Formation and Morphology of Al_2O_3 Inclusions at the Onset of Liquid Fe Deoxidation by Al Addition

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The initial stage of deoxidation and the influence of the oxygen level on the inclusion features were examined. Liquid Fe with various dissolved oxygen content (O) was brought into contact with Al in a quartz tube for a short time, *i.e.* 1, 5, 30 and 60 s. Microscopic investigations of the quenched samples revealed the formation of Al_2O_3 inclusions in the Fe–Al reaction zone, resulting from the motion of the diffusion front with time. Specific attention is given to inclusion size, location and morphology as a function of interaction time and Q content. The latter was found to influence the inclusion characteristics. The inclusion number increased drastically with Q content, which is related to the degree of supersaturation of the melt, one of the most important factors influencing the formation of inclusions. The inclusion morphology evolved from angular to spherical with increasing Q content.

KEY WORDS: deoxidation; Al_2O_3 inclusion; morphology.

1. Introduction

Steel cleanliness is a major issue regarding the production of high quality steels. Non-metallic inclusions are often considered as harmful to product quality and productivity. Another approach is to beneficially utilize non-metallic inclusions to produce steels with enhanced and even tailored properties. In both cases, the key is to control the characteristics of the inclusion population in the steel, such as number, composition, morphology, size and spatial distribution. The degree of supersaturation, S , the temperature and the presence of impurities are essential factors that influence the formation and growth of the inclusions, which yield distinctive inclusion morphologies and size distributions. It is therefore crucial to understand the relation between process variables and inclusion formation and growth soon after nucleation in order to control their size distribution throughout the deoxidation process.

Few studies were dedicated to the observation of the early stage of deoxidation. Numerical approaches^{1–3)} give insight to predict the size distribution of inclusions from the nucleation stage. The predictions reveal that, at the initial stage, the growth of inclusions is mainly determined by dissolved oxygen (O) and deoxidizer (*e.g.* Al, Si), diffusion and Ostwald ripening. Deoxidation is a fast and complex process. The observation of the inclusions soon after nucleation is an experimental challenge. By measuring the inclusion size distribution from 60 s after deoxidation, Suito and Ohta⁴⁾ identified the interfacial energy between oxide and liquid Fe to be a critical parameter in predicting the inclusion size, enabling to modify the spread of the size distribu-

tion by selecting appropriate deoxidant and supersaturation conditions. Beskow and Du Sichen⁵⁾ studied experimentally the homogeneous nucleation and agglomeration of Al_2O_3 inclusions in a melt quenched at 5, 15, 30 and 120 s after Al deoxidation. In the areas supersaturated with Al, the formation of small spot-like Al_2O_3 inclusions took place, 5 s after deoxidation, followed by agglomeration. The effect of the amount of Al addition on the formation of these inclusions was more pronounced compared to the initial Q content. It was explained by the slow diffusion of Al under limited convection, causing a high local supersaturation. Wakoh and Sano⁶⁾ measured the initial size distribution of Al_2O_3 inclusions by sampling the steel 1 s after deoxidation. They observed a larger inclusion size with increased Q content and concluded that inclusion growth under these conditions is controlled by Q diffusion. They reported four morphologies, *i.e.* sphere, octahedron, hexagonal and a minority of coagulated inclusions. By adding rimming steel to Al in an ingot, Tiekink *et al.*⁷⁾ observed a repetitive sequence of several Al_2O_3 morphologies and explained it by a mechanism of local reaction and diffusion of Al and Q . Small Al_2O_3 inclusions were formed under high Q conditions, while needles and dendrites appear at some distance away from the former, due to counter diffusion of Q and Al maintained for some time.

