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Transient Evolution of Inclusions during Al and Ti Additions in Fe-20 Mass pct Cr Alloy

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Abstract: The transient evolution of inclusions during Al and Ti additions in a Fe-20 mass pct Cr alloy was investigated using polished cross sections and electrolytic extraction. After Al addition, the evolution of Al_2O_3 -based inclusions based upon the area and particle size passed through the following three main stages with time: Particle agglomeration, inclusion floating, and a slow decrease of the remaining Al₂O₃-based inclusions. Titanium wire was fed into the steel at the end of the floating stage after Al addition when the Ostwald ripening process was finished. Immediately after Ti addition, the transient phase of Ti oxide was readily generated on the existing Al₂O₃-based inclusion and disappeared due to Al reduction as time progressed. The formation of the transient TiO_x phase was affected by the low disregistry between Al_2O_3 and TiO_x and the local Ti supersaturation, which cannot be predicted by the equilibrium relations of Ti-O-N or Ti-Al-O in the high-Cr-containing melt. Because of the local supersaturation of dissolved [%Ti] and [%N] shortly after Ti addition, TiN associated with existing inclusions and three types of individual TiN including single cubes, twinned inclusions, and clusters were identified. In order to minimize the Ti loss caused by the formation of Ti-rich zones during the transient stages, the removal of large Al₂O₃-based particles including aggregates, clusters, and flower-shaped inclusions should be promoted by stirring before Ti addition. After Ti addition, Brownian and turbulent were the major factors affecting the collision of particles smaller than the threshold of 2.7 µm. The agglomeration of inclusions larger than this threshold was mainly dominated by turbulent and Stokes' collisions.

Keywords: Al₂O₃ inclusion; Ti oxide; inclusion evolution; electrolytic extraction; thermodynamic calculation; three-dimensional investigations

1. Introduction

Aluminum and titanium are both important alloying elements in steels. Aluminum provides one of the most economical and efficient approaches for deoxidation in steels. However, the Al_2O_3 inclusions formed as deoxidation products are likely to deteriorate the steel castability due to their high hardness and high melting point [1,2]. Titanium has a strong affinity with carbon and nitrogen and, therefore, is commonly added into steels, as a stabilizing alloying element, to improve the mechanical properties via grain refinement during hot rolling. In particular, fine TiN and TiO_x as second-phase particles with a dispersive distribution can raise the percentage of equi-axed cast structure in steels [3–6]. On the other hand, these Ti-bearing particles including TiN, TiO_x, and TiO_x–Al₂O₃ are also the possible cause of deposits [7–13]. Thus, the presence of titanium in liquid steel, unfortunately, is a risk factor for clogging in submerged nozzles during continuous casting.

There are two aspects embodied in the complexity of the transient inclusion evolution during Al and Ti additions in Cr-rich stainless steels.

First, the thermodynamic relation between aluminim and titanium in stainless steels containing high amounts of chromium is still not yet fully clarified due to the lack of accurate thermodynamic information. On one hand, there is an ongoing debate about the presence of the liquid region in the Fe–Ti–Al–O equilibrium phase diagram. Ruby-Mayer [14] employed the multiphase equilibrium code CEQCSI (chemical equilibrium calculation for the steel industry) based on a statistical thermodynamic cell model to calculate the equilibrium phase diagram, in which a liquid region was present between the Ti₂O₃ and Al₂O₃ stable regions at 1793 K. In a study investigating the thermodynamic relation between aluminim and titanium in liquid iron at 1873 K, Kim et al. [15] constructed a stability diagram for Al₂O₃, Ti₂O₃, and Ti₃O₅ phases as a function of dissolved aluminum, titanium, and oxygen contents in liquid iron. With the aid of FactSage software, Jung et al. [16] predicted the existence of a liquid oxide inclusion phase in the Fe–Al–Ti–O inclusion diagram. Kang and Lee [13,17] reassessed oxide stability diagram in the Fe–Al–Ti–O system by using CALPHAD (calculation of phase diagram) approach and further pointed out that liquid region in the stability diagram could be refined by decreasing thermodynamic stability of liquid Al₂O₃-TiO₂-Ti₂O₃ system. Nonetheless, in thermodynamic studies by Wang et al. [18], Marie-Aline et al. [19] and Masuura et al. [20], Al₂O₃, Ti₂O₃, Ti₃O₅, and Al₂TiO₅ were stable phases and the liquid phase was not taken into account. On the other hand, it has been noted that the effect of chromium on the thermodynamic description of the Fe-Al-Ti-O-N system cannot be neglected. A study conducted by Lee et al. [21] revealed that the deoxidizing power of aluminum in high-alloy melts becomes weaker than that in pure iron. Moreover, various equilibration methods including Sievert's method [22] and the sampling method described in [15], combined with various measurement techniques such as the galvanic cell technique [23] and the metal-nitride-gas equilibration technique [24], have been adopted to determine the thermodynamic interactions of chromium with aluminum [25–27], titanium [24,28,29], oxygen [30], and nitrogen [28,31] with varying Cr concentrations.

