Nucleation and Ostwald Growth of Particles in Fe-O-Al-Ca Melt

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Tremendous focus has been put on the control of particle size distribution which effects the grain structure and mechanical properties of resulting metallic materials, and thus nucleation and growth of particles in solution should be clarified. This study uses classical nucleation theory and Ostwald ripening theory to probe the relationship between the compositions of Fe-O-Al-Ca melts and the behavior of particles under the condition of no external stirring. Our experimental data suggest that decreasing the initial Ca addition and Al addition is conductive to the increase of nucleation rate for calcium aluminate particles, which exhibits a same change trend with that predicted from classical nucleation theory. Based on the experimental evidence for particles size distribution in three-dimensional, we demonstrate that Ostwald ripening is the predominate mechanism on the coarsening of particles in Fe-O-Al-Ca melt at early stage of deoxidation under the condition of no external stirring but not at later stage.

Controlling on the characteristics of particles in the metallic materials has been one of the leading subjects in the field of metallurgy which directly effects the progress of melting¹, mechanical properties and service life of final products². In spite of efforts dedicated to the utmost removal of the particles, they still exist in metallic materials³. In recent years, focus is shifting from the removal of particles to effective utilization of fine particles, aiming at refining the microstructure, and improving the strength and fracture toughness⁴–⁸. Particle-assisted microstructure control has been frequently used in the metallic materials⁹–¹¹. Ma et al.¹² reported a novel Al matrix composite with ultrahigh strength reinforced by a three dimensional network of nano-AlN particles. Hossein¹³ found that the ferrite was grain-refined to about 3 μm due to vitue of augmented nucleation and retarded growth by titanium oxide nanoparticles. Fine MgO-containing particles were found to have a facilitating effect on the formation of equi-axed crystallization and refinement of microstructure¹⁴. Yiquan Wu¹⁵ found that as Ca content increased from 2 ppm to 25 ppm in thick plates, particles in submicron scale were 6 times as much as that in conventional steel, which promoted the nucleation of acicular ferrite obviously. Integrated performance of HAZ for steel plates was improved significantly by retarding γ grain growth in the HAZ near a weld fusion line with fine dispersed oxides and/or sulfides containing Ca or Mg¹⁶,¹⁷. It should be noted that the transformation, augmented nucleation and retarded growth of grain by pinning are strongly influenced by the size distribution of fine particles. Many scholars advocate that it is particularly important to obtain the fine particles in sub-micrometer or nanometer scale whose number density is considerably large and volume fraction is small¹⁸–²⁰. From this point of view, it is critical to investigate the nucleation and growth behavior of particles in the metallic materials.

In spite of extensive studies on the nucleation of inorganic particles in many fields²¹–²⁶, it remains a matter of debates. Jian Zhang et al.²⁷ gave a numerical analysis of alumina particles by combining thermodynamics, classical homogeneous nucleation theories and dynamics of particles collision and coagulation, and reported that the nucleation process in a Fe-Al-O melt system covers only several tens of microseconds. The nucleus of alumina particles were predicted to be about 10–20 Å in diameter and their nucleation time should be in the range of 1–10 μs based on thermodynamic analysis and numerical simulation by Lifeng Zhang et al.²⁸. However, Lindberg et al.²⁹ found that the time for attending the 90% of the equilibrium of particle volume was 0.2 s based on the diffusion model in Si deoxidation. The growth mechanism of deoxidation products can be explained by the following four major processes:³⁰ diffusion growth; coagulation due to the difference in ascending velocity; the coagulation due to Brown motion and the coarsening by Ostwald ripening. It is reported that the growth of particles in molten steel by diffusion occurs very rapidly and far less than 60 s at 1600 °C³⁰. Kluken³¹ and Suzuki et al.³² concluded that the growth of particles in steel should be explained by Ostwald ripening. In addition, Ohta and Suito³³ have investigated the size distribution of CaO–Al₂O₃ particles in Fe-10mass%Ni alloy and found that

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compared with Al₂O₃, the distribution curve of CaO-Al₂O₃ was narrower and nucleation rate was higher, indicating that CaO-Al₂O₃ particles were fine and in large amount in Fe-10mass%Ni alloy. They also advocated that the supersaturation degree, and interfacial energy between oxide particles and liquid Fe, and the equilibrium deoxidation constant affect the nucleation and growth of particles in early stage of deoxidation under no coagulation of deoxidation particles by collision. However, they just compared the size distribution of deoxidation products of MgO, ZrO₂, Al₂O₃, CaO-Al₂O₃ and MnO-SiO₂ in an Fe-10mass%Ni alloy. In spite of many experiments performed to investigate the formation mechanism and composition control of particles in steel by thermodynamic and kinetic theories³⁴–³⁶, limited studies about the effect of melt composition on the nucleation and growth of particles are conducted.

