A Multi-step Thermodynamic Model for Alumina Formation during Aluminum Deoxidation in Fe–O–Al Melt

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Received: 14 July 2014 / Revised: 17 September 2014 / Published online: 7 January 2015
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Abstract Based on the two-step nucleation mechanism, a multi-step thermodynamic model for alumina inclusion formation during aluminum deoxidation process was proposed in Fe–O–Al melt. Thermodynamic properties of metastable intermediates including $(\text{Al}_2\text{O}_3)_n$ clusters for prenucleation and $\alpha\text{-Al}_2\text{O}_3$ nanoparticle for growth process were calculated using density functional theory. Furthermore, Gibbs free energy change of forming the intermediate by reaction between the dissolved aluminum ($\underline{\text{Al}}$) and oxygen ($\underline{\text{O}}$) in the melt was calculated. The results indicated that the thermodynamics of $(\text{Al}_2\text{O}_3)_n$ at steelmaking temperature are dependent on their structures, while that of $\alpha\text{-Al}_2\text{O}_3$ nanoparticle are dependent on their size. The nuclei of $\alpha\text{-Al}_2\text{O}_3$ which was originated from $(\text{Al}_2\text{O}_3)_n$ aggregated under a high supersaturation ratio of $\underline{\text{Al}}$ and $\underline{\text{O}}(R_s)$ in the melt. There existing excess oxygen because of the low R_s , but the secondary inclusions will be formed during the cooling process due to the excess oxygen. The nuclei larger than 20 nm can grow up spontaneously and instantaneously into primary inclusions because of thermodynamic drive. It is difficult to control the size of $\alpha\text{-Al}_2\text{O}_3$ to be less than 20 nm, in the aluminum deoxidation process of the current conditions of steelmaking.

KEY WORDS: Multi-step thermodynamics; Fe–O–Al melt; Aluminum deoxidation; DFT; Nano- $\alpha\text{-Al}_2\text{O}_3$

1 Introduction

Deoxidation of molten steel with aluminum is commonly used in secondary metallurgy, during which the dissolved aluminum ($\underline{\text{Al}}$) reacts with dissolved oxygen ($\underline{\text{O}}$) to form solid alumina inclusions, usually $\alpha\text{-Al}_2\text{O}_3$. The purpose of

deoxidation is not only to decrease the $\underline{\text{O}}$ content and remove inclusions as far as possible from molten steel but also to keep the inclusion size small for manufacturing high-performance steel. In order to accomplish the objectives, a good knowledge of inclusion formation could be helpful. The formation mechanism is closely related to thermodynamics of metastable alumina intermediate formed probably in the process of the nucleation [1–7] and growth at the nanoscale [8, 9] in the initial period of deoxidation. Thus, a deep knowledge about thermodynamics of the intermediate could help to clarify the formation mechanism of alumina in Fe–O–Al melt.

The aluminum deoxidation is a heterogeneous reaction resulting in nucleation and crystallization of $\alpha\text{-Al}_2\text{O}_3$ as following steps: (1) $\underline{\text{Al}}$ reacts with $\underline{\text{O}}$ to form alumina pseudo-molecule in Fe–O–Al melt; (2) the molecules aggregate stochastically into unstable clusters, probably forming the critical nucleus capable of independent existence that acts as centers of the growth; (3) the growth of α -

Available online at <http://link.springer.com/journal/40195>

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Al_2O_3 critical nucleus is immediate and spontaneous, which depends on supersaturation ratio of $\underline{\text{Al}}$ and $\underline{\text{O}}(R_s)$ [10, 11] in Fe–O–Al melt. Based on classical nucleation theory (CNT), an initial supersaturation ratio (R_s^0) above the critical supersaturation ratio ($R_{s,\text{cr}}^*$) is required for α - Al_2O_3 nucleation in the melt. The $\log R_{s,\text{cr}}^*$ was measured as 3.5 by electrochemical method [3] and was supported by CNT simulations [2]. Nevertheless, the measured oxygen content in deoxidized Fe–O–Al melt after adding aluminum for a considerable time exceeds frequently much more than the thermodynamic equilibrium level [2–4, 12–16]. The oxygen content in deoxidized melt is referred to as the excess oxygen thought to originate from both the suspension of fine alumina products [13, 14] and the supersaturation of alumina-associated compounds [2, 17]. The excess oxygen will continue to react with $\underline{\text{Al}}$ to form alumina secondary inclusions during cooling process. Wasai *et al.* [8] observed the secondary inclusions in solid iron prepared using ultra-rapid cooling, not only have various shape, such as a spherical shape with a diameter of a few to 10 nm or have a coral-like or network-like shape with a trunk thickness of approximately several hundred nanometers to a few micrometers, but also have the polycrystalline structures including stable α -alumina and metastable γ -, δ -alumina. It is remain unclear that why the excess oxygen and $\underline{\text{Al}}$ remain separate in the melt for a long time without forming a stable alumina or consumed by the nucleus growth, but react to form the secondary inclusions at lower temperatures in the ultra-rapid cooling process.