Second, although various factors including the sequence of alloy addition [18,20,32,33], titanium source [34], titanium/aluminum ratio [35], and element contents [19,36–39] have been examined their impacts on the inclusion behaviors during Al and Ti additions, several fundamental questions remain about the evolution mechanism of the inclusion behaviors. In a laboratory study of deoxidation by Al and Ti at 1873 K, Nagata et al. [40] found that alumina particles were formed with an acicular shape at first and gradually changed to clusters of granular Al₂O₃ spheres, but the inclusion characteristics were, nevertheless, not significantly affected by the subsequent Ti feeding. However, Kunisada and Iwai [41,42] pointed out that along with the existence of angular oxide products during Al and Ti additions, dual-phase oxides consisting of TiO_x and Al_2O_3 were observed after Ti addition. As argued by Masuura et al. [20] and Wang et al. [18,34,35], the inclusion chemistry after Ti addition shifted back to the thermodynamically stable Al₂O₃ region, but the change of the particle morphology from spherical inclusions to polygonal inclusions resulting from the transient reactions after Ti addition remained. Moreover, the presence of Ti oxides during the transient stages after Ti addition was reported by previous studies by Masuura et al. [20] and Wang et al. [34,35]. Aside from the traditional metallographic characterization of Al-Ti-O inclusion behaviors by investigating the two-dimensional features, various methods including the focused-ion-beam method [43], confocal scanning laser microscopy [37], and electrolytic extraction [33] have been adopted to investigate the inclusion behaviors in Al-killed Ti-bearing steels. However, the existing literature on the transient products has suffered from a lack of direct and systematic descriptions of the three-dimensional features of temporary titanium oxide inclusions during the transient stages after Ti addition, especially when they were associated with existing alumina; thus, the effect of the existing Al_2O_3 morphology on transient reactions after Ti addition has so far been unclear.

Additionally, the transient behaviors of TiN during Al and Ti additions remains poorly understood. A previous study by Wang et al. [34] showed that TiN inclusions could still be more frequently observed, even when the nitrogen content was controlled to less than 0.0019 mass pct with various Ti contents ranging from approximately 0.05 mass pct to 0.35 mass pct. Thus, for dual-phase Ti-bearing particles

with oxide cores covered by TiN, only the inner phase was measured for inclusion characterization during the two-dimensional investigations in the previous work [20,34]. In the case of Ti-stabilized stainless steel containing 0.025 mass pct N, Yin et al. [44] found that three different three-dimensional morphologies of TiN inclusions, including single particles, twinned particles, and clusters, were extracted from the sample after Ti addition.

In light of the complexity of inclusion behaviors during Al and Ti additions, further research into the transient evolution of inclusions in high-chromium melts is required. In the current work, laboratory experiments in a Fe-20 mass pct Cr alloy were carried out to clarify the evolution mechanisms of inclusion behaviors by taking samples at various times during Al and Ti additions. Electrolytic extraction was employed to extract intact inclusions from the steel matrix, allowing three-dimensional investigations of inclusion characteristics including composition, morphology, and structure during the transient stage after Ti wire feeding. The thermodynamic calculation in the Fe-20 mass pct Cr–Al–Ti–O–N system was performed to predict the formation of inclusions in stainless steels. The agglomeration mechanism of inclusions after Ti addition was also discussed in this paper.

2. Materials and Methods

2.1. Experimental Procedure

In order to obtain the Fe-20 mass pct Cr alloy, high-purity electrolytic iron (~99.99%) and superalloy degassed chromium (~99.8%) were melted in a high-frequency induction furnace (Jinzhou electric furnace Co., Ltd., Jinzhou, China) under Ar atmosphere. The original oxygen content and nitrogen content in Fe-20 mass pct was approximately 0.0113% and 0.0009%, respectively. Subsequently, approximately 450 g of Fe-20 mass pct Cr steels were melted in a MgO crucible (40 mm inner diameter, 48 mm outer diameter, and 130 mm depth) at 1873 K in a Si-Mo high-temperature tube furnace. The schematic of the experimental furnace is shown in Figure 1. Two sets of experiments (No. 1 and No. 2) were carried out under Ar atmosphere. After melting, Fe₂O₃ powders (99.999 pct) were added to the melt to adjust oxygen content to approximately 0.03%. As depicted in Figure 2, the Al alloy (>99.9%) was added into the molten steel after 30 min stabilization of the melt in experiments No. 1 and No. 2, while Ti wire (>99.5%) was added into the melt in experiment No. 2 at 20 min after Al addition. In experiment No. 1, the first sample was taken before Al addition, and other five samples were collected at 5 min, 10 min, 15 min, 20 min, and 30 min after Al addition. In experiment No. 2, the first sample was taken before Ti addition, and other three samples were collected at 2 min, 5 min, and 10 min after Ti addition. All steel samples in the present work were taken by using quartz tubes and quenched into water at room temperature.



Figure 1. Schematic of the experimental furnace.



Figure 2. Melting and sampling sequences of the current experiments.

2.2. Chemical Analysis

Each steel sample collected at different sampling locations was machined into three specimens, as shown in Figure 3. The specimen A was analyzed to obtain the chemical composition of steel. In this work, the aluminum and titanium contents were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, NCS, Beijing, China). Inert gas fusion-infrared absorptiometry (LECO, St. Joseph, MI, USA) was applied to measure the total oxygen and nitrogen contents of steel. The results are listed in Table 1.



Figure 3. Schematic of the zones used for the investigation of inclusions.

Table 1. Measured composition of steels samples (wt%).

Experiment No.	Time	Al	Ti	0	Ν
1	Before Al addition	-	-	0.0312	0.0018
	5 min after Al addition	0.082	-	0.0252	0.0020
	10 min after Al addition	0.068	-	0.0107	0.0021
	15 min after Al addition	0.056	-	0.0064	0.0022
	20 min after Al addition	0.039	-	0.0054	0.0023
	30 min after Al addition	0.053		0.0047	0.0023
2	20 min after Al addition	0.048	-	0.0067	0.0016
	10 min after Ti addition	0.055	0.15	0.0056	0.0024

