Effect of Alumina Morphology on the Clustering of Alumina Inclusions in Molten Iron

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Clustering of alumina inclusions during liquid processing of steel significantly influences its cleanliness and mechanical properties. We have therefore studied the effect of alumina inclusion morphology on their clustering behavior in molten iron. Alumina inclusions were extracted from iron samples taken at 1 min after Al addition. Dendritic, spherical, plate-like, faceted and clustered alumina inclusions were identified and their clustering degrees were measured. The clustering degree increases in the order of spherical, dendritic, plate-like and faceted inclusions. To explain this, attractive force between two alumina particles with different shape combinations, *i.e.*, sphere-sphere (S-S), sphere-plane (S-P), plane-plane (P-P), was calculated based on the theory of spontaneous cavitation. The attractive force is influenced significantly by particle shape. S-S type has the smallest attractive force and the shortest acting length. P-P type has the largest attractive force and the longest acting length. This explains that spherical inclusions have the lowest clustering degree. The lower clustering degree of plate-like inclusions, compared with faceted inclusions, is due to that molten iron wets plate-like inclusions better.

KEY WORDS: alumina inclusions; interfacial properties; morphology; clustering degree; attractive force; cavitation.

1. Introduction

Clustering of non-metallic inclusions, especially of alumina inclusions, occurs in liquid steel during deoxidization. Due to clustering, fine inclusions grow rapidly, and thus float up more easily to the slag phase. However, large clusters may deteriorate the mechanical properties of steel when they remain in the solidified steel.^{1,2)} For this reason, maximum size of non-metallic inclusions is restricted in many steel grades.³⁾ Moreover, build-up of non-metallic inclusions on the submerged entry nozzles (SENs) may interrupt the continuous casting process, leading to decreased strand speed or premature replacement of SENs.⁴⁾ Clustering of inclusions in liquid steel and build-up of inclusions on the SENs both result from strong attractive forces between the inclusions. Due to SEN clogging, expensive countermeasures have to be taken, such as Ca-treatment.^{5,6)}

Clustering of non-metallic inclusions in liquid steel has been intensively studied, mainly focusing on influencing factors, such as inclusion type, temperature, holding time, stirring and initial oxygen content.^{7–12)} Clustering was found to occur easily among inclusions that are not wetted by liquid steel. This suggests that clustering is related to the interfacial properties of inclusions and liquid steel. When inclusions are not wetted by liquid steel, withdrawal of liquid steel film between two approaching inclusions is energetically advan-

tageous, facilitating the clustering process. When inclusions are wetted by liquid steel, liquid steel film stays between the inclusions and inhibits clustering. Clustering of inclusions both on liquid steel surface and at slag/steel interfaces has been extensively studied. With confocal scanning laser microscopy (CSLM), unwetted inclusions are observed to move to each other, followed by collision and agglomeration.^{13–19)} The attractive force is considered to arise from the capillary force, which is due to the deformation of the melt surface around the inclusions.^{16,20)} In the bulk of liquid steel, however, studies of clustering of inclusions are still limited from the viewpoint of interfacial properties. Yaminsky *et al.*^{21,22)} proposed that liquid may be spontaneously expelled from the region between two approaching particles unwetted by the liquid to form a gas cavity around the contact zone, resulting in a strong attractive force. Cournil *et al.*^{23,24)} reported that unwetted particles can form bigger clusters and that fragmentation of the clusters happens less significantly, compared with wetted particles. Nakamoto *et al.*²⁵⁾ compared neck growth of alumina balls at sintering in molten iron with that in Ar atmosphere and found that neck growth in molten iron proceeds much faster. After analyzing influencing factors, they concluded that the fast neck growth is not caused by the interfacial energy, but by the non-wetting property, which induces the formation of a gas cavity between the two alumina balls. Sasai *et al.*²⁶⁾ found that the clustering of alumina inclusions is promoted when molten FeO is present in liquid steel and concluded that molten FeO forms a liquid bridge between alumina inclusions and serves

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as a binder during the clustering. Such a conclusion was also obtained by Mizoguchi *et al.*²⁷⁾ after comparing iron content in alumina inclusions sampled from liquid steel after RH-degassing and from a cast slab. However, molten FeO is thermodynamically unstable in Al-killed steel. Therefore, this conclusion should be reconsidered carefully. Recently, Sasai²⁸⁾ directly measured the attractive force between two alumina cylinders ($D = 8$ mm, $H = 30$ mm) in molten iron with a novel method and confirmed that the strong attractive force derives from a gas cavity between the two cylinders not from the van der Waals force. Based on the above literature studies, it can be concluded that the cavitation theory has attracted more and more attention to interpret the clustering phenomena of non-metallic inclusions in liquid steel. To the best of our knowledge, however, studies of the clustering of non-metallic inclusions with this theory are still limited, especially focusing on the effects of wettability, surface tension of the melt, particle size and shape.