Wasai *et al.* [4] concluded that liquid alumina probably formed in initial stage of deoxidation in Fe–O–Al melt is the precursor for secondary inclusion formation based on CNT and Ostwald's step rule, but it is difficult to prove that whether liquid alumina is present or not. Recently, a two-step nucleation (TSN) mechanisms from solution [18–22] was proposed and supported by both the experimental evidence of stable clusters [23–26] and the molecular simulation evidence of the clusters coming together [27–30] in nucleation. According to the TSN mechanisms, it was demonstrated [1] that $\underline{\text{Al}}$ reacting with $\underline{\text{O}}$ can form alumina clusters $[(\text{Al}_2\text{O}_3)_n]$ present as the metastable intermediate both for the nucleation during deoxidation process in Fe–O–Al melt and for the crystallization of secondary inclusions during cooling process, while the excess oxygen is not actually nonreactive but the equilibrium oxygen with $(\text{Al}_2\text{O}_3)_n$ cannot nucleate because of low supersaturation ratio in the deoxidized Fe–O–Al melt.

On the other hand, Masamitsu and Nobuo [9] observed the minimum diameter of α - Al_2O_3 inclusion particle in solid steel sampling at only 1 s after adding aluminum was 23 nm; however, the reliable values were obtained above 100 nm. Wasai *et al.* [8] observed the size of α - Al_2O_3

inclusion in solid iron prepared using ultra-rapid cooling is a few to several tens of micrometers. Thus, fine alumina suspensions in the deoxidized melt [13, 14] could be nanoscale α - Al_2O_3 particle or aggregate of nanoparticles, the size of which could be larger than the size of critical nucleus and the upward movement of which might be very slow in the melt. But, the experimental observation of the size of α - Al_2O_3 suspensions smaller than 100 nm in deoxidized melt for a considerable time after adding aluminum is not yet reported. Therefore, one of the reasons may be relevant to α - Al_2O_3 nanoparticle having the “surface, interface effect and small size effect” [31–33] could have an impact on α - Al_2O_3 growth at the nanoscale by affecting thermodynamics. However, thermodynamic properties and their change of nanoscale α - Al_2O_3 as metastable intermediate of the growth process at steelmaking temperature are unclear until now. Moreover, according to the experimental information and CNT, the nature of fine suspensions and the relationship between the excess oxygen and the fine suspensions are difficult to be revealed.

Thus, the two-step nucleation mechanisms of alumina cannot yet provide the whole and clearer information about the nature of the pathways of alumina inclusion formation in Fe–O–Al melt. In the present work, a multi-step thermodynamic model of alumina inclusion formation is proposed through metastable intermediate including $(\text{Al}_2\text{O}_3)_n$ for prenucleation and α - Al_2O_3 nanoparticle for the growth in deoxidation process. For verifying the model, thermodynamics of the intermediate formed in Fe–O–Al melt were calculated by density functional theory (DFT). Furthermore, the relationship between the excess oxygen and $(\text{Al}_2\text{O}_3)_n$ was discussed, while the thermodynamics of α - Al_2O_3 growth at the nanoscale was analyzed. A clearer whole picture of inclusion formation in aluminum deoxidation process is displayed.

2 Multi-step Thermodynamic Model

The aluminum deoxidation reaction to form α - Al_2O_3 crystal inclusions is usually written by the stoichiometric equation:

The Gibbs free energy change ($\Delta_r G_m^\theta(\text{cryst})$) [34, 35] is calculated by

$$\Delta_r G_m^\theta(\text{cryst}) = -1,202.00 + 0.386T \quad (\text{kJ mol}^{-1}), \quad (2)$$

where T is the temperature, in K.

Based on TSN mechanisms and the thermodynamic properties of alumina intermediate in aluminum deoxidation process in Fe–O–Al melt, a multi-step thermodynamic model for alumina inclusion formation was proposed and

in which alumina clusters and α -Al₂O₃ nanoparticle are, respectively, the intermediate of the nucleation and the growth of alumina inclusion in the melt. The multi-step thermodynamic model can be described as follows.