2.3. Inclusion Characterization

For two-dimensional inclusion analysis, one-half of a vertical section cut from the center of specimen B was polished. Afterwards, the two-dimensional characteristics (composition, number, and

size distribution) of inclusions were determined using an automated inclusion analysis system (ASPEX Explorer, 20 kV, Thermo Fisher Scientific, Waltham, MA, USA). The scanning area of each sample was approximately 10 mm². The working magnification and distance were set at ×450 and 18 mm, respectively. Inclusions larger than 1 μ m in each sample were analyzed in the backscatter electron imaging mode. In this work, the area fraction (AF) and number density (ND) were used to describe the two-dimensional characteristics of non-metallic inclusions, which can be defined by Equations (1) and (2), respectively:

$$AF = \frac{A_{\text{inclusion}}}{A_{\text{total}}},\tag{1}$$

$$ND = \frac{N_{inclusion}}{A_{total}},$$
 (2)

where AF is the area fraction of inclusions (ppm), $A_{inclusion}$ is the total area of detected inclusions (μm^2), and A_{total} is the total analysis area (mm^2); ND is the number of inclusions per unit area (per mm^2) and $N_{inclusion}$ is the number of detected inclusions within the area of A_{total} .

To manifest the three-dimensional morphologies, non-metallic inclusions were extracted by dissolving specimen C in a 10%AA (10 v/v% acetylacetone-1 wt/v% tetramethylammonium chloride-methanol) electrolyte. Figure 4 presents the schematic of the electrolysis cell. The steel sample was the anode, while a platinum loop was used as the cathode. The current density and temperature during the extraction were set at 40–50 mA·cm⁻² and 0–5 °C, respectively. Approximately 0.15 g of metal was dissolved in the electrolyte with an electrolysis time of 6 h. After extraction, the solution was filtered through a polymer filter membrane with 0.2 μ m openings. Subsequently, the membrane was mounted on an aluminum stub and sputter coated with gold. The three-dimensional characteristics of the inclusions were investigated using scanning electron microscopy (SEM, Supra 55, Zeiss, Oberkochen, Germany) combined with energy dispersive spectroscopy (EDS, INCA, Oxford, UK). At least 30 typical inclusions were observed using secondary electron image mode (instrument conditions: 10~15 keV, 18 mm working distance, and lithium drifted silicon detector at 45 deg elevation).



Figure 4. Schematic illustration of apparatus used for electrolytic extraction.

3. Results and Discussion

3.1. Two-Dimensional Characteristics of Inclusions after Al Addition

By scanning an area of approximately 10 mm^2 , inclusions larger than $1 \mu \text{m}$ were characterized using ASPEX. Figure 5 shows the area fraction (AF) and mean size of inclusions after Al addition. Since the AF of inclusions after melting was approximately 0.87 ppm, the influence of existing after melting on the inclusion behaviors after Al addition could be ignored. Meanwhile, the size statistical analysis after Al addition as a function of holding time is presented in Figure 5. The solid symbols in Figure 6 represent the number density and mean size of each size group. The distribution curves based on the lognormal distribution model were also plotted in the figure, which are consistent with the experimental observations. On the basis of the statistical data collected in Figures 5 and 6, the evolution of inclusions after Al addition was classified into three stages as follows:



Figure 5. Evolutions of AF and average size of inclusions after Al addition.



Figure 6. Size distribution of inclusions at each holding time after Al addition.

(1) In the early stage after Al addition, the AF of inclusions decreased dramatically, while the opposite trend was observed for inclusion size. Notably, the percentage of inclusions in the size range of $5 \sim 10 \,\mu$ m increased with time, revealing the effect of particle collision and agglomeration on inclusion growth within the first stage. Consequently, the average size of inclusions reached a peak value of approximately 4.2 μ m at the end of stage I (10 min after Al addition).

(2) From 10 to 20 min after Al addition, the statistical results including the AF and average size of Al_2O_3 inclusions exhibited a downward trend. With rapidly decreasing inclusions in the size range of 5~10 µm due to the removal by preferential floatation, the mean size of inclusions declined to approximately 3.7 µm at the end of stage II. Therefore, the inconsistency between the AF and particle size during the first two stages after Al addition indicates that the floatation of particles was accompanied by the dramatic aggregation of inclusions in the first stage and then became dominant in the next stage.

(3) Within stage III, the AF and ND of inclusions experienced a continuous but slow decrease, whereas no significant changes in the particle size were observed.

3.2. Three-Dimensional Characteristics of Inclusions after Al Addition

The electrolytic extraction technique offers an effective means of elucidating the three-dimensional characterization of Al₂O₃-based inclusions by eliminating the interference associated with the steel

matrix. Figure 7 shows the three-dimensional morphologies of typical inclusions in the sample with a holding time of 10 min after Al addition. Aggregated, faceted, and plate-like inclusions were identified among the dominant morphologies. It is also noted that at this moment, a neck, resulting from the sintering process and leading to the densification of the aggregate, was found between the colliding inclusions, as shown in Figure 7c. This observed result indicates that the diffusion of pseudomolecules was not yet completed at the end of the first stage after Al addition. Additionally, a small number of coral-like clusters were extracted from the steel sample (see Figure 7f). By contrast, in an Al-deoxidation experiment performed in the melt containing 0.293 mass pct Al with an initial O content = 297 ppm, Yang et al. reported [45] that there were plenty of spherical and dendritic inclusions within 9 min after Al addition under no-stirring conditions.



Figure 7. Three-dimensional morphologies of inclusions with a holding time of 10 min after Al addition: (**a–c**) Aggregated inclusions; (**d**) faceted inclusion; (**e**) plate-like inclusion; (**f**) dendritic inclusion.