This paper is the second part of an experimental study of the phenomena involved in the early steps of the deoxidation process, when Al rich melts are brought into contact with oxidized Fe. In the first part,⁸⁾ the interactions between Fe and Al shortly after the deoxidation stage were investigated through the interpretation of the quenched mi-

microstructures of the diffusion couple, to identify the interactions and the nature of the phases at the experimental temperature. In the present study, the formation of Al_2O_3 inclusions with respect to the inclusion size, location and morphology as a function of interaction time and $\underline{\text{O}}$ content in liquid Fe, was studied at the early stages of deoxidation in the Fe–Al reaction zone. A piece of Al was brought in contact for several seconds with liquid Fe held at 1600°C, in which the total oxygen content was changed from 160 to 1800 ppm. The samples were evaluated with electron microscopy on the sample cross section and on the extracted inclusions.

2. Experimental

The experimental procedure is described in detail in a previous paper.⁸⁾ 100 g of electrolytic Fe (99.97% Fe) was melted in a high temperature vertical tube furnace at 1600°C under purified Ar atmosphere. The oxygen content in the melt was increased by the addition of Fe_2O_3 powder, followed by stirring with an Al_2O_3 rod. A piece of Al (99% Al) cut in a cubic shape (5 mm side) was placed inside a quartz tube. The end of the quartz tube was narrower in order to maintain the Al piece inside. After 30 min at 1600°C to stabilize the temperature of the melt, the quartz tube with the Al piece was quickly introduced in the liquid Fe. A small volume of molten metal was sucked in the tube and brought into contact with Al (Fig. 1(a)). Except for sample 4, the contact between Fe and Al took place at the lower facet of the cubic piece of Al. In sample 4, the contact was made at a corner of the Al piece. After the desired interaction time, the quartz tube was rapidly withdrawn from the metal bath, removed from the furnace and quenched in water. The detailed conditions for each test are listed in Table 1. $\underline{\text{O}}$ is assumed equal to total O owing to the low impurity level of the electrolytic Fe. The total O content was determined by combustion analysis on the bulk Fe of the samples. With samples 2, 3 and 4 (and 5), the influence of increasing the $\underline{\text{O}}$ content from 450 ppm to 1800 ppm on the inclusion characteristics was studied with fixed interaction time (~1 s). The comparison between

samples 4, 5 and 6 emphasises the effect of changing the interaction time from, respectively, 1 s, 5 s and 60 s on the inclusion population at high initial $\underline{\text{O}}$ content, whereas samples 1 and 2 provide the influence of interaction times of 1 and 30 s at lower $\underline{\text{O}}$ content.

The upper part of the samples was cut along the longitudinal axis and prepared for SEM investigation (SEM XL30 FEG, equipped with an EDAX EDS spectrometer). After SEM investigation of the polished cross sections, the inclusions were extracted by dissolving the metal matrix in HCl (1:1). The non-dissolved inclusions collected on a membrane were investigated with SEM for size and morphology assessment.

3. Results

3.1. Fe–Al Interactions

The interaction between Fe and Al and the development of the reaction zone were investigated in detail.⁸⁾ Due to the large temperature difference and the heat transfer between Fe and Al, solid Al in contact with Fe heats up and melts. At the same time, liquid Fe solidifies at the interface, forming a Fe shell.⁹⁾ During the shell period, interactions between solid steel and liquid Al may lead to the formation of Fe–Al intermetallic compounds with melting points intermediate between those of steel and Al. Once the solid shell melts, Al is released in the melt. As illustrated in Fig. 1(b), interdiffusion of Fe and Al results in the formation of a reaction zone, which is characterized by a composition intermediate between pure Fe and pure Al. The reaction zone (noted Fe–Al) is bounded by two diffusion fronts, indicated by the dashed lines in Fig. 1(b). Since our main interest lies in the interactions occurring between oxidized Fe and Fe–Al, the term diffusion front will be used to designate the Fe/Fe–Al interface (*i.e.* diffusion front 1 in Fig. 1(b)). The diffusion couple involves a third component, O, which is present in liquid Fe at a given concentration. Due to their high affinity, $\underline{\text{Al}}$ and $\underline{\text{O}}$ react to form solid Al_2O_3 inclusions at the reaction front, which is indicated by the dotted line in Fig. 1(b). Since both $\underline{\text{Al}}$ and $\underline{\text{O}}$ must be available for the reaction to take place, the reaction front is located in the reaction zone. The reaction zone consisted in several layers of solidified Fe–Al intermetallic compounds. Based on the microstructure, the concentration profiles, diffusion processes in solid and liquid phases, and on the behavior of Al_2O_3 inclusions in the reaction zone, it was shown that the reaction zone was completely liquid and that the Fe shell disappeared in samples 1 and 6 with longer holding time.