The first step, the prenucleation stage, that is, the formation of metastable alumina clusters having various species, (Al₂O₃)_n, by the reaction between Al and O in Fe–O–Al melt, as represented by

where n is the number of Al₂O₃ in an alumina cluster, which is chosen as 1, 2, ..., 10, 15 and 30 in the current work.

The second step, the clusters come together and crystallize into metastable α -Al₂O₃ nanoparticles. At the beginning of this step, the nucleation of α -Al₂O₃ first occurs. The critical nucleus is the minimum nanoscale α -Al₂O₃ crystal which has the capacity of independent existence in the melt. This step can be described as follows,

The last step, α -Al₂O₃ nanoparticles grow up into stable α -Al₂O₃ inclusions. The growth mechanisms are, respectively, diffusion growth, Ostwald growth and collision growth [10, 11] in turn, with the increasing of α -Al₂O₃ size. The change from nanoparticle to crystal particle can be written as follows,

Thus, total Gibbs free energy change of α -Al₂O₃ inclusion formation by the reaction between Al and O in Fe–O–Al melt can be described as the sum of Gibbs free energy changes of Eqs. (3), (4) and (5) as follows,

$$\Delta_r G_m^\theta (\text{cryst}) = \Delta_r G_m^\theta (\text{cluster}) + \Delta_r G_m^\theta (\text{cluster} \rightarrow \text{nano}) + \Delta_r G_m^\theta (\text{nano} \rightarrow \text{cryst}). \quad (6)$$

In addition, in cooling and solidification process of the melt, (Al₂O₃)_n cannot nucleate and will crystallize into secondary inclusion probably having polycrystalline structures including γ -Al₂O₃ and δ -Al₂O₃ [8]. The change can be described as follows,

3 Method of Calculation

3.1 Thermodynamic Properties Calculation Using DFT

The structures and thermodynamic properties of (Al₂O₃)_n used for calculation can be found in detail in the previous

work [1]. In the present work, in order to calculate thermodynamic properties of nanoparticle, a nanoparticle of α -Al₂O₃ is divided into two parts: One is the inner of the nanoparticle, and the other is the surface of the nanoparticle. Thus, thermodynamic properties of a nanoparticle could be regarded as the sum of thermodynamic properties of the inner and the surface parts. The various thermodynamic property of a nanoparticle, Y^{nano} , can be written as follows,

$$Y^{\text{nano}} = (1 - x)Y^{\text{in}} + xY^{\text{sur}}, \quad (8)$$

where Y^{in} and Y^{sur} are thermodynamic property of the inner and the surface of a nanoparticle, respectively; x is the fraction of the surficial atom numbers divided by the total atom numbers,

$$x = \frac{N_{\text{sur}}}{N_{\text{in}} + N_{\text{sur}}} = \frac{V_{\text{sur}} \cdot n_{\text{sur}}}{V_{\text{in}} \cdot n_{\text{in}} + V_{\text{sur}} n_{\text{sur}}},$$

where N_{in} and N_{sur} are the inner and the surface atom numbers, respectively, V_{in} is the total volume of the inner atoms, V_{sur} is the total volume of surficial atoms, n_{in} is atom numbers per unit volume of the inner ($n_{\text{in}} = 22.049$), n_{sur} is atom numbers per unit volume of the surface ($n_{\text{sur}} = 26.316$). The values of nanoparticle with various sizes are shown in Table 1.

In consideration of ignoring the interaction between the surficial atoms and inner atoms of nanoparticle, the inner thermodynamic properties of α -Al₂O₃ nanoparticle are the same with that of α -Al₂O₃ crystal, that is, $Y^{\text{in}} = Y^{\text{cryst}}$. On the other hand, according the symmetry of crystals, three crystal planes of structural model of α -Al₂O₃ including (0 1 0), (1 0 0) and (0 0 1) planes were established, as shown in Fig. 1a–c. Therefore, $Y^{\text{sur}} = [Y^{(0\ 1\ 0)} + Y^{(1\ 0\ 0)} + Y^{(0\ 0\ 1)}]/3$. Thermodynamic properties of the three crystal planes, $Y^{(0\ 1\ 0)}$, $Y^{(1\ 0\ 0)}$ and $Y^{(0\ 0\ 1)}$, and α -Al₂O₃ crystal (Y^{cryst}) were calculated based on DFT, respectively. The calculation is achieved by using CASTEP procedure code based on plane wave pseudopotential theory (PWPP). The initial structure model of α -Al₂O₃ crystal is shown in Fig. 1d.

