquid and unstable alumina nucleation will be accelerated again in the supercooling process.

The results based on the modified homogeneous nucleation theory also depend on the values of the interfacial free energies. Especially, Eq. (3-21) is uncertain for the case where a nucleus contains only a few molecules. However, as mentioned in a previous report, the calculated nucleation rates of α-alumina for various oxygen and aluminum contents in liquid iron are consistent with experimental trends. The present results calculated for unstable and liquid alumina nuclei could also reflect the real trends.

4. Discussion

4.1. Network-like and Coral-like Inclusions

The network-like inclusions observed in aluminum-deoxidized iron which was solidified ultra rapidly or quenched into a copper mold sometimes extend to a wide region like a plane. Shibata et al. reported, from in-situ observations of alumina inclusions with a confocal laser scanning microscope that fine alumina particles tend to be pushed by advancing interface between the melt and cellular crystal. If liquid alumina is formed during cooling before solidification front, it would tend to be pushed from the interface and the following mechanism would occur. The fine several liquid alumina particles, which are formed in the solidification front, are pressed by the iron grains with the advance of the front, and finally, gather at the grain boundary, where they are pressed and solidified into a network-like plane connected with each other.

However, the network-like and coral-like inclusions in the sample quenched in water were roundish in contrast to those with angular shape which were observed in a sample solidified ultra rapidly or quenched in copper mold. The roundish coral-like inclusions seemed to be the result of multiple union of liquid spherical inclusions with high viscosity. The network-like inclusions in the same sample seemed to be formed when several coral-like inclusions were superimposed upon one another. Thus, in a sample quenched in water, the spherical liquid inclusions formed during cooling would have time to float upward, collide and coalesce with each other in liquid iron, since the cooling speed is rather slow, and finally, they could solidify as the network-like or coral-like inclusions. The above process for the network-like or coral-like inclusion in the sample quenched in water might occur during the early stage of aluminum deoxidation process in liquid iron with a composition which exceeded the critical point of supersaturation. If the inclusion is formed at this stage, it should be the primary phase.

The above elucidation of the morphology of the network-
like and coral-like inclusions supports the significant formation of liquid alumina. If the liquid alumina is present, it will act as a binder of solid alumina particles which would result in a large alumina cluster. Thus, the care must be taken at every place where the supercooling or the reoxidation may occur, for instance, around the wall of mold, if cluster formation is to be prevented.

4.2. Possibility of Liquid Alumina Formation

Figures 1, 4, 5, 7 and Table 1 indicate the possibility of liquid alumina formation from the supersaturated state without a temperature rise exceeding the melting point of alumina. Although established evidence for the presence of liquid alumina is currently insufficient, there is a strong possibility of liquid formation. For instance, the spherical inclusion of amorphous silica can not be explained without the formation of liquid silica. The present authors have already pointed out the amorphous silica is formed in copper during cooling from 1423 K. The temperature of 1423 K is lower than the glass transition temperature of silica (1443 K). Thus, supersaturated silica and oxygen, or the silica-associated compound in liquid copper participate as a form of liquid silica during cooling, and it subsequently transforms into amorphous silica.

From the standpoint of controlling the morphology of alumina, it is an important topic as to whether the liquid alumina is present or not. More detailed investigations and deliberations are necessary if the formation of liquid alumina is to be verified.

5. Conclusion

The process of unstable alumina (δ, γ, κ, and θ-alumina) formation has been discussed on the basis of the Ostwald’s Step Rule and two homogeneous nucleation theories. One of the homogeneous nucleation theories is the simplified theory in which the Gibbs free energy change of parent iron phase is taken into consideration. All the theories show the possibility of both unstable alumina and liquid alumina being formed. The details are follows;

The chemical potentials of supersaturated states, \( \mu_{\text{s.s.}} \), \( \mu_{\text{g}} \), \( \mu_{\text{d}} \), \( \mu_{\text{k}} \), \( \mu_{\text{a}} \), \( \mu_{\text{m}} \), and \( \mu_{\text{l}} \), were larger than any chemical potential of δ, γ, κ and liquid alumina. From the standpoint of the Ostwald’s Step Rule, this result indicates that unstable alumina or liquid alumina could be formed from liquid iron in the supersaturated state.

From the former simplified homogeneous nucleation theory, it was concluded that the nucleation rate of the liquid, δ and γ-alumina were larger than δ-alumina; the nucleation rate of liquid-alumina was greatest followed by those for δ and γ-alumina.

From the modified homogeneous nucleation theory, in which the dependence of interfacial free energy on nuclea-

us size and oxygen contents in liquid iron is considered in apparent form, one can calculate nucleation rate of liquid and unstable aluminas at any content of oxygen and alumina in liquid iron. It was found that the nucleation of liquid and unstable aluminas (δ and γ-alumina) from the liquid iron containing 0.1 mass% \( \text{Al} \) and an oxygen content exceeding the critical value of supersaturation (about 0.0150 mass% \( \text{O} \) at 1873 K) were possible in addition to α-alumina. In contrast, the nucleation of every type of alumina is rare with oxygen contents below the critical value. However, the nucleation of δ and α-alumina began again during cooling process of iron due to the reduction of the critical oxygen content with decrease in temperature. When liquid iron is supercooled strongly, the nucleation rate of liquid and unstable alumina would be accelerated due to the oxygen enrichment at the solidification front resulting from the lower solubility of oxygen in solid iron.

The morphology of the network-like and coral-like inclusion can be described by assuming that liquid alumina is formed. If liquid alumina is present, it will act as the binder of alumina solid particles and create large alumina clusters. The liquid alumina is a key point for considering alumina morphology and its control.

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