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The Formation Mechanisms and Evolution of Multi-Phase Inclusions in Ti-Ca Deoxidized Offshore Structural Steel

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Abstract: To understand and clarify the formation mechanisms and evolution of complex inclusions in Ti-Ca deoxidized offshore structural steel, inclusions in industrial steel were systematically investigated. The number density of total inclusions generally decreased from Ladle Furnace (LF), Vacuum Degassing (VD), Tundish to the final product except for Ti and Ca addition. The major inclusions during the refining process were $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ inclusion initially originated from the combination of $\text{CaO-SiO}_2\text{-(MgO)}$ in refining slag or refractory and deoxidization product Al_2O_3 and TiO_2 . With the refining process proceeding and Ca addition, the Al_2O_3 concentration in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ inclusions gradually dropped while the CaO and TiO_2 concentrations gradually increased. The $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ inclusions originally came from refining slag, existing as $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, and maintained a liquid state during the early stage of LF. After Ca treatment, it was gradually transferred to $2\text{CaO} \cdot \text{SiO}_2$ due to Al_2O_3 continuously being reduced by Ca. The liquidus of $2\text{CaO} \cdot \text{SiO}_2$ inclusion was higher than that of molten steel, so they presented as a solid-state during the refining process. After welding thermal simulation, $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ inclusions were proven effective for inducing intragranular acicular ferrite (IAF) while $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ was inert for IAF promotion. Additionally, $\text{Al}_2\text{O}_3\text{-MgO}$ spinel in multiphase $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ inclusion has different formation mechanisms: (1) initial formation as individual $\text{Al}_2\text{O}_3\text{-MgO}$ spinel as a solid-state in molten steel; (2) and it presented as a part of liquid inclusion $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ and firstly precipitated due to its low solubility.

Keywords: oxide metallurgy; high heat input welding; Ti-Ca deoxidation; inclusion evolution; formation mechanism



Citation: Rong, Z.; Liu, H.; Zhang, P.; Wang, F.; Wang, G.; Zhao, B.; Tang, F.; Ma, X. The Formation Mechanisms and Evolution of Multi-Phase Inclusions in Ti-Ca Deoxidized Offshore Structural Steel. *Metals* **2022**, *12*, 511. <https://doi.org/10.3390/met12030511>

Academic Editor: Mark E. Schlesinger

Received: 17 February 2022

Accepted: 14 March 2022

Published: 17 March 2022

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1. Introduction

With the development of large-scale engineering structures, high heat input welding has been widely used in shipbuilding, marine engineering, and oil container fields due to its advantages, such as high efficiency and high stability. However, the increment in the heat input will result in the coarsening of grains in the heat affect zone (HAZ), the origin of a tiny cleavage crack, and a heterogeneous microstructure, thereby significantly deteriorating the toughness [1].

To address these problems, researchers have started to focus on inclusions that are inevitable in metal products. Some non-metallic inclusions can have positive impacts on the steel microstructure and mechanical properties [2–4]. Initially, in the 1970s, nanosized TiN particles were found to be effective at inhibiting the growth of austenite grains and beneficial for the mechanical property of steel [5]. They were formed during the cooling

process after solidification due to their relatively low solubility. In the 1990s, titanium oxide-containing inclusions, formed in the molten steel and solidification process, were reported to act effectively as intragranular nucleation sites for acicular ferrite, contributing to a smaller grain size and consequently improving the weldability of steel. These practical inclusions were formed during the second refining process and had a relatively high liquidus, so they had excellent thermostability. The technology of titanium oxides and their positive effect on the steel microstructure and phase transformation behaviour was proposed and termed “oxide metallurgy” [6–9]. Since then, the understanding of inclusions in the steelmaking industry has been rejuvenated. Harmful inclusions, such as large-sized and Al_2O_3 inclusions that may cause clogging, should be removed as much as possible while those with a small size and particular chemical composition can be maintained and utilized to achieve outstanding mechanical properties [10,11]. Oxide metallurgy has been one of the most effective methods used to address the toughness problem in HAZ.