In view of the grain growth, the morphology of Al_2O_3 inclusions depends on the growth conditions of the particles, i.e., the supersaturation degree of the dissolved Al and O contents, holding time, liquid flow conditions, grain surface roughness, and impurity particles [46,47]. Upon increasing the initial supersaturation in the melt, the generation sequence of alumina inclusions is polyhedral first, then plate-like, dendritic, and spherical successively [48] on the basis of the classification of inclusion morphologies by Braun et al. [46] and Dekkers et al. [47]. Therefore, in a previous Al deoxidation study under the condition of higher supersaturation by Yang et al. [45], unstable growth along with variable supersaturation gradient directions was the leading cause of the dendritic particles, whereas the presence of spherical Al_2O_3 -based inclusions was due to the coarsening and breaking of dendrite arms [49]. In turn, the polyhedral and plate-like particles obtained in the current work are the consequences of the low supersaturation of dissolved Al and O. With respect to dendritic inclusions observed in samples, their formation may be likely attributed to a local high supersaturation degree after Al addition.

In the sample with a holding time of 20 min after Al addition, aggregated and single inclusions were by far the dominant morphologies. Looking at Figure 8a–d, it is apparent that the surface contours of inclusions became smoother due to the Ostwald-ripening effect [46] (the diffusion of pseudomolecules). That is, small inclusions and the sharp edges of inclusions were dissolved, whereas larger inclusions grew. The three-dimensional features of the Al₂O₃-based particles in Figure 8 show that Ostwald-ripening can be finished within 20 min, which is in agreement with Yang's findings [45]. The dendritic morphology of the particles was hardly observed in the sample at 20 min after Al

addition. In addition to the floatation of inclusions, Van Ende et al. [50] reported that the dendritic Al_2O_3 inclusion that usually appeared in the early deoxidation stage could subsequently change into a polyhedral shape with the decrease of supersaturation. Considering the smaller rising velocity and the transformation from dendrites, small polyhedral inclusions, therefore, could be observed long after Al addition.



Figure 8. Three-dimensional morphologies of inclusions extracted from the sample with a holding time of 20 min after Al addition: (**a**–**d**) Aggregated inclusions; (**e**) faceted inclusion; (**f**) plate-like inclusion.

3.3. Two-Dimensional Inclusion Characteristics after Ti Addition

Since titanium is an expensive alloying element, in commercial production, titanium is commonly added after Al deoxidation to diminish the Ti loss due to oxidation [51]. In this study, the Ti wire was fed into the melt at 20 min after Al addition, when most of the Al₂O₃-based inclusions had reached the melt surface and the Ostwald-ripening had almost been completed. Figure 9 shows the changes of the AF and average size of inclusions after Ti addition. As shown in Figure 9, the evolution of inclusion behaviors after Ti addition consisted of two main stages. (I) Within 5 min after Ti addition, the AF of inclusions first peaked at 2 min and then decreased drastically. The changes of the mean size of inclusions were approximately synchronous with those of the AF of inclusions. (II) Thereafter, no considerable changes in the AF were observed over time in contrast with the particle size, which gradually decreased.



Figure 9. Evolutions of AF and average size of inclusions after Ti addition.

Figure 10 shows the particle size distribution of the inclusion population as a function of holding time after Ti addition. In the figure, the open symbols correspond to the number density and mean size of each size group, which are in reasonable agreement with the fitted curves based on the lognormal distribution model. As presented in Figure 9, the value of ND at each holding time passed through a peak and tended towards zero with increasing inclusion size. In other words, the number of inclusions in the size range of 2–3 μ m was much larger than the number of inclusions in the other size distributions. Besides, the value of ND experienced an increase shortly after Ti addition, followed by a rebound at a holding time of 5 min after Ti addition.



Figure 10. Particle size distribution of inclusions after Ti addition.

Distributions of the inclusion composition during Al and Ti additions are shown in Figure 11. Since the nitrogen content in oxide–nitride duplex inclusions cannot be quantitatively determined by ASPEX system [52], the inclusion composition data were collected in the Mg–Al–Ti system. Previous studies [53,54] have confirmed that small amounts of Mg and Al can lead to the generation of magnesium aluminate spinel in liquid steel, and thus, the magnesium-containing oxide phase in inclusions was identified as MgO·Al₂O₃. Accordingly, the dashed line in the figure corresponds to the mass ratio of titanium and aluminum in xMgAl₂O₄·yAl₂TiO₅.

Before titanium addition, the inclusion compositions were mainly concentrated close to the Al₂O₃ corner of the MgO–Al₂O₃ binary system, as visible in Figure 11a. According to ASPEX results, the Mg content in inclusions, which was normalized in the Mg–Al–Ti system ([Mass pct Ti] = 0) was 3.97% on average and varied from 2.22% and 23.88% before Ti addition, indicating that a little MgO was formed in inclusions because of reactions between soluble Al and MgO in the crucible. It should be pointed out that, according to the FactSage predictions, the Al₂O₃-based inclusions can be fully transformed into spinels when the Mg content in the Mg–Al system exceeds approximately 18.33%. Thus, in addition. Figure 11b shows a dramatic increase in the Ti content in inclusions at a holding time of 2 min after Ti wire feeding. In addition, there were a few smaller inclusions ($\leq 3 \mu m$) located close to the dashed line in the diagram but no pure titanium-containing particles were observed. This suggests the possibility of the discrete Al₂TiO₅ particle after Ti feeding.

Figure 12 exhibits the two-dimensional composition mappings of typical Ti-bearing inclusions at 2 min after Ti addition. The mapping pattern in Figure 12a confirms the inference about the presence of Al_2TiO_5 from ASPEX results. As can be seen from Figure 12b–d, the zones of concentrated Ti were present in association with Al_2O_3 -based body. Taken together, these results clearly point to the existing Al_2O_3 -rich inclusions providing the major heterogeneous nucleation sites for the Ti-bearing phase.



Figure 11. Inclusion composition map during Ti addition: (**a**) 20 min after Al addition; (**b**) 2 min after Ti addition; (**c**) 5 min after Ti addition; (**d**) 10 min after Ti addition.