This paper is a follow-up study of the effect of interfacial properties of alumina inclusions and molten iron on the clustering of alumina inclusions. To modify the interfacial properties, Te, which is a strong surface active element in molten iron, was added to molten iron before Al deoxidization. In our previous paper,²⁹⁾ we found that the extent of clustering increases with Te addition from 0 to 250 ppm and thereafter decreases with further Te addition especially in the samples taken at 10 min after Al addition. To explain this, we proposed that the clustering of alumina inclusions has a close relationship with alumina morphology, which is modified considerably due to Te addition.

In the present work, we focus on the effect of alumina morphology on the clustering of alumina inclusions. Alumina inclusions were extracted from iron matrix and observed with a high resolution SEM. Clustering degrees of spherical, dendritic, plate-like and faceted inclusions were measured, respectively. The effect of alumina morphology on the clustering is quantitatively analyzed based on the theory of spontaneous cavitation between unwetted particles. Influencing factors on the clustering of alumina inclusions, such as wettability, surface tension of melt and particle size, are also discussed.

2. Experimental Methods

2.1. Procedure

A detailed description of the experiments is given in our previous paper.²⁹⁾ The experiments were carried out in a vertical tube furnace (heating element MoSi₂) under purified Ar atmosphere (flowrate 0.5 L/min, $P_{O_2} < 10^{-20}$ atm). 80 g of electrolytic iron (99.99%, Mairon SHP, Toho Zinc Co. Ltd.) together with reagent grade Fe₂O₃ powder used to adjust the initial oxygen content was filled in a magnesia crucible (27 mm ID and 50 mm H) and melted at 1 873 K. After homogenizing for 30 min, Te was added through a quartz tube (8 mm ID), followed by stirring for 30 s with an alumina rod. 3 min later, Al (99.99 %) was added in the same way, followed by stirring for 0 or 30 s. Then, the melt was held at 1 873 K. Iron samples were taken with a quartz tube (6 mm ID) at 1, 3, and 10 min after Al addition, and rapidly quenched in water. Detailed experimental conditions are listed in **Table 1**. The additions of 3.2, 20 and 80 mg Te

Table 1. Details of the experimental conditions.

Test No.	Fe ₂ O ₃	Te	Al	Stirring
	(g)	(mg)	(g)	(s)
L1	0	0	0.08	0
L2		80		
LS1		0		
LS2		80		
HS1	0.11	0	0.13	30
HS2		3.2		
HS3		20		
HS4		80		

to molten iron correspond to 40, 250 and 1 000 ppm Te in molten iron, respectively.

2.2. Observation of Inclusion Morphology

0.1 g of iron was dissolved in a HCl–HNO₃ acid solution (HCl/HNO₃/H₂O = 10/1/10) at 90°C. After complete dissolution (4 h), the solution was filtered on a polycarbonate membrane with 0.2 μ m pore size. The membrane was washed, dried and coated with Au–Pd. Alumina inclusions on the membrane were subjected to SEM (Philips XL 30 FEG) observation. Successive micrographs were taken at a magnification of 5 000. For each sample, more than 500 particles with a diameter larger than 0.8 μ m were measured for studying morphology distribution and clustering tendency of alumina inclusions.

3. Results and Discussion

3.1. Morphology Distribution of Alumina Inclusions

During SEM observation, dendritic, spherical, faceted, plate-like and clustered alumina inclusions were identified. The classification in the present work follows that of Braun *et al.*¹¹⁾ Dendritic inclusions develop with a typical multi-branching form; spherical inclusions are singular and in the shape of sphere; faceted inclusions have well-developed crystal faces and are three-dimensional; plate-like inclusions also have well-developed crystal faces but appear as two-dimensional, showing a platy {222} form; clusters consist of two or more individual particles of the above mentioned morphologies. **Figure 1** shows the representative morphologies of the inclusions observed in this work. The origin of different morphologies of alumina inclusions in liquid steel has been reviewed by Dekkers *et al.*³⁰⁾

The morphology of a crystal is determined intrinsically by its internal structure.³¹⁾ External factors, such as supersaturation degree, holding time, temperature, stirring, impurity and solvent, can cause large changes to the growth rates of individual faces and hence modify the morphology.³¹⁾ In the present work, an obvious effect of impurity Te on the morphology of alumina inclusions was observed. To evaluate the extent of morphological modification by Te, morphology distribution of alumina inclusions was measured after acid extraction. The morphology distribution represents the relative frequency of dendritic, spherical, plate-like and faceted inclusions. Particles in clusters were also included in the

Fig. 1. Alumina morphologies after acid extraction: spherical (S), dendritic (D), faceted (F), plate-like (PL) and clustered (C).