3.2. Inclusion Type

Next to alloying and interdiffusion between Fe and Al, non-metallic inclusions were observed in the reaction zone. Variations in size, type, morphology and relative occurrence were observed between samples containing different $\underline{\text{O}}$ levels. Three different types of inclusions were identified, based on their composition.

- (1) Pure Al_2O_3 inclusions were observed in the region between the initial Fe/Al interface and the diffusion front (Fig. 2(a)).
- (2) Large Al_2O_3 inclusions containing traces of Si and Fe were found near the $\text{FeAl}_2/\text{Fe}_2\text{Al}_5$ interface (Fig. 2(a)).

Fig. 1. Schematic representation of (a) the experimental setup with Fe suction inside the quartz tube and (b) the reaction zone development in the diffusion couple Fe–Al(O).

Table 1. Details of the experimental procedure.

Sample	Initial $\underline{\text{O}}$ content (ppm)	Contact time (s)
1	160	30
2	450	1
3	780	1
4	1800	1
5	1800	5
6	1800	60

They are located the furthest away from the diffusion front, in the vicinity of the initial Fe/Al interface.

- (3) FeO_x inclusions were found in the bulk Fe in samples 4 to 6 containing high initial $\underline{Q}$ contents (Fig. 2(b)).

3.3. Inclusion Size and Number

With increasing initial $\underline{Q}$ content in liquid Fe, an increase in the number of precipitated inclusions was observed. The inclusion number was low in samples 1 and 2 with, respectively, 160 and 450 ppm initial $\underline{Q}$ content, as inclusions are relatively difficult to find in the reaction zone shown in Figs. 3(a) and 3(b). The inclusion number increased drastically with sample 3 (780 ppm $\underline{Q}$) as evidenced by the high

Fig. 2. Overview of the inclusion types observed on polished cross sections (SEM images): (a) Al_2O_3 inclusions in the reaction zone of sample 6 (60 s, 1 800 ppm $\underline{Q}$), categorized in pure Al_2O_3 inclusions (inclusion type 1) and large Al_2O_3 inclusions with traces of Si and/or Fe (inclusion type 2); (b) FeO inclusions in the bulk Fe of sample 4 (1 s, 1 800 ppm $\underline{Q}$).

Fig. 3. Comparison of the relative amount of inclusions as a function of the initial $\underline{Q}$ content: (a) and (b) are SEM images of polished cross sections of the reaction zone with Al_2O_3 inclusions appearing black for (a) sample 1 (1 s, 160 ppm $\underline{Q}$); (b) sample 2 (1 s, 450 ppm $\underline{Q}$). (c) is a SEM image of Al_2O_3 inclusions (appearing white) on the filtration membrane after extraction of sample 3 (1 s, 780 ppm $\underline{Q}$). The white arrows indicate the direction of the Al side.

number of inclusions collected on the filtration membrane after their acid extraction from the reaction zone (Fig. 3(c)). For samples 4 to 6, the very high initial $\underline{Q}$ content (1 800 ppm $\underline{Q}$) gave rise to very high inclusion number, all along the area covered by the trace of the diffusion front (Fig. 4).

For interaction times of 1 and 5 s, the inclusion size tends to decrease with increasing $\underline{Q}$ content in liquid Fe. The average inclusion size was about 2.1 μm at 160 and 450 ppm $\underline{Q}$ (samples 1 and 2), and decreased to below 1 μm with increasing $\underline{Q}$ content to 780 ppm (sample 3).