In current study, the relationships between compositions of Fe-O-Al-Ca melts with not only the particle type, but also the particle size distribution were analyzed. The nucleation and growth by Ostwald ripening of particles in Fe-O-Al-Ca melt were estimated and verified by experimental data. This study will provide information to predict the nucleation and growth of particles in the melt and will be helpful for controlling behavior of particle.

Results and Discussion

Experimental results. The average compositions and morphologies of particles in Fe-O-Al-Ca melt during the deoxidation process are shown in Fig. 1. [% Ca_i] = 0.25, 0.4, 0.78 (i represents initial addition of metal) were added in the melts with [% Al_i] = 0.05, 0.25 in order to study the effect of deoxidants amount on the behavior of calcium aluminate particles in the melt. The yield rates of Al and Ca in this experiment are about 90% and 1.6%, respectively. The chemical compositions of samples are analyzed and presented in Tables 1–2. The energy dispersive spectroscopy results reveal that the major particles in the Fe-O-Al-Ca melt are Al₂O₃-CaO. The content of CaS is no more than 5%, thus, it is ignored. Figure 1a presents the SEM images of typical particles and their average composition evolution during whole deoxidation process at 1600°C. (b) Average compositions of particles in steels after deoxidation at 1600°C for 3900 s.

Table 1. Experimental condition and main chemical compositions of samples in deoxidation experiments.
The composition of the particles in the melts with various contents of deoxidants at 3900 s is illustrated in Figure 1b. It can be seen that the average CaO content of particles increases with increasing amount of Ca addition. Most of particles are composed of CaO·6Al2O3 and CaO·2Al2O3 after melting for 3900 s, except for the melts with initial Ca addition of 0.78% which exhibits predominantly CaO·2Al2O3 + CaO·Al2O3 particles.

Figure 2 depicts the particle size distribution in three-dimensional for the experimental samples at 3900 s based on the stereological analysis. It can be seen that the peak of the curves in Figure 2 tends to decrease with the increasing amount of initial Ca addition, indicating that the number density of particles decreases with increasing Ca at 3900 s. Besides, the size of particles corresponding to the peaks of curves in the samples containing higher Ca content is smaller than that in the melts containing lower Ca content. It is concluded that the number density and size of particles tend to decrease with an increase of initial Ca addition after deoxidation for 3900 s. The particle size distribution for different samples after deoxidation at 1600 °C for 360 s, 600 s and 1800 s are plotted in Figure 3. The particles with size less than 260 nm can’t be detected due to the limitation of resolution of SEM. Therefore, the curves of particle size distribution in Figure 3b,c are incomplete. However, it still can be seen that the primary particles are smaller and in significantly larger amount in the melt with high initial Ca addition ([Ca%]i = 0.78%), compared with those in the melt with low initial Ca addition ([Ca%]i = 0.25%). The number of particles decreases significantly and large particles form with the proceeding of deoxidation, attributing to the flotation, aggregation and growth of particles.

Calculation results. Nucleation of Calcium Aluminates. In order to study the contents of Al, Ca and O on the nucleation rates of calcium aluminates, \( I_{CaO} \) (cm\(^{-3}\) s\(^{-1}\)), it was estimated as the following relationship based on the classical nucleation theory:

\[
\ln I_{CaO} = \frac{16\pi \gamma_{CaO}^{3}}{3k_{B}R^{2}T^{3}} \left( \frac{1}{\ln S_{Ca}^{2}} - \frac{1}{\ln S_{CaO}^{2}} \right)
\]

(1)

| Exp. No | C   | Si   | Mn   | P    | S    | Cu   | Ni   |
|---------|-----|------|------|------|------|------|------|
| A1C1    | 0.0015 | 0.0026 | 0.01 | 0.004 | 0.0019 | 0.0038 | 0.0035 |
| A1C2    | 0.0014 | 0.0029 | 0.01 | 0.005 | 0.0016 | 0.0036 | 0.0035 |
| A1C3    | 0.0016 | 0.0028 | 0.01 | 0.004 | 0.0014 | 0.0037 | 0.0038 |
| A2C1    | 0.0016 | 0.0029 | 0.01 | 0.007 | 0.0017 | 0.0035 | 0.0037 |
| A2C2    | 0.0015 | 0.0025 | 0.01 | 0.005 | 0.0014 | 0.0036 | 0.0039 |
| A2C3    | 0.0017 | 0.0028 | 0.01 | 0.006 | 0.0013 | 0.0036 | 0.0034 |