Table 2. Morphology distribution of alumina inclusions in samples taken at 1 min after Al addition.

Sample No.	Te (ppm)	Morphology distribution/%			
		Spherical	Dendritic	Faceted	Plate-like
L1	0	68.0	1.6	21.6	8.8
L2	1 000	33.9	3.6	32.1	30.5
LS1	0	23.7	4.2	55.4	16.7
LS2	1 000	4.0	6.2	43.2	46.6
HS1	0	3.1	19.7	66.0	11.2
HS2	40	3.7	4.7	78.2	13.5
HS3	200	4.8	4.1	75.9	15.2
HS4	1 000	8.3	3.0	68.1	20.6

Table 3. Clustering degree of different types of alumina inclusions.

Sample No.	Clustering degree/%				
	Spherical	Dendritic	Plate-like	Faceted	Overall
L1	9.9	28.6	55.3	71.0	27.4
L2	16.6	38.9	64.5	77.5	51.6
LS1	6.0	20.0	35.6	68.4	46.1
LS2	23.1	15.0	24.5	72.1	44.4
HS1	14.3	33.8	51.3	83.5	68.0
HS2	20.0	50.0	64.6	87.2	80.0
HS3	32.5	42.9	72.3	94.2	85.8
HS4	29.3	47.6	72.2	92.0	81.4

distribution. Since long holding time facilitates sintering and densification of clustered particles, leading to difficulties in determining the number and morphology of individual alumina particles in clusters, only samples taken at 1 min after Al addition were analyzed. The results were shown in **Table 2**.

It is clear that Te considerably modifies the morphology of alumina inclusions. Te tends to make the morphology of alumina inclusions evolve from dendritic or spherical, via faceted, to plate-like. The effectiveness of Te on the morphological modification closely relies on the experimental conditions. Stirring strengthens the effectiveness of Te, resulting in more plate-like inclusions. On the contrary, increasing the supersaturation degree expressed as $(a_{\text{Al}}^{2/3} \cdot a_{\text{O}}) / (a_{\text{Al}}^{2/3} \cdot a_{\text{O}})_{\text{eq}}$ weakens the effectiveness of Te, decreasing the amount of plate-like inclusions. Mechanism of Te action on the morphology of alumina inclusions will be studied in a following paper.

3.2. Clustering Degree of Different Morphologies of Alumina Inclusions

To study the extent of clustering of alumina inclusions, clustering degree C_D is defined as the ratio of the number of clustered particles to the total number of particles. The C_D values for the samples taken at 1 min after Al addition are listed in the rightmost column of **Table 3**. It was found that Te considerably enhances the clustering of alumina inclusions. This is consistent with 2D measurements in our

Fig. 2. Schematic illustration of determining the clustering degree of alumina inclusions.

previous paper.²⁹⁾ To clarify whether this enhancement is related to the morphological modification of the inclusions shown in **Table 2**, clustering degree of each type of alumina inclusions was measured. The measurement approach is schematically illustrated in **Fig. 2**. The results are presented both in **Fig. 3** and **Table 3**. For a high reliability of the results, more than 500 particles in each sample were carefully analyzed with respect to their morphologies.

Figure 3(a) shows the C_D results of samples L1 and L2. In both samples, the C_D values increase in the order of spherical, dendritic, plate-like and faceted inclusions. The same phenomenon was also observed in samples LS1, LS2 and HS1 to HS4, as shown in Figs. 3(b) and 3(c). **Figure 4** shows the average clustering degree of each type of alumina inclusions based on the results of samples HS1 to HS4. The