Figure 12. Two-dimensional composition mapping patterns of Ti-bearing inclusions at 2 min after Ti addition: (a) Mapping of discrete Al₂TiO₅; (b) mapping of Al₂O₃ wrapped by TiO_x; (c) mapping of TiO_x associated with irregular Al₂O₃-based polygon; (d) mapping of TiO_x associated with Al₂O₃ aggregate.

In the steel sample taken at 5 min after titanium wire feeding as shown in Figure 11c, the chemistry of inclusions shifted back towards MgO-Al₂O₃ binary system, implying that the Ti in inclusions was

re-dissolved into the bulk steel. Consequently, the critical factor behind the rapid change in the Ti content is the presence of the Ti-bearing phase that functions as a transient product after Ti addition.

With increasing holding time, there were slight increases in the contents of Ti and Mg as presented in Figure 11d. As a result, the mean inclusion chemistry contained up to approximately 18 mass pct and 12 mass pct Ti (in Mg–Al–Ti system) at the ends of stage I and stage II after Ti addition, respectively. Strikingly, Matsuura et al. [20] reported that at 4 min after Ti addition, approximately 5 to 20 mol% Ti could be detected in the Al–Ti deoxidation experiments performed in IF steels ([mass pct Ti] = 0.12). This discrepancy can be partially attributed to the influence of the melt composition, including from Cr, N, and Mg. A second possible explanation for this difference is that the inclusion chemistry in the previous work was normalized in the Ti–Al–O system, rather than in the Ti–Al–Mg system used in this study. Third, the phase of TiN were not distinguishable according to the inclusion chemistry in this study because the typical particles in the previous work were Al–Ti–O oxides covered by a rectangular nitride phase in lieu of the irregular distribution of Ti-rich zones associated with Al₂O₃-based inclusions shown in Figure 11, and thus the Ti content determined by ASPEX represents the whole content in inclusions.

3.4. Three-Dimensional Characteristics of Inclusions after Ti Addition

One principal aim of this work is to establish a better understanding of the impact of existing Al₂O₃-based inclusions on the transient inclusion evolution during Ti addition. The electrolytic extraction technique provides revealing insight into the actual size and morphology of inclusions, with emphasis on the distribution of the Ti-bearing particles on the surface of Al₂O₃-based inclusions and the joining of individual particles during agglomeration.

It should first be pointed out that even though the N content was controlled to approximately 0.0020 mass pct, individual TiN inclusions were still identified after extraction from steel samples. As shown in Figure 13a–c, on the basis of the three-dimension morphologies, the individual TiN particles at 2 min after Ti addition can be classified into three general types: Single cubes, twinned inclusions, and clusters. In Figure 13a, a single TiN inclusion lying on the surface of the membrane exhibited a cubic habit. Twinned TiN with an irregular shape was also observed, as presented in Figure 13b, which is likely to originate from the growth of two nucleates [55]. Furthermore, the extracted TiN clusters comprised of sub-micron Ti-bearing particles (Figure 13c) were significantly smaller than Al₂O₃-based aggregates before Ti addition (Figure 8). The present classification of TiN based upon their three-dimensional morphologies is similar to that applied in stainless steel containing 0.307 mass pct Ti and 0.0251 mass pct N (Figure 13d–f) [44]. By comparison, the typical TiN inclusions observed in the high-N liquid steel. This difference is probably due to the excessive concentrations of Ti and N for TiN formation in the previous work.

The three-dimensional morphologies of typical Ti-containing particles associated with Al_2O_3 -based inclusions at 2 min after Ti addition are illustrated in Figure 14. In contrast to the sharp edges of TiN aggregates (Figure 14c), the curved boundary lines of these Ti-rich regions in Figure 14 combined with EDS results indicate the existence of TiO_x . However, considering the interference from the Al_2O_3 matrix, it is exceedingly difficult to identify the accurate form of Ti in these regions according to the irregular inclusion shape or the semi-quantitative EDS analysis. So, the region of Ti-bearing particles adhering on the surface of the Al_2O_3 -based body was simply considered to be the Ti-rich zone (TZ) during three-dimensional investigations.



Figure 13. Three-dimensional morphologies of TiN inclusion after Ti addition: (a-c) TiN observed in this work with a holding time of 2 min after Ti addition; (d-f) TiN observed in high N steels.

Figure 13a–c exhibits the three-dimensional morphologies of Ti-rich zones associated with Al₂O₃-based clusters. This type of Ti–Al-containing inclusion may be the result of the growth of clusters by collision with separate inclusions or with other clusters during their ascension to the liquid surface (Figure 14a,b). Figure 14c is an enlarged partial view of the Ti-rich zone shown in Figure 14b. As seen from Figure 14c, a sintering process, driven by minimization of the surface energy [56], took place between Ti-rich particles and the Al₂O₃-based body, which led to densification of the aggregate.

Figure 14d–f shows the three-dimensional features of the Ti-bearing Al₂O₃-based aggregates after Ti addition. The Al₂O₃-based aggregate originated from the agglomeration of inclusions. Because of the diffusion of pseudomolecules, the aggregating boundary line almost disappeared, and the surface of the aggregate became smoother. After Ti feeding, small Ti-rich zones were readily observed on the surface of existing aggregates, but the sites of these zones tended to be random and unpredictable (Figure 14d–f). Moreover, larger aggregates appeared to provide more advantageous sites for Ti-rich zones (Figure 14d).

As shown in Figure 14g,h, the experimental results obtained from the three-dimensional investigations revealed the presence of polygonal inclusions in association with the Ti-bearing particles after Ti wire addition. There were small concentrated Ti zones scattered on the body of the polyhedral inclusions. This type of Ti–Al-containing inclusion might have been attributed to the collision between the Al₂O₃-based polyhedron and small-sized Ti-containing particles or to the simple generation of Ti-bearing particles onto the polyhedron.