The cross section of samples 4 to 6 was distinctive owing to the very high initial $\underline{Q}$ content (1 800 ppm). Inclusions show specific features as a function of their location, delimiting several zones depicted in Fig. 5. Two zones are found in Fe (lower part of Fig. 5 and Fig. 6(a)): one containing FeO_x , resulting from the excess $\underline{Q}$ upon cooling, and a “precipitate-free” region located between the bulk Fe and the diffusion front (zone 0). The absence of precipitates in this area suggests a lower $\underline{Q}$ content compared to the bulk Fe. As shown in Table 2, a thinner precipitate-free zone (*i.e.* high $\underline{Q}$ source closer to the diffusion front) seems corre-

Fig. 4. Overview of the reaction zone of sample 4 in contact with liquid Fe containing a high $\underline{Q}$ level (1 s, 1 800 ppm $\underline{Q}$). Numerous Al_2O_3 inclusions are formed in the reaction zone delimited by the diffusion front. A precipitate-free zone separates the reaction zone and the bulk Fe containing FeO precipitates (top right corner). In the reaction zone, individual Al_2O_3 inclusions are observed near the diffusion front, whereas aggregates of fine Al_2O_3 inclusions are found further away from the diffusion front. The white arrow indicates the direction of the Al side.

Fig. 5. Simplified representation of the Fe and reaction zone in the case of high initial $\underline{Q}$ content (samples 4 to 6), showing the different zones according to inclusion characteristics (delimited by dashed lines). Black markers represent Al_2O_3 inclusions and grey-filled markers FeO_x inclusions.

Fig. 6. (a) BSE images of the diffusion front in sample 4 (1 800 ppm $\underline{Q}$, 1 s), showing the precipitate-free zone (zone 0, delimited by the dotted lines) separating α -Fe containing FeO_x from Fe–Al containing Al_2O_3 inclusions (zone 1); (b) Aggregates of fine Al_2O_3 inclusions observed in zone 2 of sample 6 (1 800 ppm $\underline{Q}$, 60 s); (c) large angular Al_2O_3 inclusions with traces of Si, located in zone 3 of sample 6 (1 800 ppm $\underline{Q}$, 60 s).

Table 2. Extent of zones 0 and 1, inclusion characteristics in zone 1 and $\underline{\text{Al}}$ gradient at the diffusion front in samples 4 to 6 with high initial $\underline{Q}$ content. Zone 0 corresponds to the precipitate-free area and zone 1 contains individual Al_2O_3 inclusions, as depicted in Fig. 5 (a=angular; s=spherical; +++=high; ++=medium; +=low).

sample	thickness zone 0 (μm)	thickness zone 1 (μm)	average inclusion diameter (μm)	inclusion shape	$\underline{\text{Al}}$ gradient
5	1.5 - 2.5	~20	< 0.1	a	+++
4	~15	~35	0.3	a + s	++
6	~60	~70	1.0	s	+

lated with a larger $\underline{\text{Al}}$ concentration gradient near the diffusion front. This aspect was discussed in the first part of this study.⁸⁾ As regards sample 4, contact between Fe and the Al piece was made at a corner of the Al piece, in place of the lower facet for all the other samples. As shown in the first part of this study,⁸⁾ such difference results in much thicker layers compared to other samples with similar holding time, due to Fe penetrating deeper in the Al. Therefore, sample 4 with a contact time of 1 s has a thicker zone 0 and a less steel Al gradient than sample 5 with a contact time of 5 s (Table 2).

In the reaction zone, three regions containing inclusions were identified, as illustrated in Fig. 5. The first one (zone 1) is located just above the diffusion front and comprises individual Al_2O_3 inclusions (Figs. 4 and 6(a)). Table 2 gathers the thickness and inclusion characteristics measured in this area. Also the layer thickness and the inclusion size in this area seem correlated with the $\underline{\text{Al}}$ concentration profile. The steeper it is at the diffusion front, the smaller the inclusions and the thinner the layer.