error bars represent the lowest and the highest clustering degrees in the samples. The average C_D values are 24.0%, 43.6%, 65.1% and 89.2% for spherical, dendritic, plate-like and faceted inclusions, respectively. These results show that faceted inclusions have the highest tendency of forming clusters while spherical inclusions have the lowest tendency, as seen clearly from the SEM images in Fig. 5. Similar results were also noticed by Braun *et al.*,¹¹⁾ who found that the extent of clustering of alumina inclusions in high oxygen ingots, where the inclusions are mostly spherical, is much less than in low oxygen ingots, where the inclusions are predominantly faceted. Compared with spherical inclusions, the higher clustering degree of dendritic inclusions is due to the larger size, resulting in larger effective collision volume.¹¹⁾ In practice, the relative amount of dendritic inclusions should be much larger due to the extremely high local supersaturation degree resulted from the Al addition. Because of their multi-branching feature, dendritic inclusions can capture each other easily. Consequently, the clustering degree of dendritic inclusions is much higher. The clustering of plate-like inclusions is quite complex. Some plate-like inclusions are very thin and large, mostly exhibiting a hexagonal form, as shown in Fig. 1(b). This type inclusions were occasionally observed in clusters in all samples. On the contrary, some are quite thick and relatively small in size, as shown in Figs. 5(b) and 5(c). A large number of such inclusions were observed in samples L2, HS2, HS3 and HS4. These inclusions frequently cluster edge by edge.

The clustering degrees of different morphologies of alumina inclusions were measured quantitatively for the first

time. Different alumina morphologies were found to have quite different clustering tendencies. Since Te affects the morphology distribution of alumina inclusions, the overall clustering degree of alumina inclusions is changed correspondingly. For example, in samples where Te increases the amount of faceted inclusions, which have the highest clustering tendency, the overall clustering degree increases and vice versa. Essentially, the clustering of alumina inclusions results from strong attractive forces between alumina inclusions. It is implied that alumina morphology affects the attractive forces. This will be discussed in the follow-

Fig. 4. Average clustering degree as a function of the morphology of alumina inclusions from samples HS1 to HS4.

Fig. 3. Clustering degree as a function of the morphology of alumina inclusions. (a) L1 and L2; (b) LS1 and LS2; (c) HS1 to HS4.

Fig. 5. SEM images of alumina inclusions after acid extraction.²⁹⁾ (a) L1; (b) L2; (c) HS4.

ing sections.

3.3. Thermodynamic Considerations on the Clustering of Alumina Inclusions

3.3.1. Spontaneous Cavitation between Unwetted Particles

High clustering tendency of non-metallic inclusions unwetted by liquid steel indicates that strong attractions exist between the inclusions. Due to the opaque property and the high temperature of liquid steel, attractive forces between non-metallic inclusions in the bulk of liquid steel cannot yet be determined experimentally. However, interactions between unwetted particles in aqueous solutions have been extensively studied,³²⁾ revealing the existence of strong attractions of much longer range than the van der Waals force.^{32–36)} Several mechanisms have been proposed to account for these strong attractions: (i) electrostatic interactions;³⁷⁾ (ii) bridging of submicroscopic bubbles adhering to the surface;^{34,36,38)} (iii) disturbed water structure³⁹⁾ and (iv) spontaneous formation of cavities between unwetted surfaces.^{21,22,40,41)} Well-designed experiments have excluded the first two mechanisms.^{42–44)} Of the remaining mechanisms, the proposal that in non-wetting systems the liquid may be spontaneously expelled from the gap between two approaching particles to form a gas cavity, as shown in **Fig. 6**, is the most attractive and has been validated experimentally.^{45–47)} Therefore, the effect of alumina morphology on the clustering of alumina inclusions will be discussed based on the cavitation theory.

For two approaching alumina particles in molten iron, the negative change of Gibbs free energy of an alumina-molten

iron interface replaced by an alumina-gas interface, as seen from Eq. (1), is the driving force for the gas cavity formation.²¹⁾ Once the gas cavity is formed, an attractive force between the two alumina particles develops. This attractive force is the summation of the forces due to the surface tension of molten iron and the pressure drop across the molten iron-gas interface, as expressed in Eq. (2).⁴⁸⁾

$$\gamma_{sg} - \gamma_{sl} = \gamma_{lg} \cdot \cos \theta \quad \text{..... (1)}$$

$$F = 2\pi\gamma_{lg}l + \pi l^2 \Delta P \quad \text{..... (2)}$$

The pressure drop across the molten iron-gas interface can be calculated with the Laplace-Young equation expressed with Eq. (3).

$$\Delta P = \gamma_{lg}(1/r - 1/l) \quad \text{..... (3)}$$

where γ_{sg} is the alumina surface tension, γ_{lg} is the surface tension of molten iron, γ_{sl} is the alumina-molten iron interfacial energy, θ is the contact angle, F is the attractive force, ΔP is the pressure drop, and l and r are the principle radii of the gas cavity, as shown in **Fig. 6**.