In recent decades, the use of strong deoxidizers, such as Ca, Mg, Zr, and rare Earth metals (REMs) [10,12–15], has attracted considerable research interest due to their stronger affinity with O and S and higher thermal stability of inclusions. Traditionally, Ca treatment is mostly used for modifying Al_2O_3 inclusions with a high melting point into $\text{CaO-Al}_2\text{O}_3$ with a lower melting point, thereby solving the nozzle clogging problem [16–18]. Kobe Steel also reported that modified inclusion of $\text{CaO-Al}_2\text{O}_3$ could help prohibit the coarse TiN precipitating on oxides and facilitate the formation and dispersive distribution of fine TiN particles [19]. So far, research has mainly focused on Ca treatment in Ti-bearing Al-killed steel. Wang et al. [20] compared Al-Ca deoxidized steel and Ti-Ca deoxidized steel in the lab, pointing out that $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2\text{-MnS}$ -related inclusions were dominant and active in facilitating fine IAF formation [21,22]. $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2$ will act as a nucleation core while MnS will precipitate around the core during the cooling process and form a manganese depletion zone (MDZ) to induce IAF formation [23–25].

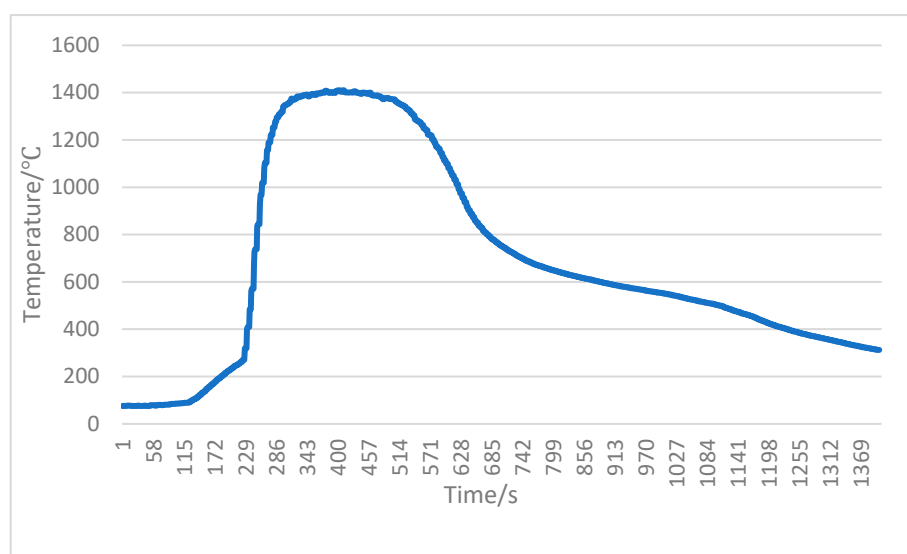
Although several investigations regarding Ti-Ca deoxidized steel have been reported, they mainly focused on the effect of different deoxidizers on inclusions in final products or the effect of inclusions on the microstructure in HAZ. However, few studies harnessing the integrated understanding of inclusion evolution in each step of actual industry practice are available. In this paper, the inclusion characteristics regarding categories, number density, and evolution were systematically investigated to understand and clarify the formation mechanisms and evolution of complex inclusions in Ti-Ca-treated offshore structural steel, which will benefit the translation Ti-Ca oxide metallurgy of offshore steels.

2. Materials and Methods

Steel samples were obtained from an industrial process for offshore structural steel, which followed the sequential steps through a basic oxygen furnace (BOF)→ladle furnace (LF)→vacuum degassing (VD)→continuous casting (CC)→thermomechanical control process (TMCP) in Wusteel, HBIS. Ferrosilicon ($\text{Si} \geq 75.0\%$, $\text{Al} \leq 1.5\%$, $\text{Fe} \geq 21.0\%$) and ferromanganese (65.0–72.0% Mn, $\text{Si} \leq 2.5\%$, $\text{C} \leq 7.0\%$) alloys together with lime were added to the molten steel during BOF tapping. Then, the molten steel was transferred into LF for refining and bottom argon blowing was adopted for homogenizing the steel composition and accelerating the removal of large-sized inclusions. LF refractories were composed of MgO-C bricks. After refining in LF at 1650 °C, the molten steel was transferred to VD at 1600 °C and was eventually transported into tundish for continuous casting. In particular, samples were collected at the beginning of LF 1 min after Ti addition (Ti-Fe: 25.0–35.0%Ti, $\text{Al} \leq 8.0\%$, $\text{Si} \leq 4.5\%$), 1 min after Ca addition, VD soft blowing, tundish, and hot-rolled plate (final products). The chemical compositions of the steel samples from different stages are shown in Table 1. The product sample underwent heat treatment as welding thermal simulation at a peak temperature of 1400 °C. The measured temperature curve of the welding thermal simulation is shown in Figure 1. The welding samples were held at 1400 °C for 180 s, and the cooling rates of the 1400–800 °C and 800–500 °C range were approximately 3 and 0.75 °C/s ($t_8/5 = 400$ s), respectively.