Table 1 Fraction of the surficial atom (x) and expression of $\Delta_r G_m (\text{nano})$ in the nanoparticles with different sizes

Nanoparticle size	x (%)	$\Delta_r G_m$ (kJ mol ^{−1})
2	16.631	$-861.361 + 37.780 \times 10^{-2} T$
5	6.653	$-1,065.744 + 38.272 \times 10^{-2} T$
10	3.326	$-1,133.872 + 38.436 \times 10^{-2} T$
20	1.663	$-1,167.936 + 38.518 \times 10^{-2} T$
30	1.109	$-1,179.291 + 38.545 \times 10^{-2} T$
40	0.832	$-1,184.968 + 38.559 \times 10^{-2} T$
50	0.665	$-1,188.374 + 38.567 \times 10^{-2} T$
75	0.444	$-1,192.916 + 38.580 \times 10^{-2} T$
100	0.333	$-1,195.187 + 38.584 \times 10^{-2} T$

Fig. 1 Structural model for DFT calculation: **a** (0 1 0) plane; **b** (1 0 0) plane; **c** (0 0 1) plane; **d** crystal

The calculation processes of three crystal planes were the same: The geometry optimization of the initial structural model was done using BFGS [36] (the abbreviation of the first letter of names for these researchers, Broyden, Fletcher, Goldfarb and Shanno) method based on quasi-Newton algorithm. The precisions of BFGS method were set as follows: energy per atom $\leq 1 \times 10^{-5}$ eV, tension $\leq 1 \times 10^{-2}$ eV/Å and shift $\leq 1 \times 10^{-3}$ Å. Hybrid density functional BLYP [37, 38] (the abbreviation of the first letter of names for these researchers, Becke, Lee, Yang and Parr) method based on Generalized Gradient Approximation (GGA)-PBE is an exchange–correlation potential function. Brillouin zone integral is done by Monkhorst–Pack method with grid size of K -points of $3 \times 3 \times 2$. The precision of Brillouin integral was set as fine. Norm-conserving PWPP based on reciprocal space was used [39].

The calculation of α -Al₂O₃ crystal can be described as follows: the initial structure of α -Al₂O₃ crystal is from the structural database of MS 6.0. The geometry optimization of the initial structural model was processed using BFGS method which is based on quasi-Newton algorithm. The precision of BFGS were set as follows: energy per atom $\leq 1 \times 10^{-5}$ eV, tension $\leq 1 \times 10^{-2}$ eV/Å and shift $\leq 1 \times 10^{-3}$ Å. Hybrid density functional BLYP method based on GGA-PBE is an exchange–correlation potential function. Brillouin zone integral is done by Monkhorst–Pack method with grid size of K -points of $4 \times 4 \times 2$. The precision of Brillouin integral was set as fine. Norm-conserving PWPP based on reciprocal space was used.

The calculated density of phonon states, $D(\omega(q))$, is shown in Fig. 2. According to $D(\omega(q))$, thermodynamic properties of the three crystal planes and α -Al₂O₃ crystal can be calculated by the following equations [40]:

$$F_V = \frac{1}{2} \int D(\omega(\mathbf{q})) \hbar \omega(\mathbf{q}) d\omega + k_B T \int D(\omega(\mathbf{q})) \ln \left[1 - \exp \left(-\frac{\hbar \omega(\mathbf{q})}{k_B T} \right) \right] d\omega, \quad (9)$$

Fig. 2 Density of phonon states of α -Al₂O₃ crystal

$$\omega(\mathbf{q}) = \int D(\omega(\mathbf{q})) d\omega, \quad (10)$$

$$S(T) = k_B \left\{ \int \frac{\frac{\hbar \omega(\mathbf{q})}{k_B T}}{\exp \left(\frac{\hbar \omega(\mathbf{q})}{k_B T} \right) - 1} D(\omega(\mathbf{q})) d\omega - \int D(\omega(\mathbf{q})) \left[1 - \exp \left(-\frac{\hbar \omega(\mathbf{q})}{k_B T} \right) \right] d\omega \right\},$$

$$C_V = k_B \int \frac{\left(\frac{\hbar \omega(\mathbf{q})}{k_B T} \right)^2 \exp \left(\frac{\hbar \omega(\mathbf{q})}{k_B T} \right)}{\left[\exp \left(\frac{\hbar \omega(\mathbf{q})}{k_B T} \right) - 1 \right]^2} D(\omega(\mathbf{q})) d\omega, \quad (12)$$

where k_B is the Boltzmann's constant and $\hbar$ is the Planck's constant. For the crystals, Helmholtz vibrational free energy (F_V) is equal to Gibbs vibrational free energy (G_V),

$$F_V = G_V. \quad (13)$$

The Gibbs free energy (G) and enthalpy (H) can be calculated as follows:

$$G = G_V + U_0 = F_V + U_0 = F, \quad (14)$$

$$H = G + TS. \quad (15)$$

where F is the Helmholtz free energy, U_0 is the zero-point vibrational energy at the temperature of 0 K, S is entropy.