In the adjacent zone 2 (Fig. 5), aggregates of fine Al_2O_3 inclusions are found (Fig. 6(b)), as a result of inclusion collision and coagulation. Owing to the high inclusion number density, collisions are much more likely compared to the samples with lower initial $\underline{Q}$ contents. As seen in Fig. 7, when moving away from the diffusion front, the size of the aggregates increases as the number of collisions increases with time. On the other hand, the size of the inclusions forming the aggregates decreases in the first 400 μm from the diffusion front and then remains approximately constant at 0.5 μm .

Finally, zone 3 (Fig. 5) comprises large Al_2O_3 inclusions with traces of Si and Fe (Fig. 6(c)). Oxide inclusions are hardly found above area 3, suggesting that $\underline{Q}$ was not conveyed beyond this point.

Fig. 7. Evolution of (a) the size of the individual inclusions and that of the particles forming the aggregates and (b) the aggregate size as a function of the distance from the diffusion front for sample 6 (1 800 ppm $\underline{Q}$, 60 s).

Fig. 8. Evolution of the Al_2O_3 morphologies after extraction: (a) and (b) angular inclusions are dominant at low initial $\underline{Q}$ content (sample 2: 450 ppm $\underline{Q}$, 1 s), (c) small spherical inclusions increase in number (d) and dendritic shaped inclusions are found with increasing the initial $\underline{Q}$ content (sample 3: 780 ppm $\underline{Q}$, 1 s).

3.4. Inclusion Morphology

The $\underline{Q}$ content available at the diffusion front was found to influence the inclusion number by acting on the inclusion formation process. The growth process is also greatly influenced by the supersaturation degree S nearby the crystal.

Fig. 9. (a)–(c): Morphology of individual Al_2O_3 inclusions in zone 1 (Fig. 5) for samples (a) 4 (1 s), (b) 5 (5 s) and (c) 6 (60 s) with 1 800 ppm initial $\underline{Q}$ content. (d)–(f): aggregates of fine Al_2O_3 inclusions found in zone 2 (Fig. 5) of samples (d) 4 (1 s), (e) 5 (5 s) and (f) 6 (60 s) with 1 800 ppm initial $\underline{Q}$ content.

Fig. 10. Overview of Al_2O_3 inclusion morphologies after extraction from (a) to (c): sample 4 (1 s, 1 800 ppm $\underline{Q}$); (d) to (f): sample 5 (5 s, 1 800 ppm $\underline{Q}$) and (g) to (i): sample 6 (60 s, 1 800 ppm $\underline{Q}$).

Therefore, a modification in the initial $\underline{Q}$ content is expected to influence growth and morphology of the inclusions.

Angular inclusions with a mean size of $2.1\ \mu\text{m}$ were dominant in samples 1 and 2, often as individual particles (**Fig. 8(a)**). Spherical inclusions were hardly found. Small and sparse agglomerated angular inclusions were found as well (Fig. 8(b)). When increasing the $\underline{Q}$ content to 780 ppm (sample 3), numerous small spherical inclusions, mainly pure Al_2O_3 with a size less than $1\ \mu\text{m}$, were found (Fig. 8(c)), together with larger Al–Fe–O inclusions (Fe $\sim 10\text{at}\%$) with an average size of $3.9\ \mu\text{m}$. Small clusters were occasionally found.

Figures 9 and 10 show an overview of the inclusion morphologies observed in samples 4 to 6 with 1 800 ppm initial $\underline{Q}$ content based on the polished cross sections (Fig. 9) and

on extracted inclusions (Fig. 10). The individual inclusions (originating from zone 1) in sample 6 are spherical (Figs. 9(c) and 10(g)). Those in sample 4 have a shape between spherical and angular (Figs. 9(a), and 10(a) and 10(b)). Facets appear but are not well defined. As seen in Fig. 9(b), those in sample 5 were too small to obtain an average size and to evaluate easily their shape.