Table 1. Chemical composition of samples taken from different stages (wt%).

No.	C	Si	Mn	P	S	Nb	V	Al	O	Ti	Ca
LF begin	0.025	0.089	1.29	0.013	0.025	-	-	0.0062	0.0110	-	-
Ti added	0.032	0.201	1.31	0.013	0.0070	0.02	0.039	0.0065	0.0068	0.0042	-
Ca added	0.048	0.200	1.43	0.013	0.0034	0.02	0.039	0.0058	0.0031	0.015	0.0015
VD	0.066	0.214	1.47	0.013	0.0022	0.022	0.043	0.0052	0.0035	0.010	0.0026
Tundish	0.065	0.216	1.47	0.013	0.0021	0.023	0.043	0.0047	0.0032	0.010	0.0016
TMCP	0.069	0.222	1.52	0.013	0.0021	0.023	0.044	0.0040	0.0031	0.014	0.0014

**Figure 1.** The measured temperature curve of welding thermal simulation.

Steel samples were mounted in resin and ground, polished, and etched for inclusion composition analysis and microstructure observation. Composition analysis of inclusions was conducted by using a JXA 8200 electron probe microanalyzer (EPMA, JEOL, Akishima, Japan) with wavelength-dispersive spectrometers (WDSs).

The EPMA operating details are as follows: the standard samples are CaSiO_3 for Ca and Si, pure MgO for Mg, pure Al_2O_3 for Al, pure TiO_2 for Ti, Spessartine for Mn, Fe_2O_3 for Fe, and FeS for S. An acceleration voltage of 15 kV, probe current of 15 nA, probe diameter of “zero” (the smallest operating probe diameter achieved by the focused electron beams), peak measuring time of 30 s, and background measuring time of 10 s were used. Backscattered electron imaging and EDS analysis were utilized to recognize the non-metallic inclusions, especially those complex inclusions with multiple phases. Then, WDS was conducted on the inclusions to analyze the inclusion composition accurately. EPMA can accurately determine the composition of inclusions exceeding 1.5 μm . Field emission scanning electron microscopy (FE-SEM) was used to analyze inclusions sized 1.5 μm or less by element spot analysis, line scanning, and map scanning to demonstrate the elementary distribution of multiphase inclusions.

To describe the number densities of inclusions, 20 photos were taken randomly under 500 magnifications for each sample to ensure reliable statistics. The area of each photo was $0.246 \text{ mm} \times 0.196 \text{ mm} = 0.0482 \text{ mm}^2$, so the total observation area of each sample was 0.964 mm^2 .

3. Results and Discussions

3.1. Characteristics of the Inclusions at Different Stages

Due to complex alloy systems including Si, Mn, Al, Ti, and Ca related to the deoxidization process, the inclusions can be classified into nine groups: Al_2O_3 -MnO, Al_2O_3 -

SiO₂-MnO, CaO-Al₂O₃-SiO₂-MnO, CaO-SiO₂, CaO-Al₂O₃-SiO₂, CaO-Al₂O₃-SiO₂-TiO_x, Al₂O₃-MnO-TiO_x, SiO₂-MnO, and CaO-TiO_x, as shown in Table 2. Generally, several valences of Ti, such as TiO, TiO₂, Ti₂O₃, and Ti₃O₅, exist in steel, and it is assumed that Ti-oxide was mainly TiO₂ when analyzing the inclusion composition, so a TiO₂ standard sample was used during the EPMA analysis. Among these inclusions, Al₂O₃-MnO, Al₂O₃-SiO₂-MnO, and CaO-Al₂O₃-SiO₂-MnO are either primary deoxidization products or those that contacted with lime, which was added during the BOF tapping process. CaO-SiO₂ and CaO-Al₂O₃-SiO₂ are grouped into slag entrapment products (large-sized inclusions) and reduction products (small-sized inclusions). CaO-Al₂O₃-SiO₂-TiO_x and CaO-TiO_x belong to the refining products. Al₂O₃-MnO-TiO_x and SiO₂-MnO inclusions are considered to be secondary oxidization products during the vacuum break of VD and Tundish processes.