The plate-like Al₂O₃-based inclusions can, likewise, provide a direct site for Ti-based particle formation. At a holding time of 2 min after Ti wire feeding, for an individual plate-like inclusion as depicted in Figure 14i, titanium was concentrated around the periphery rather than in the interior. Also, the Ti-rich zone was frequently located at the end of a single elongated platelet (i.e., bar shape during two-dimensional investigations) as shown in Figure 14j. Additionally, the outer edges of the base and the plate-like arms of flower-shaped Al₂O₃-based inclusions could act as nucleation sites for Ti-rich particles (Figure 14k,l).

As presented in Figure 14, compared with small aggregates with smooth surface contours and single polyhedral inclusions, larger Al₂O₃-based inclusions, including clusters, aggregates, and some flower-shaped inclusions, can provide favorable sites for Ti-rich zones during the transient stage. These newly produced Ti-bearing particles may increase the Ti loss because of the adsorption of refining slag in practical production. Hence, along with the steel chemistry (Al, Ti, and O contents) [39], the

morphology of existing Al₂O₃-based inclusions is a contributing factor affecting the Ti yield. This means the large Al₂O₃-based particles including larger aggregates, clusters, and some flower-shaped inclusions, should be eliminated by stirring to the extent possible before Ti addition.



Mass%: Al: 35.02 Ti: 14.37 O:50.61

Mass%: Al:38.64 Ti:15.35 O:46.01

Mass%: Al: 34.58 Ti: 14.88 O:50.54

Figure 14. Three-dimensional morphologies of Ti-rich particles in association with Al_2O_3 -based inclusions with a holding time of 2 min after Ti addition: (**a**–**c**) Ti-rich zones associated with clusters; (**d**–**f**) Ti-rich zones associated with aggregated inclusions; (**g**,**h**) Ti-rich zones associated with faceted inclusions; (**i**–**l**) Ti-rich zones associated with plate-like inclusions.

Figure 15 exhibits the three-dimensional morphologies of Ti-rich zones associated with Al₂O₃-based inclusions at 10 min after Ti feeding. Note that Al₂O₃-based clusters containing Ti-rich zones almost disappeared long after Ti feeding. This is due to the preferential floatation of larger inclusions. As depicted in Figure 15, aggregated, faceted, and plate-like inclusions with Ti-rich zones were identified among the dominant morphologies. Even though no nitrogen was detected in inclusions by EDS, compared with the irregular boundary lines of the Ti-rich zones at 2 min after Ti addition, the sharp

edges and right angles of these zones, shown in Figure 15, provided an indication of the TiN phase long after Ti feeding. Moreover, most of the Ti-rich zones in Figure 15 were in sub-micrometer.



Figure 15. Three-dimensional morphologies of Ti-rich particles in association with Al_2O_3 -based inclusions with a holding time of 10 min after Ti addition: (**a**,**b**) Ti-rich zones associated with aggregated inclusions; (**c**,**d**) Ti-rich zones associated with plate-like inclusions; (**e**,**f**) Ti-rich zones associated with faceted inclusions.

3.5. Thermodynamic Conditions in the Fe-20 Mass pct Cr-Al-Ti-O-N System

The calculated deoxidation equilibria for Al in high-Cr stainless steel and pure iron at 1873 K by using thermodynamic software FactSage 7.0 (ThermFact LTD, Montreal, QC, Canada and GTT-Technologies, Herzogenrath, Germany) is shown in Figure 16. The equilibrium curve in the Fe-20 mass pct Cr–Al–O system is higher than that in pure iron, suggesting that the deoxidation power of aluminum in stainless steel is reduced by the addition of chromium. One deeper reason for this difference may be the strong attraction between chromium and oxygen ($e_O^{Cr} = -0.032$ [30]), particularly in a Fe–Cr alloy containing up to 20 mass pct Cr.



Figure 16. Equilibrium relationship between Al and O for Al₂O₃ formation at 1873 K.

Figure 17 shows the equilibrium relationship between Ti and N for TiN formation in the Fe-20 mass pct Cr–Ti–N–O melt. According to the thermodynamic prediction, the contents of titanium and

nitrogen play a crucial role in the formation of TiN in molten steel and, therefore, should be controlled at levels below the equilibrium values to avoid the generation of stable TiN. Within the range of Ti content studied here, the concentrations of Ti and N in the bulk melt containing 0.0020 mass pct N at 1873 K are located in the area below the Ti–N equilibrium curve. Hence, it is believed that the observed TiN in this work was not a thermodynamically stable compound. Additionally, in the case of [mass pct N] = 0, Ti₂O₃ becomes dominated when the Ti content exceeds a threshold of approximately 0.21% in the Fe-20% Cr–Ti–O melt and this threshold slightly increased with the nitrogen content.



Figure 17. Equilibrium relationship between Ti and N for TiN formation at various oxygen contents at 1873 K.

The stability diagram in Fe-20 mass pct Cr–Al–Ti–O melt at 1873 K was calculated by using FactSage 7.0 with the FactPS, FToxid, and FSstel databases, as presented in Figure 18. The experimental data listed in Table 1 are located in the region of Al_2O_3 , indicating that Al_2O_3 was the thermodynamically stable phase in the current deoxidization tests. In this figure, there lies a liquid region among Al_2O_3 , Ti_2O_3 , and Ti_3O_5 at 1873 K, which narrows to disappearance with increasing [mass pct Al]. Furthermore, the value of the critical Ti content between the Ti_2O_3 and Ti_3O_5 regions slightly decreases with increasing Al content. Nevertheless, the threshold of the Ti content between the Ti-bearing inclusion region and the stable Al_2O_3 region shows an opposite trend. That is, with increasing Ti addition, more aluminum should be added into the liquid steel to prevent Ti oxidation.