Table 2. Other chemical compositions of final samples.
where $V_{O(CaAl)}$ is the molar volume of oxide (m$^3$/mol), $k_B$ is the Boltzman constant (1.38 × 10$^{-23}$ J·K$^{-1}$), $R$ is the gas constant (8.314 J·mol$^{-1}$·K$^{-1}$) and $T$ is the absolute temperature (K). $\gamma_{CxAy-Melt}$ is interfacial energy between calcium aluminates and metallic melt (J/m$^2$).

According to the research of Li$^{40}$ and Suito$^{32}$, supersaturation degree of calcium aluminate $S_{CxAy}$ can be expressed by Eq. (2). $K_{CaO}$ is calculated from the relation: $\log K_{CaO} = -9.0841$ (1600 °C). In this calculation, the effect of melt compositions on the activity coefficient of Ca and O is not considered.

$$S_{CxAy} = \frac{a_{Ca} \cdot a_{O}}{a_{CaO}} \cdot K_{CaO}$$

$S_{CxAy}^*$ is the critical supersaturation degree which is the value of $S_{CxAy}$ at $I = 1$ (cm$^{-3}$·s$^{-1}$) and it is derived from Eq. (3). $A$ is the frequency factor ($10^{26}$ cm$^{-3}$·s$^{-132}$). $a$ and $b$ are used to modify the calculated values by matching that with the experimental critical supersaturation degree$^{32}$ ($a = 0.026, b = 1.25$). The values of $S_{CxAy}^*$ obtained by Eq. (3) are shown in Table 1.

$$S_{CxAy}^* = \exp \left( \frac{V_{O(CaAl)}}{RT} \cdot \frac{16\pi \gamma_{PL}^3}{3k_B T \ln A} \right) \times a + b$$

The interfacial energy between solid particles and metallic melt can be expressed by Young’s equation:

$$\gamma_{CxAy-Melt} = \gamma_{CxAy} - \gamma_{Melt} \cos \theta$$

The interfacial energy between liquid particle and metallic melt can be calculated by Neumann’s relation$^{42}$:

$$\gamma_{CxAy-Melt} = \gamma_{CxAy} \gamma_{Melt} \cos \varphi$$

where $\gamma_{CxAy}$ and $\gamma_{Melt}$ are the surface energies of calcium aluminate and metallic melt (J/m$^2$), $\theta$ is the contact angle between solid particle and melt, $\varphi$ is the visible contact angle of liquid particle. The relation between $\varphi$ and $\theta$ (the contact angle between liquid particle and melt) can be expressed by Eq. 6$^{42}$ if vertical equilibrium is considered.

$$\gamma_{CxAy-Melt} \sin (\theta^* - \varphi) = \gamma_{CxAy} \sin \varphi$$
The surface energy of metallic melt (J/m²) used in this study was calculated at 1600 °C as following:

$$\gamma_{\text{Melt}} = 1.75 - 0.279 \ln(1 + 140 \cdot a_i)$$  \hspace{1cm} (7)

The relevant parameters used in the calculation of nucleation rates for calcium aluminates are shown in Table 3. The activities of Al₂O₃ and CaO in particles were estimated by Factage Software 7.0 of "Equilib" module. The calcium aluminates with mole ratio of Al₂O₃/CaO at the range from 1 to 3 are almost in liquid state at 1600 °C and their visible contact angle is calculated by Eq. 6. In this study, CA type particle is treated as liquid because it often is partially or totally molten state in the experiments of measuring wettability and it is observed to be spherical or semi-spherical in the samples. The surface energies of solid calcium aluminates are estimated by the relation:

$$\gamma_{CxAy} = x \cdot \gamma_{\text{CaO}} + y \cdot \gamma_{\text{Al}_2\text{O}_3}$$  \hspace{1cm} (8)

where x and y are the molar fractions of CaO and Al₂O₃ in calcium aluminates. \(\gamma_{\text{CaO}}\) and \(\gamma_{\text{Al}_2\text{O}_3}\) are the surface energies of solid CaO (0.74 J/m²) and solid Al₂O₃ (0.94 J/m²) at 1600 °C.