Table 2. Classification of inclusions based on the chemical compositions (wt%).

Inclusions	Chemical Composition					
	CaO	Al ₂ O ₃	SiO ₂	MgO	TiO ₂	MnO
Al ₂ O ₃ -MnO	<10%	>60%	<10%	<10%	<10%	>10%
Al ₂ O ₃ -SiO ₂ -MnO	<10%	>10%	>20%	<10%	<10%	>10%
CaO-Al ₂ O ₃ -SiO ₂ -MnO	>10%	>10%	>10%	<10%	<10%	>10%
Al ₂ O ₃ -MnO-TiO _x	<10%	>20%	<10%	<10%	>30%	>10%
SiO ₂ -MnO	<10%	>30%	<10%	<10%	<10%	>30%
CaO-SiO ₂	>40%	<10%	>10%	<10%	<10%	<10%
CaO-Al ₂ O ₃ -SiO ₂	>20%	>20%	>20%	<10%	<10%	<10%
CaO-Al ₂ O ₃ -SiO ₂ -TiO _x	>20%	>10%	>10%	<10%	>10%	<10%
CaO-TiO _x	>30%	<10%	<10%	<10%	>30%	<10%

The initial inclusions in the LF-entry sample include Al₂O₃-MnO, Al₂O₃-SiO₂-MnO, CaO-Al₂O₃-SiO₂-MnO, and CaO-SiO₂. Among these inclusions, Al₂O₃-MnO and Al₂O₃-SiO₂-MnO are primary deoxidization products with small sizes generally less than 3 µm. Although Fe-Si and Fe-Mn ferroalloys are mainly used as pre-deoxidizer in industrial practice, inevitably a small amount of Al impurities exist in alloys. As Al has a stronger ability to combine with oxygen than Si and Mn, almost all the primary deoxidization products contained Al₂O₃. CaO-Al₂O₃-SiO₂-MnO can be considered as the coalescence between primary deoxidization products and CaO from lime and CaO-SiO₂ from refining slag that was added to molten steel during BOF tapping. CaO-SiO₂ inclusions in the LF entry stage were generally larger than 10 µm, but the proportion of CaO-SiO₂ inclusions in this stage was very low. They originated from slag entrapment. After Ti was added to LF, the main inclusion types were CaO-Al₂O₃-SiO₂ and CaO-Al₂O₃-SiO₂-TiO_x 1–10 µm in size. The dissolved aluminium coming from continuous reaction of ferroalloys with CaO-SiO₂ from refining slag then formed CaO-Al₂O₃-SiO₂ inclusions. The additive Ti entered molten steel, reacting with CaO-Al₂O₃-SiO₂ inclusions and forming CaO-Al₂O₃-SiO₂-TiO₂ inclusions. After Ca was added to the molten steel, a considerable proportion of CaO-SiO₂ inclusions was observed apart from CaO-Al₂O₃-SiO₂ and CaO-Al₂O₃-SiO₂-TiO_x inclusions due to the severe slag entrapment caused by the splashing of the Ca addition, and the reduction of Al₂O₃ by additive calcium. In the following VD and Tundish, until the final products, CaO-SiO₂, CaO-Al₂O₃-SiO₂, and CaO-Al₂O₃-SiO₂-TiO_x inclusions remained the main types. The most significant difference was that Al₂O₃-MnO-TiO_x and SiO₂-MnO inclusions were observed after the vacuum break of VD and Tundish. In general, these were typical re-oxidization products due to the excessive surface turbulence during molten steel teeming into the Tundish ladle. However, these kinds of re-oxidization products were seldom found in the final products, which indicated that most of them floated upwards into the mold flux and were removed effectively. In the final products, CaO-TiO_x inclusions

were found apart from CaO-SiO_2 , $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_x$ inclusions. They may be generated from either the enrichment of the CaO component and the reduction of Al_2O_3 and SiO_2 , or the precipitation of CaO-TiO_x from $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_x$ inclusions during the cooling process.