From above equations, thermodynamic properties of α - Al_2O_3 nanoparticle can be obtained using Eq. (8).

3.2 Gibbs Free Energy Change Calculation

The Gibbs free energy change of forming alumina clusters (Eq. 3) can be calculated by

$$\Delta_r G_m^\theta(\text{cluster}) = \Delta_r G_m^\theta(\text{cryst}) - (G^{\text{cryst}} - G^{\text{cluster}}), \quad (16)$$

where G^{cluster} and G^{cryst} are, respectively, Gibbs free energy of $(\text{Al}_2\text{O}_3)_n$ cluster and α - Al_2O_3 crystal. The calculation process and results can be found in detail in Ref. [1].

The reaction of forming various scale α - Al_2O_3 nanoparticles by $\underline{\text{Al}}$ reacting with $\underline{\text{O}}$ in Fe–O–Al melt is represented by $2\underline{\text{Al}} + 3\underline{\text{O}} = \alpha\text{-Al}_2\text{O}_3(\text{nano})$. $\Delta_r G_m(\text{nano})$. (17)

According to Eq. (5), during α - Al_2O_3 grow from nanoparticle to crystal inclusion, the Gibbs free energy change can be calculated by

$$\Delta_r G_m(\text{nano} \rightarrow \text{cryst}) = G^{\text{cryst}} - G^{\text{nano}}, \quad (18)$$

where, G^{nano} is the Gibbs free energy of α - Al_2O_3 nanoparticle.

The Gibbs free energy change of forming α - Al_2O_3 nanoparticle, $\Delta_r G_m(\text{nano})$, can be calculated by

$$\begin{aligned} \Delta_r G_m(\text{nano}) &= \Delta_r G_m^\theta(\text{cryst}) - \Delta_r G_m(\text{nano} \rightarrow \text{cryst}) \\ &= \Delta_r G_m^\theta(\text{cryst}) - (G^{\text{cryst}} - G^{\text{nano}}). \end{aligned} \quad (19)$$

4 Results and Discussion

4.1 Thermodynamic Properties of α - Al_2O_3 Crystal

The calculated thermodynamic properties of α - Al_2O_3 crystal are shown in Fig. 3. The C_V and S were, respectively, plotted

as black and green solid curves in Fig. 3a. The F_V , H and G were, respectively, plotted as color solid curves in Fig. 3b. The experimental data of S [41] are also plotted in Fig. 3a. It can be seen from Fig. 3a that the calculated S are in agreement with the experimental results, only a small deviation between the calculated value and experimental data at higher temperature. The calculated U_0 of α - Al_2O_3 crystal is $-136,820.680$ kJ/mol.

4.2 Thermodynamic Properties of α - Al_2O_3 Nanoparticle

The calculated thermodynamic properties of α - Al_2O_3 nanoparticle are plotted in Fig. 4. Figure 4a shows that heat capacity (C_V^{nano}) of α - Al_2O_3 nanoparticles increases with the temperature increasing at a constant size, while C_V^{nano} decreases with the size increasing at a constant temperature. The change rate of C_V^{nano} with nanoparticles size (d) at a constant temperature, $[\delta(C_V^{\text{nano}})/\delta(d)]_T$, decreases with the size increasing at the nanoscale, while the change rate of C_V^{nano} with temperature at a constant size, $[\delta(C_V^{\text{nano}})/\delta(T)]_d$, decreases with the temperature increasing at 0–2,000 K. Figure 4b shows that the change pattern of enthalpy (H^{nano}) with the size and the temperature is similar to that of C_V^{nano} . Figure 4c shows that entropy (S^{nano}) increases with the temperature increasing at a constant size, while S^{nano} decreases with the size increasing at a constant temperature. Figure 4d shows Helmholtz vibrational free energy (F_V^{nano}) decreases with the temperature increasing at a constant size, while F_V^{nano} increases with the size increasing at a constant temperature. The change rates of C_V^{nano} , H^{nano} , S^{nano} and F_V^{nano} with size show similar tendency at the nanoscale at a constant temperature. On the other hand, at low temperature (below 200 K), the values of C_V^{nano} , H^{nano} , S^{nano} and F_V^{nano} of nanoparticles with

Fig. 3 Thermodynamic properties of α - Al_2O_3 crystal: **a** S and C_V ; **b** F_V , H and G

Fig. 4 Thermodynamic properties of α - Al_2O_3 nanoparticle: **a** C_V^{nano} versus temperature; **b** H^{nano} versus temperature; **c** S^{nano} versus temperature; **d** F_V^{nano} versus temperature; **e** U_0^{nano} versus nanoparticle size; **f** G^{nano} versus temperature

various sizes are close to each other, but become different with the temperature increasing, gradually. At the steel-making temperature, the difference is very great, especially for the nanoparticles which size in the smaller range.