According to Eqs. (2) and (3), to calculate the attractive force between two alumina particles, the principle radii l and r , i.e., the profile of the molten iron-gas interface, should be determined first. Determining exact interface profile requires complex numerical procedures, even for the simple case of two identical spheres.⁴⁸⁾ Methods of optimizing the interface profile of the cavity confined by two identical spheres are available in literature.^{21,22,36,49,50)} For approximate calculations, the interface is usually described by a piece of a circle.^{35,48)} This method is known as the toroidal approximation and it will be used in the present paper.

By describing the interface profile with a piece of a circle with radius r , the principle radii l and r can be expressed as a function of the filling angle α . As morphology combinations of two alumina particles are various in liquid steel, here we only consider three cases: sphere and sphere (S-S), sphere and plane (S-P), and plane and plane (P-P). As seen in **Fig. 6**, only the particle surface geometry around the contact region affects the gas cavity formation. Therefore, the word “sphere” here indicate the surface around contact region is curved, such as spherical and dendritic inclusions. The word “plane” indicates the surface around contact region is flat, such as faceted and plate-like inclusions. The principle radii l and r are listed in **Table 4**. In the present paper, the formulas with references are taken from literatures. The formulas

Fig. 6. Basic geometries of the gas cavities of different contact types.

Table 4. The principle radii l and r of a gas cavity for different contact types.

Contact types	Principle radii	
	r	l
S-S	$r = -\frac{R_1(1 - \cos \alpha_1) + R_2(1 - \cos \alpha_2) + h}{\cos(\theta - \alpha_1) + \cos(\theta - \alpha_2)}$	$l = R_1 \sin \alpha_1 - r[1 - \sin(\theta - \alpha_1)]$
S-P ³⁵⁾	$r = -\frac{R(1 - \cos \alpha) + h}{\cos(\theta - \alpha) + \cos(\theta)}$	$l = R \sin \alpha - r[1 - \sin(\theta - \alpha)]$
P-P ³⁶⁾	$r = -\frac{h}{2 \cos(\theta')}$	$l = x - r(1 - \sin \theta')$

Note: R , R_1 and R_2 are the radii of particles; α , α_1 and α_2 are the filling angle; h is the separation distance between the two particles; x is the radius of the contact rim (**Fig. 6(c)**).

without references are derived by the authors.

The key step of calculating the attractive force F is to determine the filling angle α . For rough calculation, the filling angle α can be obtained by inserting the principle radii l and r (as shown in Table 4) into Eq. (3) at constant pressure drop ΔP .^{26,28)} Since this method can not guarantee the formed gas cavity is in thermodynamically stable state, in the present work, the filling angle α was determined by minimizing the Gibbs free energy of the gas cavity,^{21,49)} as expressed with Eq. (4).³⁶⁾

$$G = P_0 V - N k_B T \ln V + \gamma_{lg} A_{lg} + (\gamma_{sg} - \gamma_{sl}) \cdot A_{sg} \dots\dots (4)$$

where P_0 is the pressure in the molten iron, V is the volume of the gas cavity, N is the number of gas molecules inside the cavity, A_{lg} is the molten iron-gas area, and A_{sg} is the alumina-gas area.

Expressing V , A_{lg} and A_{sg} as a function of the filling angle α , the equilibrium value of filling angle α can be obtained from $dG = f(\alpha) = 0$. Then the attractive force F can be calculated. V and A_{lg} are expressed with Eqs. (5) and (6). The expressions of A_{sg} are listed in Table 5.

$$V = \pi \int_{y_1}^{y_2} (r + l - \sqrt{r^2 - y^2})^2 dy - V_s \dots\dots\dots (5)$$

$$A_{lg} = 2\pi \int_{\theta_1}^{\theta_2} r(r + l + r \cos(\theta)) d\theta \dots\dots\dots (6)$$

The parameters used in the calculations are listed in Table 6. The number of gas molecules N in the gas cavity is set to 0, considering that the partial pressure of molten iron and other elements, such as oxygen, is very low. The pressure in the molten iron P_0 is set to 1 atm, considering that the depth of the molten iron in the MgO crucible is very

Table 6. Parameters used in the calculations of the attractive force.