The fine Al_2O_3 inclusions forming aggregates in zone 2 are much smaller than $1\ \mu\text{m}$ and exhibit spherical and angular shapes. Even when the holding time changes between samples 4 to 6, the aggregates are very similar in shape (Figs. 9(d) to 9(f)). However, the size of the particles forming the aggregates tends to be larger in sample 6 compared to samples 4 and 5. After extraction from the metal matrix, the individual inclusions forming the aggregates are easily distinguishable. In samples 4 and 5, the latter are mainly

angular shaped (Figs. 10(a) and 10(b); 10(d) and 10(e)). In sample 6, both angular and spherical morphologies are found numerously (Figs. 10(g) and 10(h)).

The third distinct morphology that was identified in every sample concerns the large, compact angular inclusions (Fig. 10(c), 10(f) and 10(i)) located in the vicinity of the initial Fe/Al interface. Contrasting with the other inclusions, they show well defined and smooth facets and tend to be larger and more compact with time (Fig. 10(i)). The absence of intermediate morphologies between aggregates (network structure) to such compact shapes suggests that these large angular inclusions are formed by a distinct mechanism.

4. Discussion

4.1. Sequence of Inclusion Formation

Due to the significant temperature difference between liquid Fe at 1600°C and solid Al initially at 25°C (Fig. 11, $t=0$), a solid Fe shell forms at the interface with colder Al (Fig. 11, $t=t_1$). During solidification of the Fe in the shell, the oxygen solubility in Fe decreases, causing the formation of FeO precipitates.⁸⁾ With pure liquid Fe, mainly FeO_x is generated when liquid Fe cools down in contact with colder Al. Also some SiO₂ crystals arising from devitrification of the fused quartz above 1000°C may be carried away with the liquid Fe flow during sampling (Fig. 2(b)). These solid oxide inclusions may provide preferential sites for heterogeneous nucleation of Al₂O₃, generating large inclusions in the vicinity of the initial Fe/Al interface (e.g. Figs. 2(a) and 6(c)). With the diffusion of Fe and Al and the subsequent formation of Fe–Al intermetallic compounds in this area (Fig. 11, $t=t_2$), the FeO_x precipitates and SiO₂ crystals initially contained in the shell would undergo a reduction by Al, forming solid Al₂O₃ inclusions with a SiO₂ or FeO_x core. Because these precipitates represent an important O source in a limited volume, the Al₂O₃ inclusion formed by reduction of the precipitates might be larger than those formed later through Al and O diffusion to the diffusion front. Remaining traces of Si and Fe were detected in such large crystals. Those tend to decrease with time, confirming the ongoing reduction by Al.

Fig. 11. Schematic illustration of the interactions between Fe and Al during the shell period. $t=0$: initial conditions; $t=t_1$: Al melting and formation of the solid shell upon contact between cold Al and liquid Fe. FeO_x precipitates and SiO₂ are present in the solid shell; $t=t_2$: formation of Fe–Al liquid and Fe–Al solid phases due to interdiffusion of Fe and Al. FeO_x precipitates and SiO₂ inclusions are reduced by Al to form large Al₂O₃ inclusions; $t=t_3$: melting of the shell.

An increase of the Si content was not measured (or detected) in Fe nor in Al (the detection limit of the EDS system is about 1 wt%). SiO₂ from the quartz tube could not be reduced by Al due to the short contact time and the limited contact surface between Al and the SiO₂ tube.