3.2. Number Density and Size Distribution of Inclusions

The number density of all inclusions in industrial steel is shown in Figure 2. The primary inclusions in the LF entry sample were generally primary deoxidization products, such as $\text{Al}_2\text{O}_3\text{-MnO}$ and $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-MnO}$, featuring a high proportion of fine inclusions that were less than $1\text{ }\mu\text{m}$ and had a number density of $1560/\text{mm}^2$. With ladle furnace refining processing, when Fe-Ti alloy was added to the molten steel, the total amount of inclusions decreased dramatically to about $300/\text{mm}^2$, especially those with a small size ($<1\text{ }\mu\text{m}$). This is due to the coalescence of small inclusions, floating upward into the refining slag. When Si-Ca wire was added to the molten steel and the end of LF refining, the total amount of inclusions increased slightly to higher than $400/\text{mm}^2$ owing to the severe splashing during Si-Ca wire feeding. It also featured a higher proportion of $1\text{--}2\text{ }\mu\text{m}$ and $2\text{--}5\text{ }\mu\text{m}$ inclusions, and this can be explained by inclusion coalescence and growth to be larger ones. In the VD section, the total amount of inclusions dropped gradually to around $200/\text{mm}^2$, small-sized inclusions of less than $1\text{ }\mu\text{m}$. This is because small-sized inclusions kept coalescing and gathering during the vacuum break and soft blowing process of VD. From VD to Tundish and products, the total amount of inclusions decreased steadily, and the main factor was the decrease in the inclusions with small sizes less than $1\text{ }\mu\text{m}$.

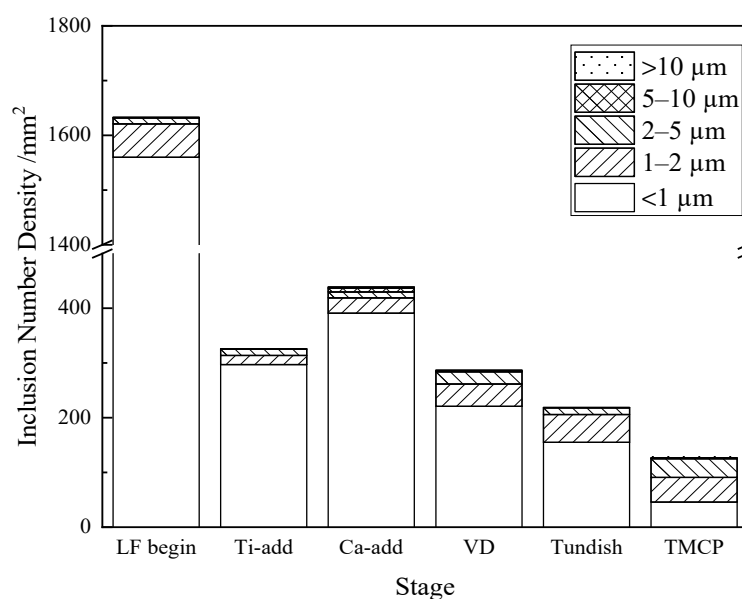


Figure 2. The number density of inclusions at different stages.

The oxide components in inclusions at different stages are shown in Figure 3. As can be seen, Al_2O_3 and MnO , as primary deoxidization products, accounted for the majority initially when LF began. With the LF refining processing, when Fe-Ti and Si-Ca alloys were added to the molten steel, CaO and SiO_2 were substituted for Al_2O_3 and MnO , accounting for more than 50% and 30%, respectively. Therefore, the content of Al_2O_3 and MnO dramatically decreased to less than 10%. From the Ca addition to vacuum degassing, the CaO content dropped a little to 40% due to the evaporation effect of Ca, and accordingly, the Al_2O_3 content increased a little to about 20%. However, the CaO content increased gradually to about 50% after the vacuum break of VD, which was due to extra Si-Ca alloy being added to the molten steel. The TiO_2 concentration fluctuated from 10% to 15% after Ti-Fe addition.

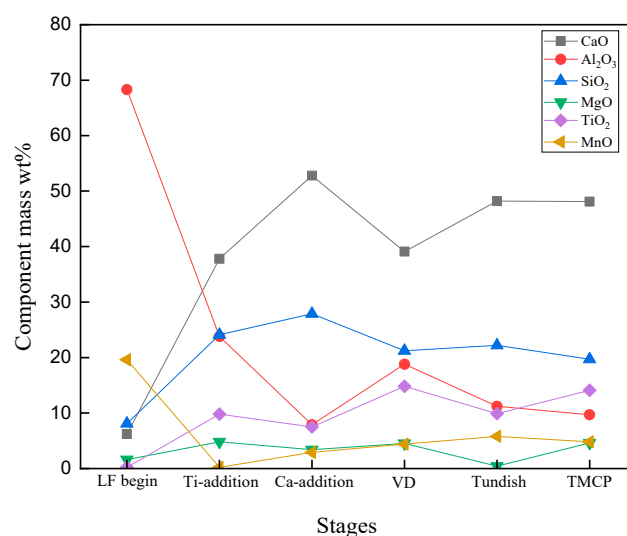


Figure 3. Oxide component in the inclusions at different stages.