Combining Eqs (1–8) at 1600 °C, the effect of melt compositions \(a_o\) and \(a_{Al}\) on the nucleation rate of each type of calcium aluminate, including CaO-6Al₂O₃, CaO-2Al₂O₃, CaO-Al₂O₃, and 12CaO-7Al₂O₃ is shown in Fig. 4a–d, respectively. The nucleation rate of CaO-2Al₂O₃ for given activities of Ca and O is larger than that of CaO-6Al₂O₃, and the nucleation rates of various types of calcium aluminates in the region with high supersaturation degree \(a_o > 0.03\) and \(a_{Al} > 10^{-6}\) increase in the order of CaO-2Al₂O₃ < CaO-6Al₂O₃ < CaO-Al₂O₃ < 12CaO-7Al₂O₃.

Figure 4e,f is obtained by adding the nucleation rates of all types of calcium aluminates together which means that it is assumed that these calcium aluminates nucleate simultaneously. Assuming that [Al] is in equilibrium with [O] before calcium aluminates nucleate, the effect of \(a_o\) on the nucleation rates of calcium aluminates can be calculated based on the thermodynamic equilibrium relation: Al₂O₃ = 2[Al] + 3[O] \(\log K_{\text{Al}_2\text{O}_3} = -12.57\) \(41\)). \(a_{Al}\) is determined from the relationship: \(K_{\text{Al}_2\text{O}_3} = \frac{a_{Al}^3}{a_o^6}\). Figure 4a–d suggests that the nucleation rate of each type of calcium aluminates increases with an increase of \(a_o\) and \(a_{Ca}\) and decrease of \(a_{Al}\). Figure 4e,f indicates that in the region where \(a_o\) is larger than 2 \(\times\) 10⁻³ or \(a_{Al}\) is smaller than 2 \(\times\) 10⁻³, the total nucleation rate is mainly dependent on the value of \(a_o\) or \(a_{Al}\) and it reaches the maximum (about 1800) when \(a_o\) is 6 \(\times\) 10⁻².

In order to verify the guiding significance of the nucleation theory on the metal smelting, the theoretical nucleation rates changed little as shown in Table 4 obtained by considering the effects of \(a_o\), \(a_{Ca}\), \(a_{Al}\) separately, which verifies that Eq. (2) is well applied in this study and the reaction between O and Al reaches equilibrium state nearly before adding Ca in this condition. The reason why the theoretical nucleation rate of calcium aluminates in the melt with lower amount of Ca addition is larger than that with higher amount of Ca addition is mainly attributed to the discrepancy of particle composition.

Where \(a_i = \frac{f_i(\text{mass \%})}{\text{mass \%}}\)

$$\log f_i = \sum e_i^{j}(\text{mass \%}) + r_i^{-k}(\text{mass \%})^{j}(\text{mass \%})^{k}$$  \hspace{1cm} (10)

where \(a_i\), \(f_i\), and \([\text{mass \%}]\) are the 1 mass% activity, 1 mass% activity coefficient, and the concentration of i in mass fraction, respectively. \(e_i^{j}\) is the first-order interaction coefficient and \(r_i^{-k}\) is the second-order interaction coefficient.

The mean values of experimental nucleation rates (\(\bar{I}\)) in Exp. A1C1, Exp. A1C3 and Exp. A2C3 were obtained with Eqs. (11 and 12):

$$\bar{I} = \frac{f_{v(Al)}}{5 \pi^3 C(C_{CA}) \cdot \tau}$$  \hspace{1cm} (11)

Table 3. Relevant parameters of calcium aluminates used in this study. \(\rho\) is density. \(V_o\) is molar volume of oxide. \(\gamma_{CxAy}\) is surface energy, \(\theta\) is the contact angle between solid particle and melt. \(\phi\) is the visible contact angle of liquid particle. \(\theta^*\) is the contact angle between liquid particle and melt. \(a\) is activity. \(C_o\) is oxygen or calcium concentration in oxide expressed by weight per unit volume. \(S_o^*\) is the critical supersaturation degree.