With the melting of the shell (Fig. 11, $t=t_3$), the interactions between the two liquid regions are intensified as Fe, Al and O transports are enhanced. According to homogeneous nucleation theory, the supersaturation S of the melt must reach a critical value S^* to initiate nucleation of a new inclusion. As a result, diffusion of O from bulk Fe to the reaction zone proceeds, creating a Fe–Al–O melt in the reaction zone near the diffusion front where the O and the Al concentration profiles overlap (solid lines in Fig. 12). The local supersaturation S increases gradually in the reaction zone near the diffusion front, as diffusion of both Al and O progresses (dashed line in Fig. 12). Once the local S value reaches S^* at a specific location, nucleation takes place in that area, defining the reaction front position (Fig. 12). During the high temperature interaction, the reaction front is therefore located behind the diffusion front, in the reaction zone. As the Al availability is high in the reaction zone, the O availability at the reaction front, which is controlled by the initial O content in liquid Fe and by O transport to the reaction zone, is believed to determine the inclusion nucleation and growth conditions at the reaction front. As observed in the samples, the inclusion number increased with increasing the O content, since nucleation of numerous small Al₂O₃ inclusions is kinetically favored by an increase of supersaturation. The supersaturation buildup in the Fe–Al–O melt located between the diffusion and reaction fronts is governed by diffusion processes, i.e. by concentration gradients. As diffusion and reaction proceed, the O and Al gradients become less steep, resulting in a decrease of the diffusion and reaction fronts velocity, which may affect the inclusion nucleation and growth conditions.

4.2. Inclusion Growth Mechanisms

Once nucleation occurs at the reaction front, supersaturation is rapidly consumed by growth, decreasing the Al

Fig. 12. Schematic view of the reaction zone during high temperature interaction, representing the overlap between the Al and O concentration profiles and the buildup of the supersaturation curve in the reaction zone (Fe–Al(l)) near the diffusion front, and the distinct position of the reaction and diffusion fronts. The reaction front appears when S reaches S^* .

and/or $\underline{Q}$ contents to their equilibrium contents at the reaction front. Simultaneously, $\underline{Al}$ diffuses further in Fe, resulting in the displacement of the diffusion front towards bulk Fe. The latter causes the newly formed inclusions to be surrounded by the Al-rich melt. Also $\underline{Q}$ is transported from the bulk Fe to the reaction zone owing to the concentration gradient. Diffusion growth is significantly influenced by the velocity of the reaction front, which controls the $\underline{Q}$ availability to the growing crystal. Owing to the lower $\underline{Q}$ available near the inclusions, growth by diffusion, which is reported as the main growth mechanism shortly after nucleation, is significantly slowed down. The growth process is limited owing to the limited transport of $\underline{Q}$ to the reaction front, as demonstrated by the small inclusion size in the reaction zone. Other growth mechanisms, such as collision-coagulation growth, might become more important. These mechanisms are governed by inclusion motion, which determines the probability that several inclusions collide and form a single inclusion.

In the absence of melt turbulences, the inclusion velocity is determined by considering buoyancy forces and Brownian motion. The buoyancy forces creating a rising velocity are governed by the inclusion size and the density difference between the inclusions and the surrounding liquid. Given the small size of the inclusions, the short contact time before solidification and the decreasing density of the Fe–Al melt in the direction of the surface, the inclusion rising velocity is insignificant. Brownian motion describes the random motion of very small inclusions suspended in a fluid. For a 0.1 and 1 μm diameter inclusion at 1 600°C, the mean value of inclusion displacement in 1 s is, respectively, about 3.96 and 1.25 μm .¹⁰ Also the moving distance of the inclusions is very limited. The contribution of collision-coagulation mechanism to inclusion growth is small under such conditions, unless the distance separating the inclusions is less than their moving distance. It results that inclusion growth is principally controlled by the availability of $\underline{Q}$ and $\underline{Al}$ at the reaction front and by the vicinity of other inclusions.

4.3. Influence of $\underline{Q}$ Content on Inclusion Morphology

Inclusion shape depends on the conditions during formation and growth. One of the most important parameters is the melt supersaturation, which increases with the $\underline{Q}$ and $\underline{Al}$ content. Clusters and dendrites, bars and globular inclusions are typically found at high supersaturation, whereas angular and compact shapes are observed at low supersaturation.^{11–19} The inclusion shape evolution from faceted prevailing at low initial $\underline{Q}$ content (samples 1 and 2) to spherical appearing at higher initial $\underline{Q}$ content (samples 3) can be explained by higher supersaturation conditions.