The U_0 of (100), (010) and (001) crystal planes are $-133,765.769$, $-133,899.046$ and $-136,624.362$ kJ/mol, respectively. The average value of the U_0 of the three crystal planes, U_0^{sur} , is $-134,763.059$ kJ/mol. The zero-point vibrational energy of α - Al_2O_3 nanoparticle, $U_0^{\text{nano}} = (1-x)U_0^{\text{in}} + xU_0^{\text{sur}}$. Thus, U_0^{nano} and G^{nano} of α - Al_2O_3 nanoparticle are plotted in Fig. 4e, f, respectively. It can be seen that the U_0^{nano} and G^{nano} increase with the nanoparticle size increasing.

4.3 Gibbs Free Energy Change of Alumina Intermediate Formation

The $\Delta_r G_m(\text{nano})$ at the temperature range of 1,800–2,000 K are plotted in Fig. 5. In order to compare the thermodynamic

stabilities of various alumina intermediates at steelmaking temperature, the $\Delta_r G_m^\theta(\text{cryst})$ [1] are also plotted in Fig. 5. The fitting expressions of $\Delta_r G_m(\text{nano})$ are listed in Table 1.

From Fig. 5, it can be found that $\Delta_r G_m(\text{nano})$ at 1,800–2,000 K increases with the temperature increasing at a constant nano- α - Al_2O_3 size, while $\Delta_r G_m(\text{nano})$ decreases with the nanoparticle size increasing at a constant temperature. Furthermore, the change rate of $\Delta_r G_m(\text{nano})$ with nanoparticle size, $[\partial(\Delta_r G_m(\text{nano}))/\partial(d)]_T$, decreases with α - Al_2O_3 size increasing at a constant temperature. $\Delta_r G_m(\text{nano})$ at the nanoparticle sizes of 20–100 nm are very close to each other to the $\Delta_r G_m(\text{cryst})$. It indicated that the effect of thermodynamics depending on size is very obvious when α - Al_2O_3 size is smaller, but the effect becomes weaker gradually with α - Al_2O_3 particle growing up. The thermodynamic drive for α - Al_2O_3 growth decreases with the α - Al_2O_3 size increasing. The nucleus of α - Al_2O_3 can grow up spontaneously and instantaneously when its size less than 20 nm along with the supersaturation ratio of Al and O is rapidly

Fig. 5 Gibbs free energy changes of various metastable phases' formation by Al reacting with $\underline{\text{O}}$ in Fe–O–Al melt

consumed, while thermodynamic drive would approach zero when $\alpha\text{-Al}_2\text{O}_3$ size larger than 20 nm. This could provide a reasonable explanation for why $\alpha\text{-Al}_2\text{O}_3$ inclusion with the size less than 20 nm in the melt cannot be observed until now. Meanwhile, it could suggest that the size of $\alpha\text{-Al}_2\text{O}_3$ inclusion is controlled to the size within 20 nm is difficult under the current conditions of steelmaking.

4.4 The Stable Region and Multi-step Pathway Leading to Inclusion Formation

For the aluminum deoxidation reaction in Fe–O–Al melt, the deoxidation constant, K'_i , can be written as

$$K'_i = 1/K_i = (a_{\text{Al}}^2 a_{\text{O}}^3) / a_i = (f_{\text{Al}} \times c_{\text{Al,eq}})^2 \times (f_{\text{O}} \times c_{\text{O,eq}})^3 / a_i, \quad (20)$$

where, K_i is the equilibrium constant of the reaction; a_{Al} , a_{O} and a_i are the activities of $\underline{\text{Al}}$, $\underline{\text{O}}$ and deoxidation products in the melt, respectively; f_{Al} and f_{O} are the activity coefficients of $\underline{\text{Al}}$ and $\underline{\text{O}}$, respectively; $c_{\text{Al,eq}}$ and $c_{\text{O,eq}}$ are the contents of $\underline{\text{Al}}$ and $\underline{\text{O}}$ (in wt%), respectively. The value of $f_{\text{Al}}^3 \times f_{\text{O}}^3$ is approximately 1 in a dilute Fe–O–Al melt. In the standard state, the activity of deoxidation product is 1. Thus, K'_i can be written as

$$K'_i = c_{\text{Al,eq}}^2 \times c_{\text{O,eq}}^3. \quad (21)$$

According to the expressions in Table 1 and the Eq. (21), the equilibrium relationships of $\log[c_{\text{O}}]$ versus $\log[c_{\text{Al}}]$ at 1,873 K in the melt corresponding to $(\text{Al}_2\text{O}_3)_n$ [1], $\alpha\text{-Al}_2\text{O}_3$ nanoparticle and $\alpha\text{-Al}_2\text{O}_3$ crystal are, respectively, plotted in Fig. 6. Meanwhile, the equilibrium curve of $c_{\text{O,cr}}$ (when