| Type  | \(\rho\), g/cm²⁻¹ | \(V_o\), m³/mol | \(\gamma_{CxAy}\), J/m² | \(\theta\), deg | \(\theta^*(\varphi),\ deg\) | \(a_{Al}\) | \(a_{Ca}\) | \(C_o\), kg/m³ | \(C_{P(Ca)}\), kg/m³ | \(S_o^*\) |
|-------|-------------------|-----------------|--------------------------|----------------|-------------------------|--------|--------|--------------|-----------------|--------|
| CA    | 3.79⁶⁶           | 9.3             | 0.9₅⁴⁵                   | 126            | 1                       | 0.005  | 125      | 227          | 1.9–5.3         |
| CA    | 2.92⁶⁶           | 12.7            | 0.8₇₄⁶¹                  | 120⁻⁶          | 0.88                    | 0.011  | 125      | 448          | 1.9–4.8         |
| CA    | 2.56⁶⁶           | 15.4            | 0.6₂²¹                   | —              | 7₄⁻⁶⁺(69)              | 0.264  | 0.113    | 1037         | 1.9–25          |
| C₇₃A₇ | 2.69⁶⁶           | 15.6            | 0.6₃⁴²                   | —              | 5₉⁽⁶⁾(40)              | 0.047  | 0.449    | 1025         | 1.3–1.4         |

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Figure 4. Calculated nucleation rates of calcium aluminates in Fe-O-Al-Ca melt at 1600 °C. (a–d) Relationship of $a_{Ca}$ and $a_{O}$ when CaO·6Al$_2$O$_3$, CaO·2Al$_2$O$_3$, CaO·Al$_2$O$_3$ and 12CaO·7Al$_2$O$_3$ nucleate at various rates, respectively. (e) Relationship of $a_{Ca}$ and $a_{O}$ when all kinds of calcium aluminates nucleate at various rates simultaneously. (f) Relationship of $a_{Ca}$ and $a_{Al}$ when all kinds of calcium aluminates nucleate at various rates simultaneously. The nucleation rate in (e) and (f) represents the total nucleation rate of all types of calcium aluminates.

Table 4. Experimental and calculated nucleation results. $a_{O}$, $a_{Al}$, $a_{Ca}$ is activity of O, Al and Ca. CA$_x$ is the weight percentage of various calcium aluminate particles in samples. ln I-$a_{O}$ is theoretical nucleation rate of particles based on the relationship of $a_{O}$ and $a_{Ca}$. ln I-$a_{Al}$ is theoretical nucleation rate of particles based on the relationship of $a_{Al}$ and $a_{O}$. ln I is mean values of experimental nucleation rates for particles in samples. $f_{V(n)}$ is volume fraction of particles in samples. $r_{(CxAy)}$ is critical size of nuclei for particles.
Table 5. First-order and second-order interaction coefficients $\varepsilon_i^{(j,k)}$ and $r_e^{(j,k)}$ of various elements in liquid steel at 1600 °C.

| $i/j$ | $C$ | Si | Mn | P | S | O | Al | Ca, Ca | O, Al | Al, Al | Ca, O | O, O |
|-------|-----|----|----|---|---|---|---|--------|-------|-------|-------|-------|
| O     | −0.421 | −0.066 | −0.021 | 0.07 | −0.133 | −0.174 | −1.17 | −313 | 570000 | 302 | −0.01 | −18000 | — |
| Al    | 0.091 | 0.056 | −0.004 | 0.033 | 0.035 | −1.98 | 0.043 | −0.047 | — | −0.0284 | — | — | 39.8 |
| Ca    | −0.34 | −0.095 | −0.007 | −0.097 | −28 | −780 | −0.072 | −0.002 | — | — | — | −90000 | 650000 |

$f_{V(n)}$ is the equilibrated volume fraction of nucleus and it can be estimated by the following relationship:

$$f_{V(n)} = f_{V(cao)} - f_{V(al)}$$

$f_{V(cao)}$ is the volume fraction of all particles in the melt after Ca adding, that is, the volume fraction of particles at 360 s. $f_{V(al)}$ is the volume fraction of Al$_2$O$_3$ just before Ca adding. The time for equilibrium of nucleus volume is 0.2 s\(^{18}\) and the critical size of nuclei $r_{C(C_{A,O})}$ is the given by

$$r_{C(C_{A,O})} = \frac{2\gamma(C_{A,O}) \cdot V_0(C_{A,O})}{RT \cdot \ln S_{C_{A,O}}}$$

(12)

The calculated results suggest that the critical size of nuclei for calcium aluminates is about 0.2–0.3 nm. The experimental nucleation rates of calcium aluminates decrease in the order of experiments A1C1 < A1C3 < A2C3, exhibiting a same change trend with theoretical values, which indicates that decreasing the initial Ca addition and Al addition is conductive to the increase of nucleation rate for calcium aluminate. The average nucleation rate of calcium aluminates is smaller than that predicted from classical nucleation theory, presumably attributed to the underestimation of $t$ and overestimation of local composition of melt.