Parameters	Values
Radius of a sphere R	10 μm
Radius of a plane (round shape) R	10 μm
Number of gas molecules N	0
Pressure drop P_0	1 atm
Surface tension of molten iron γ_{lg}	1.80 (N/m) ⁵²⁾
Contact angle θ	137 ($^\circ$) ⁵²⁾
The surface tension of Alumina inclusions γ_{sg}	0.75 (N/m) ⁵²⁾

small around 18 mm. The particle radius R is set to 10 μm due to the limitation of the toroidal approximation approach. For smaller particle size, the two principle radii l and r are almost at the same size. Thus, it is not possible to keep the pressure drop ΔP approximately constant.⁵¹⁾ For the S-S and S-P contact types, the contact angle at the three-phase line equals the bulk contact angle when the Gibbs free energy of the cavity is minimized.³⁶⁾ It is therefore kept constant during calculation. For the P-P contact type, the contact angle at the three-phase line is allowed to vary, which can be understood from Fig. 7(c) in section 3.3.2. Instead, the pressure drop ΔP is kept constant.

3.3.2. Gibbs Free Energy of A Gas Cavity between Two Alumina Particles

Figure 7 shows the calculated Gibbs free energy of a gas cavity as a function of the filling angle α or the cavity radius l at different separation distances. For the contact types S-S (Fig. 7(a)) and S-P (Fig. 7(b)), at small separation distance, the Gibbs free energy always has a minimum value, where the gas cavity is thermodynamically stable. This implies that a gas cavity forms spontaneously when the distance between two approaching alumina particles is small enough. Increasing the separation distance makes the gas cavity thermodynamically metastable and finally unstable, which means that the gas cavity will break and the attractive force will disappear. For the contact type P-P (Fig. 7(c)), the Gibbs free

Fig. 7. Variation of Gibbs free energy of a gas cavity with filling angle α or cavity radius l at different separation distances for different contact types. (a): S-S; (b): S-P; (c): P-P.

Table 5. A_{sg} , A_{lg} and V for different contact types.

Contact types	Alumina-gas area A_{sg}	Molten iron-gas area A_{lg}		Volume of gas cavity V		
		θ_1	θ_2	y_1	y_2	V_s
S-S	$2\pi R_1^2 (1 - \cos \alpha_1) + 2\pi R_2^2 (1 - \cos \alpha_2)$	$\frac{3\pi}{2} - \theta + \alpha_1$	$\frac{\pi}{2} + \theta - \alpha_2$	$r \cos(\theta - \alpha_2)$	$r \cos(\alpha_1 - \theta)$	$\frac{\pi}{3} R_1^3 (2 + \cos \alpha_1) (1 - \cos \alpha_1)^2$ $\frac{\pi}{3} R_2^3 + (2 + \cos \alpha_2) (1 - \cos \alpha_2)^2$
S-P	$2\pi R_1^2 (1 - \cos \alpha) + \pi(r + l - r \sin \theta)^2$	$\frac{3\pi}{2} - \theta + \alpha$	$\frac{\pi}{2} + \theta$	$r \cos \theta$	$r \cos(\alpha - \theta)$	$\frac{\pi}{3} R^3 (2 + \cos \alpha) (1 - \cos \alpha)^2$
P-P	$2\pi x^2$	$\frac{3\pi}{2} - \theta'$	$\frac{\pi}{2} + \theta'$	$r \cos \theta'$	$-r \cos \theta'$	0

energy varies differently. When the separation distance is small, the Gibbs free energy has no minimum value, which means that the gas cavity can grow unlimitedly. In practice, the growth of the gas cavity is limited by the particle size. With the increase of separation distance, the cavity becomes metastable and finally unstable.

3.3.3. Attractive Force and Rupture Energy

The calculated attractive force between two alumina particles as a function of the separation distance is shown in Fig. 8(a). The P-P type has the strongest attractive force and the longest critical separation distance (9.20 μm). The S-S type has the weakest attractive force and the shortest critical separation distance (1.56 μm), which is still approximately two orders of magnitude longer than the van der Waals force (Fig. 9(c)). To the best of our knowledge, this is the first quantitative calculation of the attractive force between alumina inclusions in liquid steel based on spontaneous cavitation theory, especially focusing on the effect of morphology. The dependence of forces on particle shape is known as Derjaguin's approximation, according to which the force due to atomic or molecular interactions (for example, van der Waals force) of a S-S type is half of that of a S-P type.³³⁾ In the present work, the ratio of the attractive force between the S-S type and S-P type is calculated to be 0.52 when two particles contact. Figure 8(b) shows the attractive forces arising from surface tension and pressure drop, separately, for the S-S contact type. As seen, the force due to surface tension dominates.