$\log R_s^* = 3.5$) [2] corresponding to critical nucleus and the experimental data of the measured excess oxygen [12, 14, 15, 42, 43] in deoxidized melt are also plotted in Fig. 6, respectively. There are four stable regions meaning four continuous evolution stages of $\alpha\text{-Al}_2\text{O}_3$ nucleation and growth process from the top to the bottom in Fig. 6: nucleation region, clusters and aggregation region, growth region, crystal region. The schematic illustration of alumina product formation pathways based on CNT and TSN mechanisms is shown, respectively, in Fig. 7.

Nucleation region is the region above $c_{\text{O,cr}}$ curve in Fig. 6. In this region, the critical nucleus of $\alpha\text{-Al}_2\text{O}_3$ can form because the supersaturation ratio of $\underline{\text{Al}}$ and $\underline{\text{O}}$ ($R_{s,1}$ in Fig. 7) is higher than the supersaturation ratio for critical nucleation ($R_{s,cr}^*$ in Fig. 7). According to TSN mechanisms, during the nucleation processes, $\underline{\text{Al}}$ reacts with $\underline{\text{O}}$ to form stable alumina clusters firstly; then, the clusters come together to form aggregation changing further into the critical nucleus.

Clusters and its aggregation region are the regions between $(\text{Al}_2\text{O}_3)_8$ and $(\text{Al}_2\text{O}_3)_2$ curves in Fig. 6. The supersaturation ratio ($R_{s,2}$ and $R_{s,3}$ in Fig. 7) is higher than the supersaturation ratio of most stable cluster formation ($R_{s,cl}^*$ of $(\text{Al}_2\text{O}_3)_8$ in Fig. 7) but lower than that of critical nucleation ($R_{s,cr}^*$). Stable alumina clusters can form by $\underline{\text{Al}}$ reacting with $\underline{\text{O}}$ in the melt. The clusters show two kinds of behaviors depending on the supersaturation ratio: One is that clusters could come together to form aggregation, but the aggregation cannot change into critical nucleus ($R_{s,2}$ curve); the other is that clusters cannot aggregate because of a lower supersaturation ratio ($R_{s,3}$ curve). This indicates that the new $\alpha\text{-Al}_2\text{O}_3$ primary inclusions cannot form in the region, but secondary inclusions with polycrystalline structures involving α -, γ - and $\delta\text{-Al}_2\text{O}_3$ can form because of the

Fig. 6 Relationship between $\log c_O$ versus $\log c_{Al}$ at 1,873 K corresponding to various deoxidation products in Fe–O–Al melt

Fig. 7 Schematic illustration of nucleation and crystallization of deoxidation product from Fe–O–Al melt

clusters or its aggregations crystallizing in the cooling and solidification process. Meanwhile, the formed nucleus or nanoparticles of α - Al_2O_3 can keep on growing up, and new alumina clusters can form in the region.

Growth region is the region between $c_{O,cr}$ and $c_{O,\alpha-Al_2O_3}$ curves in Fig. 6. The supersaturation ratio ($R_{s,2}$, $R_{s,3}$ and $R_{s,4}$ in Fig. 7) is higher than the supersaturation ratio of α - Al_2O_3 crystal inclusion equilibrium, but lower than that for critical nucleation ($R_{s,cr}^*$). The formed critical nucleus in nucleation region can keep on growing up by in-suit diffusion and Ostwald ripening in this region. Meanwhile, alumina clusters, aggregation and crystal-like could form according to various supersaturation ratio ranges in the region. Thus, there are four coexisting metastable phases including alumina clusters, aggregations, nanoparticle in growth and crystal-like in the region.

The crystal region is the region below $c_{O,\alpha-Al_2O_3}$ curve in Fig. 6. The α - Al_2O_3 crystal is the only product in the region. The growth behavior of α - Al_2O_3 inclusion including collision and aggregation growth can usually be described by Stokes model according to buoyancy force effect in liquid iron.