Growth of Calcium Aluminates by Ostwald Ripening. Ostwald growth of calcium aluminates in Fe-O-Al-Ca melt controlled by oxygen diffusion can be expressed as following\(^{18}\):

$$\bar{r}_n^3 - \bar{r}_o^3 = \alpha \cdot k_{d(O)} \cdot t$$

(13)

$$k_{d(O)} = \frac{2\gamma(C_{A,O}) \cdot D_O \cdot V_0(C_{A,O}) \cdot C_O}{RT(C_{P(C_{A,O})} - C_O)}$$

(14)

where $\bar{r}_n$ and $\bar{r}_o$ are the mean radius of particles at time $t$ (m) and that at the start of Ostwald growth (m), respectively. $k_d$ is coarsening rate ($\mu$m$^3$s$^{-1}$). $D_O$ is the diffusion constant of oxygen (2.91 × 10$^{-9}$ m$^2$s$^{-1}$). $C_O$ is the dissolved oxygen concentration expressed by weight per unit volume (kg·m$^{-3}$) and $C_{P(C_{A,O})}$ is the oxygen concentration in oxide expressed by weight per unit volume (kg·m$^{-3}$). $\alpha$ is the coarsening rate coefficient. In previous study\(^{18}\), it is found that calculated coarsening rate is more accurate by using $\alpha_{LSW}$ from LSW theory instead of $\alpha_{CN}$ from communicating neighbour (CN model). Therefore, $\alpha$ values as 4/9 in this study.

The coarsening rate $k_d$ of each type calcium aluminate was calculated by substituting the relevant data listed in Table 3 into Eq. (14) and are plotted with oxygen content as shown in Fig. 5. As can be seen, the coarsening rate increases with increasing dissolved oxygen content. Besides, for a given dissolved oxygen (less than 300 ppm), an increase of $C/A$ ratio in calcium aluminates increases their values of $k_d$ (except for CA) which increases in the order of $CA_6^-$ < $CA_2^-$ < $CAl_5$ < $CA_O$ < $CA_2$.

The effect of Ca addition on the Ostwald growth of particles in Fe-O-Al-Ca melt with [Al], of 0.04% and 0.2% was obtained by considering the oxygen diffusion and calcium diffusion as shown in Fig. 6. The coarsening rate $k_{d(Ca)}$ can be expressed by Eq. (15) in which the notations are similar to Eq. (14). $D_{Ca}$ is assumed to be equal to the $D_O$ because the solute diffusivities in liquid Fe is considered to be the same order of magnitude\(^{18}\).

$$k_{d(Ca)} = \frac{2\gamma(C_{A,Ca}) \cdot D_{Ca} \cdot V_{Ca(C_{A,Ca})} \cdot C_{Ca}}{RT(C_{P(C_{A,Ca})} - C_{Ca})}$$

(15)

Ca diffusion will be the rate determining step when $k_{d(Ca)}$ is smaller than $k_{d(O)}$ and vice versa. Figure 6 is obtained based on Eqs (14) and (15), in combination with FactSage modeling. Equilibrium compositions of melt with Ca addition are estimated by FACTSAGE 7.0 with the FactPS and FToxid and FTmisc databases. (based on the compositions of raw materials). “Equilib” module is used, and pure solids, and Fe-liq and Al liquid slag in solution phases are selected as products. Calculated temperature and pressure are set as 1600 and 1 atm, respectively. Al diffusion will not be the rate determining step due to its high concentration in this work. It is found that with the increasing amount of added Ca (0–0.015%), the content of soluble Ca at equilibrium increases at the range from 0 to 0.6 ppm, and the coarsening rate of particles derived from Ostwald ripening decreases firstly and then increases as the liquid calcium aluminates form and increase. The Ostwald growth of Al$_2$O$_3$ is determined by O diffusion, while Ca diffusion is the rate determining step for the coarsening of calcium aluminates at equilibrium which is marked by blue line in Fig. 6. The value of $k_d$ decreased slightly with an increase of Ca addition in the “CA6 + CA2” region ([% Ca]$_i$ = 0.0027–0.0068) due to the increasing proportion of CA2. Besides, it indicates that the optimum amount of Ca addition for inhibiting the Ostwald growth of calcium aluminate particles is 0.0027–0.0068%. In addition, when the amount of initial calcium addition is larger than 0.0027%, the coarsening...
The observed coarsening rates are obtained by substituting the experimental data into Eq. (13) and are plotted with the calculated values (obtained by substituting the relevant data in Table 3 and the composition of samples in Tables 1–2 to Eqs (14 and 15)) as shown in Fig. 7. It is found that $k_{d\text{(cal.)}}$ tends to increase with increasing $k_{d\text{(obs.)}}$ during the first 600 s of deoxidation process. The data at 360 s and 600 s in Fig. 7 fall around the line $k_{d\text{(cal.)}} = k_{d\text{(obs.)}}$, although there is some deviation in those data probably caused by error of measurement for particle size (nano scale particles are excluded by Image-Proplus during the analysis of particle characteristics). In addition, it should be noted that the triangular points in Fig. 7 at later stage of melting are out of line completely. It can thus be concluded that the Ostwald ripening is the predominate mechanism of coarsening for calcium aluminate particles in Fe-O-Al-Ca melt during the first 600 s after aluminum addition under the condition of no external stirring but not at later stage of Al-Ca deoxidation. The mechanism on coarsening of calcium aluminate particles in Fe-O-Al-Ca melt at later stage of deoxidation is still going on.