The area under the force-separation distance curve is a measure for the energy required to rupture the gas cavity. The larger the rupture energy, the more difficult it is to separate alumina particles. The rupture energies of different contact types are shown in Fig. 8(c). The rupture energy of P-P type is 16.4 times and 4.2 times as large as that of S-S type and S-P type, respectively. This suggests that non-metallic inclusions with large flat faces, such as faceted and plate-like inclusions, should form clusters more easily than spherical inclusions. This explains why the clustering degree of faceted alumina inclusions is much larger than that of spherical inclusions. The ratio of average cluster-

ing degree between faceted and spherical inclusions in tests HS1 to HS4 is calculated to be 3.7. This value is very close to the rupture energy ratio between P-P type and S-P type. As the relative amount of spherical inclusions is very low (3.1–8.3%), spherical inclusions mainly cluster with faceted inclusions. The consistency further confirms the occurrence of spontaneous cavitation between approaching alumina inclusions. Moreover, break-up of large clusters in liquid steel depends on the balance between the force due to fluid flow and the attractive force between inclusions. The calculation suggests that faceted inclusions can form large clusters more easily. This is beneficial to the removal of inclusions, as confirmed by Horigome *et al.*⁵³⁾

3.3.4. Comparison with the Capillary Force on Melt Surface and the van der Waals Force

To have a better understanding of the attractive force due to gas cavity formation, we compare this force with the capillary force on melt surface and the van der Waals force, as shown in Fig. 9. The van der Waals force between two spherical particles is expressed with Eq. (7).⁵⁴⁾

Fig. 9. Comparison of different attractive forces between two spherical alumina particles. (a) attractive force due to gas cavity formation; (b) capillary force and (c) van der Waals force.

Fig. 8. Calculated attractive force and rupture energy for different contact types. (a) and (b) attractive force; (c) rupture energy.

$$F_{VDW} = \frac{A_{121}}{6h^2} \cdot \frac{R_1 R_2}{(R_1 + R_2)} \dots\dots\dots (7)$$

where A_{121} is the Hamaker constant, h is the inter-particle distance and R_1 and R_2 are the radii of spherical particles. As calculation of the capillary force between two particles on melt surface is quite complex, the capillary force is taken directly from Ref. 18). For consistency, parameters used in the comparison are taken from the same reference. They are listed in **Table 7**.

As seen in the figure, the attractive force due to gas cavity formation is the strongest, 10^{-5} to 10^{-4} N, with acting length around $2.5 \mu\text{m}$. The capillary force is the weakest, 10^{-16} to 10^{-15} N, however, with the longest acting length up to $100 \mu\text{m}$. This is confirmed by in-situ observation by CSLM.¹⁵⁾ The van der Waals force, 10^{-11} to 10^{-8} N, is several orders of magnitude stronger than the capillary force, however, with the shortest acting length. Different attractive forces play different roles in the clustering of non-metallic inclusions in liquid steel. On the surface of liquid steel, unwetted inclusions apart tens of micrometers are observed to move to each other. The capillary force is believed to be responsible for the long-range attraction on melt surface.¹⁵⁾ In the bulk of liquid steel, the capillary force disappears due to the absence of gas-liquid-solid interfaces. As clustering occurs mainly among unwetted inclusions, the van der Waals force can be ruled out. At present, the strong attractive force due to gas cavity formation seems to be the only reasonable explanation for the clustering among unwetted inclusions in the bulk of liquid steel.

3.3.5. Influence of Surface Tension, Contact Angle and Particle Size on the Attractive Force

To elucidate the factors that influence the attractive force, we take surface tension, contact angle and particle size into account. **Figure 10(a)** shows that the rupture energy between two identical spherical alumina particles increases linearly with increasing surface tension of the melt. **Figure 10(b)** shows that the rupture energy increases slowly with increasing contact angle to 120° , thereafter it increases sharply with contact angle. This can explain why the clustering of Al_2O_3 is more severe compared with SiO_2 (115°),⁵⁵⁾ ZrO_2 (122°)⁵²⁾ and MgO (125°).⁵²⁾

According to **Fig. 10(a)**, clustering of non-metallic inclusions in liquid steel might be weakened by adding surfactants, which decrease the surface tension of liquid steel. In practice, however, this effect is not obvious as surfactants increase the contact angle simultaneously. An example of Te addition affecting the rupture energy between two spherical alumina particles in molten iron is shown in **Fig. 11**. The

parameters used are listed in **Table 8**. The rupture energy increases abruptly with increasing Te addition from 0 to 40 ppm, thereafter decreases gradually with Te addition.

Figure 12 shows that the rupture energy between two alumina particles of S-P type increases linearly with increasing the size of the spherical particle. The size of the plane is assumed to be infinite. This suggests that large particles are more likely to form clusters, as confirmed in our previ-

Fig. 10. Effects of surface tension and contact angle on the rupture energy between two identical spherical alumina particles with $R_1=R_2=10 \mu\text{m}$. (a) influence of surface tension at $\alpha=137^\circ$; (b) influence of contact angle at $\gamma_{lg}=1.80 \text{ N/m}$.