From above, it can be concluded that the excess oxygen could react with Al to form alumina clusters; meanwhile, the excess oxygen could provide the requirement of α - Al_2O_3 nucleus growing up. Alumina clusters could change further into secondary inclusions, while new alumina clusters could form by the excess oxygen reacting with Al with the temperature decreasing in the cooling process. The morphology and size distribution of secondary inclusions depend on the state of clusters and the crystallization degree of the clusters in cooling process.

4.5 The Gibbs Free Energy Change of Multi-step Pathway

The critical nucleus is a kind of metastable intermediate in deoxidation process. According to CNT, Gibbs free energy change for deoxidation product nucleation in the melt can be expressed as follows,

$$\Delta G_{cr} = \Delta_r G_m^\theta(\text{cryst}) + \Delta G_{s,m}, \quad (22)$$

where ΔG_{cr} is Gibbs free energy change of nucleation, $\Delta G_{s,m}$ is Gibbs free energy change caused by interfacial tension between new nucleus and the melt.

The maximum value of $\log R_{s,cr}^*$ for forming critical nucleus of α - Al_2O_3 in Fe–O–Al melt measured using electrochemical method is 3.5 [3]. According to $\log R_{s,cr}^* = 3.5$ and $T = 1,873$ K, ΔG_{cr} is -354.169 kJ·mol $^{-1}$. The Gibbs free energy change of forming various intermediates including $(Al_2O_3)_n$, critical nucleus and α - Al_2O_3 nanoparticles at 1,873 K by Al reacting with O in the melt is plotted in Fig. 8. From Fig. 8, it can be concluded that

$$\Delta G_{5nm} > \Delta G_{cr} > \Delta G_{10nm} \text{ and}$$

$$\begin{aligned} \Delta G_{(Al_2O_3)_1} &> \Delta G_{2nm} > \Delta G_{(Al_2O_3)_2} > \Delta G_{(Al_2O_3)_{15}} \\ &> \Delta G_{(Al_2O_3)_{30}} > \Delta G_{5nm} > \Delta G_{(Al_2O_3)_3} > \Delta G_{cr} \\ &> \Delta G_{(Al_2O_3)_n} > \Delta G_{(Al_2O_3)_8} > \Delta G_{10nm} > \dots > \Delta G_{100nm} \\ &> \Delta G_{\alpha-Al_2O_3 \text{ crystal}} \quad (n = 4, 5, 6, 7, 9, 10). \end{aligned}$$

According to the multi-step thermodynamic model of alumina inclusion formation and the Ostwald's step rule, it could be concluded that the size range of α - Al_2O_3 critical nucleus could be 5–10 nm.

The main shortage of CNT comparing to TSN mechanisms for alumina inclusion formation has two aspects. First, CNT cannot consider in nature the intermediate in the process of nucleation and the pathway of nucleation. Second, CNT is based on classical thermodynamics ignoring the effect of thermodynamic properties depending on size of alumina particle at the nanoscale. Therefore, CNT could cause the degree of deviation in dealing with the initial process of deoxidation.

Fig. 8 Gibbs free energy change of various deoxidation product formation by the reaction between Al and O at 1,873 K in Fe–O–Al melt

5 Conclusions

Thermodynamic properties of α - Al_2O_3 nanoparticle as the metastable intermediates of α - Al_2O_3 nuclei growth stage at the nanoscale in Fe–O–Al melt were calculated by DFT. According to the thermodynamic properties, Gibbs free energy change of forming various nanosize α - Al_2O_3 by deoxidation reaction between Al and O in the melt was calculated. Based on TSN mechanisms associated with the intermediate thermodynamics, a multi-step thermodynamic model for alumina inclusion formation in aluminum deoxidation process was established. It was demonstrated that four coexisting regions corresponding to four evolution stages during α - Al_2O_3 inclusion formation process: nucleation region, clusters and aggregation region, α - Al_2O_3 growth region, α - Al_2O_3 crystal region. The change of stable regions depends on the change of R_s in deoxidation process in the melt. Under a higher supersaturation, $(\text{Al}_2\text{O}_3)_n$ formed by Al reacting with O can come together to further form α - Al_2O_3 critical nucleus. The critical nucleus could spontaneously and instantaneously grow up to 20 nm because of the thermodynamic drive at the nanoscale. The control of α - Al_2O_3 inclusion size within 20 nm could be difficult in aluminum deoxidation process under the current conditions of steelmaking. On the other hand, the excess oxygen present as the equilibrium oxygen with alumina clusters intermediate in Fe–O–Al melt could crystallize into secondary alumina inclusions with polycrystalline structure and size from nanometer to micron in cooling and solidification process.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (No. 51004054) and Foundation from the Liaoning Province Education Department (No. L2013127).

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