Figure 5. Relationship of coarsening rate caused by Ostwald ripening $k_d$ for calcium aluminates and dissolved oxygen content [% O] in Fe-O-Al-Ca melt, calculated at 1600 °C.

Figure 6. Effect of Ca addition on coarsening rate caused by Ostwald ripening $k_d$ of particles and soluble Ca content in Fe-O-Al-Ca melt with various Al contents at equilibrium when $\text{Al}_2\text{O}_3$, $\text{CA}_6$, $\text{CA}_2$ and liquid calcium aluminate form as stable compounds, calculated at 1600 °C and based on FACTSAGE calculation.

Conclusion
The behavior of particles in Fe-O-Al-Ca melt under the condition of no external stirring at 1600 °C was systematically studied using experimental methods, stereological method, classical nucleation theory, as well as Ostwald ripening theory.

The nucleation rate of calcium aluminates is dependent on their type and the composition of melt. It increases with an increase of $a_{\text{O}}$ and $a_{\text{Ca}}$, and decrease of $a_{\text{Al}}$. Our experimental data suggest that decreasing the initial Ca addition and Al addition is conductive to the increase of nucleation rate for calcium aluminate, which exhibits a same change trend with that predicted from classical nucleation theory. Based on Ostwald ripening theory, for a given dissolved oxygen (less than 300 ppm), coarsening rate of particles in Fe-O-Al-Ca melt increases in the order of $\text{CA}_6 < \text{CA}_2 < \text{C}_2\text{A}_7 < \text{CA}$. The optimum amount of Ca addition for inhibiting the coarsening of calcium aluminates in Fe-O-Al-Ca melt is 0.0027–0.0068%. It is experimentally confirmed that the Ostwald ripening is the predominate mechanism of coarsening for calcium aluminate particles in Fe-O-Al-Ca melt during the first 600 s after aluminum addition under the condition of no external stirring but not at later stage of Al-Ca deoxidation. The mechanism on coarsening of calcium aluminate particles in Fe-O-Al-Ca melt at later stage of deoxidation is still going on.
Methods

**High temperature experiments.** High-purity iron was used as raw materials in the experiment and its chemical composition (wt.%) is 99.95% Fe, 0.0016% C, 0.0033% Si, 0.01% Mn, 0.0053% P, 0.0017% S, 0.003% Al, 0.0037% Cu, 0.0038% Ni. Al powder packed in iron foil (Al >99%) was first added in the molten steel at 1600 °C and after 5 min, Si-Ca alloy (59% Si, 30% Ca) was added for deoxidation, immediately stirred by a molybdenum rod for 5 s. All the experiments were carried out in Si-Mo heating electric resistance furnace without external stirring after adding Si-Ca alloy. Samples were taken by quartz tubes (Φ 6 mm) for certain holding time which were injected with Ar gas firstly to prevent molten steel from being oxidized by air, followed by rapid quenching in salt water. During the whole melting process, the argon gas was controlled at the flow rate of 5 L/min.