Fig. 11. Effect of Te addition on the rupture energy between two spherical alumina particles in molten iron.

Table 7. Parameters used in the comparison of different forces.

Parameters	Values
Surface tension of molten iron γ_{lg}	$1.80 \text{ (N/m)}^{18)}$
Contact angle θ	$133 \text{ (}^\circ)^{18)}$
Hamaker constant a_{121}	$0.45 \times 10^{-20} \text{ (J)}^{27)}$
Alumina particle radius $R_1=R_2$	$20 \mu\text{m}^{18)}$

Table 8. Interfacial properties used in the calculation of rupture energy.⁵⁶⁾

Te addition (ppm)	θ $^\circ$	γ_{lg} ($\text{N}\cdot\text{m}^{-1}$)	γ_{sg}
0	137	1.80	0.75
40	152	1.31	
250	161	1.00	
1 000	178	0.77	

ous paper.²⁹⁾

3.4. Clustering of Plate-like Alumina Inclusions

Theoretical calculations in section 3.3.5 suggest that plate-like alumina inclusions should form clusters more easily than faceted inclusions as their large flat faces can generate stronger attractive force. However, this is inconsistent with experimental results of the clustering degree of plate-like alumina inclusions, which is approximately 25% lower than that of faceted inclusions in samples HS1 to HS4. Plate-like alumina inclusions exhibit a platy {222} habit.^{57,58)} To account for this discrepancy, we think that molten iron wets plate-like inclusions better. This is confirmed by literature. Table 9 summarizes literature data

Fig. 12. Influence of particle size on the rupture energy between two alumina particles of S-P type at $\alpha=137^\circ$ and $\gamma_{\text{lg}}=1.80$ N/m.

Table 9. Contact angle of molten iron on an alumina substrate.

Contact angle/ $^\circ$	Substrate	Temperature/K	Atmos.	Ref.
132	Polycrystalline	1 873	Ar	59)
137	Polycrystalline	1 873	H ₂	56)
145	Polycrystalline	1 873	H ₂	60)
105–118	Single crystal	1 873	CO	61)
104	(222) face	1 873	H ₂ –Ar	62)
108	(222) face	1 973	Ar	63)

Fig. 13. Side view of (222) crystal face of $\alpha\text{-Al}_2\text{O}_3$ along $\langle 0\bar{1}1 \rangle$. O: large red spheres; Al: small black spheres.

on the measured contact angle between molten iron and an alumina substrate.

The contact angle between the (222) face and molten iron is approximate 30° smaller than that between polycrystalline alumina substrate and molten iron. Due to the small contact angle of $104\text{--}108^\circ$, a weak attractive force between a plate-like alumina particle and a particle of any shape is predicted. The small contact angle of molten iron on a (222) face is due to its special surface structure.⁶²⁾ As shown in Fig. 13, the (222) face has the highest density of unsaturated bonds, i.e., one broken bond for each O atom and three broken bonds for each Al atom.⁶⁴⁾ Due to such a surface structure, strong adsorption of Fe atoms is expected. This can improve the wettability of molten iron on (222) face.

4. Conclusion

The effect of alumina morphology on the clustering of alumina inclusions in molten iron was studied. The results obtained are as follows:

(1) Te addition modifies the morphology of alumina inclusions. Te tends to make the morphology of alumina inclusions evolve from dendritic and spherical, via faceted, to plate-like. Stirring strengthens the effectiveness of Te on the morphological modification of alumina inclusions, resulting in more plate-like inclusions. Increasing the super-saturation degree weakens the effectiveness of Te.

(2) Alumina morphology affects alumina clustering degree. The clustering degree increases in the order of spherical, dendritic, plate-like and faceted inclusions.

(3) Attractive force between two alumina inclusions with different shape combinations, i.e., S-S, S-P and P-P, were calculated based on the spontaneous cavitation theory. S-S type has the smallest attractive force and the shortest acting length; P-P type has the largest attractive force and the longest acting length. This can explain why spherical inclusions have the smallest clustering degree.

(4) The attractive force due to gas cavity formation was compared with the capillary force on melt surface and the van der Waals force. The attractive force due to gas cavity formation is the strongest in magnitude while the capillary force is the weakest.

(5) Plate-like alumina inclusions have 25% lower clustering degree, compared with faceted inclusions. This is due to that plate-like inclusions have better wettability by molten iron.

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