Figure 18. Stability diagram of inclusions in Fe-20 mass pct Cr-Al-Ti-O melt.

3.6. Formation Mechanism of Transient Inclusions after Ti Addition

Note that various non-stable products were observed during two-dimensional and three-dimensional investigations, indicating that the melt shortly after Ti addition was a non-equilibrium thermodynamic system. Therefore, the equilibrium calculations in Section 3.5 are not suitable for the prediction of inclusion behaviors during the transient stage.

With respect to Ti oxide observed shortly after Ti addition, according to the observed findings from the two-dimensional and three-dimensional investigations, there are two possible interpretations for their formation:

First, discrete TiO_x particles can be directly formed by reactions between dissolved but not dispersed titanium and soluble oxygen, which can be expressed as follows:

$$[Ti] + x[O] = TiO_x (s), \tag{3}$$

$$[Ti] + 2[Al] + 5[O] = Al_2 TiO_5 (s).$$
(4)

The two-dimensional statistical data and three-dimensional features revealed a small number of discrete TiO_x or Al_2TiO_5 particles after Ti feeding. It is noted that in this mechanism, the source of oxygen for TiO_x formation is offered by the current high-Cr-containing melt, wherein the equilibrium soluble oxygen concentration estimated by FactSage was approximately 3 ppm. These findings suggested a limited impact of the first mechanism by reactions (3) and (4) on the transient product generation.

The second formation mechanism of Ti oxide inclusions is that, shortly after Ti addition, TiO_x can be generated onto the existing Al_2O_3 -basedinclusions. Two factors may be linked to this mechanism:

(1) Due to the low lattice disregistry between alumina and titanium oxide [57], the existing alumina can act as a heterogeneous nucleation core of titanium oxide.

(2) Another contributing factor is the reactions between the local high titanium and existing Al_2O_3 -based inclusions, which can be understood by the following reactions:

$$3[Ti] + 5(Al_2O_3)_{inclusion} = 3(Al_2TiO_5)_{inclusion} + 4[Al],$$
(5)

$$3[Ti] + x(Al_2O_3)_{inclusion} = 3(TiO_x)_{inclusion} + 2x[Al].$$
(6)

On the basis of the stability diagram of inclusions seen in Figure 18, the occurrence of two mechanisms is, in essence, a result of local Ti supersaturation after Ti feeding but the existing Al_2O_3 -based inclusion can provide the site and oxygen for Ti-containing oxides through the second manner. The two-dimensional and three-dimensional characteristics of inclusions after Ti addition highlighted the direct effects of the second mechanism on the generation of TiO_x during the transient stage. It can be concluded that the low lattice disregistry between alumina and titanium oxide and the local Ti supersaturation play leading roles in the formation of transient TiO_x . Hence, for the minimization of Ti loss during the transient stage, the removal of existing Al_2O_3 -based particles, especially larger aggregates, clusters, and some flower-shaped inclusions, should be enhanced before Ti addition.

The newly produced TiO_x phase observed immediately after Ti feeding was, by nature, not thermodynamically stable; thus, the Ti in TiO_x phase was eventually re-dissolved into the molten steel by Al reduction according to the following reaction:

$$2x[AI] + 3(TiO_x)_{inclusion} = x(AI_2O_3)_{inclusion} + 3[Ti].$$
(7)

Consequently, the Ti content in inclusions underwent a rapid change after Ti addition. Notably, the inclusion chemistry displayed no significant changes during stage II after Ti feeding. It is concluded, therefore, that the transient evolution of most TiO_x can be finished within 5 min after titanium feeding.

Considering the N content of approximately 20 ppm and the transient non-uniform nature of soluble Ti in the melt shortly after titanium wire feeding, the generation of TiN by the local

supersaturation of dissolved [%Ti] and [%N] that exceeded the equilibrium value was very likely. However, long after Ti feeding, multiphase inclusions containing TiN and Al₂O₃ became dominant, whereas the observed TiN was not the stable phase in the current thermodynamic system, as predicted in Figure 17. Hence, the observed TiN in the sample was expected to be the secondary inclusions formed during sampling. Rapid cooling of the liquid steel primarily provided high supersaturation with respect to Ti and N and uniform growth conditions. In addition, the existing inclusions in the melt, which have low lattice disregistry with TiN (see Table 2), could act as heterogeneous nucleation cores for TiN, thereby promoting the nucleation of TiN during sampling. It should be pointed out that, due to the comparably fast solidification, the TiN formed on existing inclusions during sampling had no time to grow and, hence, maintained sub-micrometer scale as presented in Figure 15.

Table 2. Disregistry of TiN with various oxide inclusions.

Inclusion	Al ₂ O ₃	$MgO \cdot Al_2O_3$	Ti ₂ O ₃
Disregistry	17.48%	4.88%	16.17%

3.7. Agglomeration Mechanism of Inclusions after Ti Addition

According to the obtained results from three-dimensional investigations, after Ti addition, inclusion collisions took place among single inclusions, aggregates, and clusters. In this study, three major types of collisions were taken into account during the collision–agglomeration process after titanium feeding: Brownian, turbulent, and Stokes' collisions. Brownian collision, β_{ij}^B , describes the random movement of very small particles suspended in liquid steel; turbulent collision, β_{ij}^T , originates from the turbulence flow caused by convection or stirring; and Stokes' collision, β_{ij}^S , occurs in liquid steel as a consequence of the large difference in inclusion size, or to be more specific, larger inclusions have a higher settling velocity and collide with smaller ones during ascension. For a certain collision phenomenon, the collision volume (m³/s), namely, the number of inclusion collisions in molten steel per unit time, is considered to be a significant parameter relative to collision rate. The total collision volume can be expressed as the sum of each type of collision, and the separate values of $\beta_{ij'}^B$, $\beta_{ij'}^T$, and β_{ij}^S can be determined by calculation from the following equations [58,59]:

$$\beta_{ij}^{B} = \frac{2k_{B}T}{3\mu} \left(\frac{1}{r_{i}} + \frac{1}{r_{j}} \right) (r_{i} + r_{j}), \tag{8}$$

$$\beta_{ij}^{T} = 1.3 \alpha \sqrt{\pi \epsilon \rho_{Fe} / \mu} \left(r_{i} + r_{j} \right)^{3}, \qquad (9)$$

$$\beta_{ij}^{\rm S} = \frac{2\pi g(\rho_{\rm Fe} - \rho_i)}{9\mu} (r_i + r_j)^3 |r_i - r_j|.$$
(10)

In these equations, k_B is the Boltzmann constant (J/K), *T* is the thermodynamic temperature (K), μ is the absolute viscosity of steel (kg/m·s), r_i and r_j are the radii of the two colliding inclusions (m), g is the gravitational acceleration (m/s²), and ρ_{Fe} and ρ_i are the densities of the steel and inclusion, respectively (kg/m³). The parameters for the calculation are given in Table 3. The value of r_i in the computation corresponds to the mean size in the size range of 2–3 µm in Figure 10, which was set to 2.4 µm. It was assumed that the irregular particle is a sphere and can collide with other sized particles within the radius. In this case, the average size of the particle determined by ASPEX system was considered to be the inclusion diameter. Since individual particles including TiN, TiO_x, and Al₂O₃-based inclusions and their aggregations were observed after Ti feeding, the contribution of the particle density to the collision volume should be assessed.

K/(J/K)	T/K	µ/(kg/m·s)	$\alpha/(m^2/s^3)$	$\epsilon/(m^2/s^3)$
1.38×10^{-23}	1873	0.005	0.3	0.0018
$\rho_{Fe}/(kg/m^3)$	$\rho_{TiN}/(kg/m^3)$	$\rho_{Al_2O_3}/(kg/m^3)$	$\rho_{Ti_2O_3}/(kg/m^3)$	g/(m/s ²)
8000	5220	3900	4486	9.81

Table 3. Data used in calculation of collision volumes.

Figure 19 provides the predicted contribution of each type of collision to inclusion growth in terms of the collision volume. When the diameter of the particle is less than 2.7 μ m, Brownian and turbulent collisions play primary roles in particle growth. Moreover, the value of β_{ij}^{B} experiences a substantial increase with decreasing inclusion size, suggesting an increasing effect of Brownian collision on the particle growth. Consequently, the TiN clusters observed shortly after Ti addition (Figure 13c) probably results from Brownian and turbulent collisions. Note the little influence of Stokes' collision upon inclusion growth if the two colliding inclusions have the same size. Hence, the collision between the most frequently observed particles in this study, which have a mean size of 2.4 μ m, can also be associated with the same reason.



Figure 19. Collision volumes for an inclusion with a 2.4 μ m in diameter colliding with various sized particles.

When the inclusion diameter exceeds the threshold of approximately 2.7 μ m, the particle growth becomes controlled by turbulent and Stokes' collisions. As shown in Figure 19, the collision volume for Stokes' collision shows an upward trend as a function of increased size (more than 2.4 μ m), whereas turbulent collision increases over the whole range. Thus, under the influence of turbulent and Stokes' collisions, the particle with a given size can be captured by larger Al₂O₃-based inclusions, especially clusters or aggregates, and then grow into larger ones. Moreover, compared with the particle density, the collision type and the inclusion diameter appear to be the predominant factors in the collision growth of inclusions.

4. Conclusions

In this manuscript, the transient inclusion evolution during Al and Ti additions in a Fe-20 mass pct Cr alloy was investigated by two-dimensional and three-dimensional methods. The main conclusions obtained are as follows:

(1) Although the characteristics of Al_2O_3 -based inclusions are not new for low-carbon Al-killed steels, the current laboratory experiments identified that the deoxidation products in a liquid Fe-20 mass pct Cr alloy passed through three main stages with time: Particle agglomeration, inclusion floating and a slow decrease of remaining Al_2O_3 -based inclusions.

(2) After Ti addition, TiO_x was immediately generated onto the existing Al_2O_3 -based inclusion as a transitional product and thermodynamically reduced into Al_2O_3 by Al as time progressed. The generation of transient TiO_x could hardly be predicted by the equilibrium relations of Ti–O–N and Ti–Al–O in the high-Cr-containing melt but was attributed to the low disregistry between Al_2O_3 and TiO_x and the local Ti supersaturation during the transient stages.

(3) Because of the local supersaturation of dissolved [%Ti] and [%N] shortly after Ti addition, TiN associated with existing inclusions and three types of individual TiN including single cubes, twinned inclusions, and clusters were identified.

(4) The formation of Ti-rich zones during transient stages was affected by the morphology of existing Al₂O₃-based inclusions. In order to minimize the Ti loss caused by the formation of Ti-rich zones, the removal of large Al₂O₃-based particles including aggregates, clusters, and flower-shaped inclusions should be promoted by stirring before Ti addition.

(5) After Ti addition, Brownian and turbulent collisions were the primary factors in the collisions of particles smaller than the threshold of $2.7 \,\mu m$. The agglomeration of inclusions larger than this threshold was mainly dominated by turbulent and Stokes' collisions. The collision types and inclusion diameters produced more significant effects than did the inclusion densities on the collision process.

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