**Characterization of particles.** The compositions and morphologies of particles were observed using scanning electron microscopy with energy-dispersive spectrometric detection (SEM-EDS). The weight percentages of Al$_2$O$_3$ and CaO in particles were calculated based on the stoichiometric relationship and contents of Al, Ca, O which were measured by EDS. The stereological analysis (modified Schwartz-Saltykov method with the probability mass function$^{38,39}$) was adopted to obtain the particle size distribution in three-dimensional from that in two-dimensional. The details are described as below$^{54}$: the back-scattered electron pictures of each steel sample were taken under 1000 times corresponding to the area of $271 \mu m \times 271 \mu m$. 169 successive microphotographs were obtained by designating a step of $271 \mu m$. Besides, the planar size and number of inclusions were analyzed by Image-ProPlus software$^{55}$. The probability mass function (PMF) is expressed as following$^{37}$:

$$P(\gamma / R) = \frac{\gamma x}{R} \left( \frac{1}{R} \sqrt{R^2 - (\gamma - \Delta \gamma)^2} - \sqrt{R^2 - \gamma^2} \right)$$

(16)

where $P$ is the probability of a cross section with radius $\gamma (\gamma - \Delta \gamma < \gamma < r_i)$ intersecting a sphere with radius $R$ which is the actual radius of inclusions in three-dimensional, and $\Delta r$ is the interval of groups. In this study, inclusions were classified into 49 successive groups from the largest inclusions based on the measured mean radius of inclusions in two-dimensional. The diameter of largest inclusions detected in all samples is no more than 19.6 $\mu m$. Therefore, the radius of inclusions in group 1 denoted by $r = 9.8 \mu m$ or $d = 19.6 \mu m$ is in the range of 9.7–9.9 $\mu m$, group 2 is denoted by $r = 9.6 \mu m$ and group 49 is denoted by $r = 0.2 \mu m$. According to the study of Li Tao$^{38}$, the detected two-dimensional inclusions in group $j$ probably belong to the three-dimensional group $i$ ($i \leq j$) as expressed by Eq. (17).

$$N_y(j) = \sum_{i=1}^{j} d_i N_x(i) P(j, i)$$

(17)

where $N_x$ and $N_y$ are the number density of inclusions in two-dimensional and three-dimensional, respectively. The transformation from two-dimensional spherical inclusion size distribution to three-dimensional inclusion size distribution can be performed based on Eqs (18), and (19) is $P$ matrix. ($P^{-1}$ is inverse matrix of $P$ matrix)

$$\begin{pmatrix}
N_x(1) \\
N_x(2) \\
\vdots \\
N_x(n)
\end{pmatrix} = 
\begin{pmatrix}
d_1 N_y(1) \\
d_2 N_y(2) \\
\vdots \\
d_n N_y(n)
\end{pmatrix} = P^{-1}
\begin{pmatrix}
N_y(1) \\
N_y(2) \\
\vdots \\
N_y(n)
\end{pmatrix}$$

(18)
Detection of sample compositions. The compositions of samples were detected by the ICP-AES method (for the detection of Al and Ca, etc.), infrared absorption method after combustion in an induction furnace (for the analysis of sulfur) and Leco analyzer (for the measurement of total oxygen). The initial oxygen in all the experiments was 170 ± 20 ppm. The insoluble oxygen, alumina, and calcium contents were calculated based on Eqs (16–20).

\[
[O(M)]_{\text{tot}} = f_v \cdot \frac{\rho_{\text{M}_2\text{O}_3}}{\rho_{\text{Fe}}} \cdot \frac{y_{\text{M}_x\text{O}_y}}{M_{\text{M}_x\text{O}_y}} \times 10^6
\]

where \(f_v\) is the total volume fraction of oxide inclusions, \(\rho_{\text{Fe}}\) is the density of Fe and \(\rho_{\text{M}_2\text{O}_3}\) is the density of the oxide inclusions \((\rho_{\text{Fe}} = 7.8 \text{ g/cm}^3, \rho_{\text{M}_2\text{O}_3} = 3.97 \text{ g/cm}^3, \rho_{\text{CaO}} = 3.4 \text{ g/cm}^3)\), \(y_{\text{M}_x\text{O}_y} = X_{\text{M}_x\text{O}_y} + X_{\text{CaO}}\), \(M_{\text{M}_x\text{O}_y}\) and \(M_{\text{CaO}}\) are the molecular weight of \(\text{M}_x\text{O}_y\) and the molar fraction of \(\text{M}_2\text{O}_3\).

Data availability. The data that support the findings of this study are available from Linzhu Wang upon reasonable request.

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Author Contributions
Linzhu Wang and Junqi Li wrote the main manuscript text. Shufeng Yang supervised the investigation and revised the paper. All the authors contributed to discussions and analysis of the data.

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