Although four distinct inclusion morphologies are reported in literature under high supersaturation conditions, *i.e.* clusters, dendrites, bars and spheres, only the last one was observed in the present study. To obtain bars, dendrites or clusters, continuous and non uniform conditions of supersaturation must be applied, where $\underline{Al}$ and $\underline{Q}$ are supplied along one direction. In most of the above-cited studies reporting on inclusion morphologies, well-stirred and turbulent liquid steel flow is usually attained, providing high supersaturation conditions and relatively high mass transport

rates. Under the present conditions, turbulences are limited and $\underline{Al}$ and $\underline{Q}$ are transported by unidirectional counter-current diffusion process. Local growth conditions are controlled by $\underline{Q}$ and $\underline{Al}$ diffusion rates to the reaction front. In order to grow bar-like or dendritic inclusions, $\underline{Q}$ and $\underline{Al}$ must be continuously transported to the reaction front to maintain enough supersaturation. This implies that $\underline{Q}$ and $\underline{Al}$ diffusivities in Fe and Fe–Al phases must be high enough to ensure mass transport to the reaction front without cessation. In the present study, small and short-shaped inclusions were observed, suggesting that mass transport rate was too slow to obtain bar-like shapes. Nucleation and growth occurs in a confined supersaturated zone where the amount and the transport of $\underline{Q}$ are limited, providing conditions for the formation of short-shaped inclusions. It should be mentioned that, after Al addition (or injection) in the ladle, Al_2O_3 inclusions generated in the vicinity of the point of release of molten Al are transported by the liquid steel flow to other areas where they can grow further.

Since S increases with decreasing temperature, the supersaturation of the Fe–Al–O melt comprised between the diffusion front and the reaction front (Fig. 12) increases during cooling of the sample to room temperature. Formation of Al_2O_3 inclusions, which was not possible in that area at the experiment temperature, can take place upon cooling. Quenching significantly slows down the diffusion process and activates inclusion formation and precipitation, causing the reaction front to catch up with the diffusion front during cooling, as observed during the sample investigations. These inclusions would have different characteristics, such as size and morphology, compared to the inclusions formed during high temperature interaction. In view of these aspects, some of the individual inclusions found in zone 1 of the samples 4 to 6 (Fig. 5) might have formed during quenching as their characteristics, such as size and morphology (Table 2 and Fig. 9), differ from those in zone 2.

5. Conclusions

Inside a quartz tube, a piece of Al was brought in contact for 1, 5, 30, 60 s with liquid Fe containing different $\underline{Q}$ levels at 1 600°C (160 to 1 800 ppm $\underline{Q}$). The purpose was to investigate the formation and characteristics of inclusions shortly after the deoxidation stage. Microscopic investigations of the samples highlighted the following:

(1) Al_2O_3 inclusions were found in the Fe–Al reaction zone, between the position of the initial Fe/Al interface and that of the diffusion front.

(2) Large angular Al_2O_3 inclusions with traces of Si and Fe were observed near the initial Fe/Al interface, likely resulting from heterogeneous nucleation of Al_2O_3 on FeO_x and/or SiO_2 inclusions and from reduction of these oxides by Al.

(3) In the samples with high $\underline{Q}$ content, spherical and angular individual inclusions were found near the diffusion front. Aggregates of fine inclusions resulting from collisions were numerous further away from the diffusion front. It was suggested that the former were formed upon cooling of the Fe–Al–O melt located between the diffusion and reaction fronts, whereas the latter arose from homogeneous nucleation at the reaction front, once critical supersatura-

tion is reached during high temperature interactions.

(4) With lower $\underline{Q}$ content, the amount of inclusions decreases and faceted inclusions are dominant among the morphologies, owing to lower supersaturation conditions.

(5) Inclusion nucleation and growth occurred in a confined supersaturated zone where the amount and the mass transport of $\underline{Q}$ were limited, providing conditions for the formation of short-shaped inclusions.

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