CaO-SiO₂, CaO-Al₂O₃-SiO₂, and CaO-Al₂O₃-SiO₂-(MgO)-TiO_x inclusions remained the main types among all the processes after Ti addition. Particularly, CaO-SiO₂ and CaO-Al₂O₃-SiO₂ can be described in a CaO-Al₂O₃-SiO₂ system, thus CaO-Al₂O₃-SiO₂-(MgO)-TiO_x and CaO-Al₂O₃-SiO₂ inclusions were focused on and their formation mechanisms and evolutions were investigated and are discussed here.

3.3. Formation Mechanism and Evolution of CaO-Al₂O₃-SiO₂-(MgO)-TiO_x Inclusion

The initial CaO-Al₂O₃-SiO₂-(MgO)-TiO_x (MgO was marked here for discussing the formation mechanism) inclusion was found after Ti addition. Three typical inclusions (size ranged from 1 to above 10 μm) with different sizes are shown in Figure 4. The size of the three inclusions were 10.8, 5.1, and 2.5 μm, respectively. All of them belonged to CaO-Al₂O₃-SiO₂-(MgO)-TiO_x inclusions, among which the MgO content was relatively low at about 5%. The detailed chemical composition is shown in Figure 5 to demonstrate the varying trend of each oxide component with different sizes.

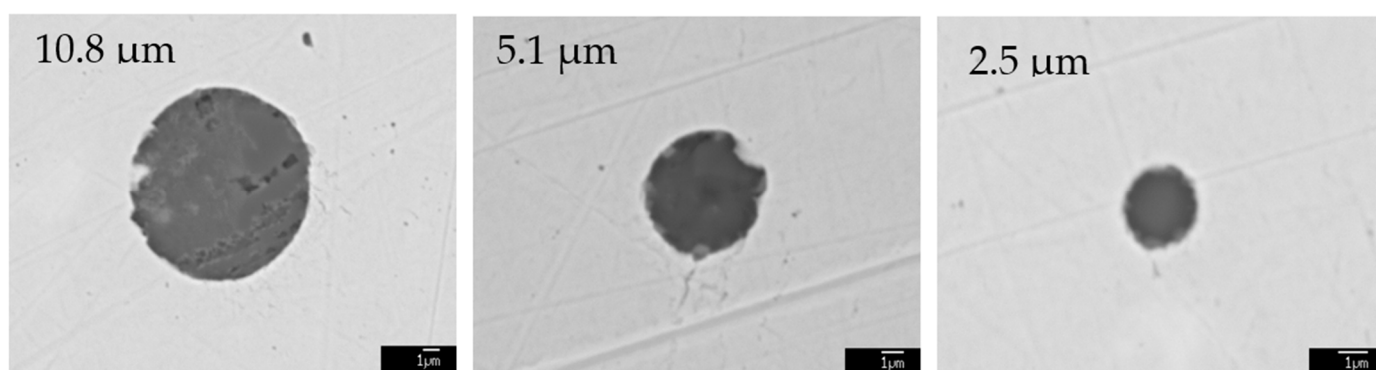


Figure 4. Morphologies of typical inclusions with different sizes after Ti addition.

It is obvious from Figure 5 that the mass proportion of CaO and SiO₂ steadily dropped with the decrease in the inclusion size. The mass proportion of MgO remained stable at a relatively low level. Adversely, the mass proportion of Al₂O₃ and TiO₂ showed a gradually increasing trend. CaO and SiO₂ were generally the main contents of the refining slag, and MgO came either from refining slag or the corrosion of MgO-C refractory and Al₂O₃, and TiO_x was a typical deoxidization product of Ti-Ca killed steel. Generally, deoxidization products are small in size while the size of particles from slag and refractory can range widely. When small-sized deoxidization products are combined with large-sized

CaO-SiO₂(-MgO) particles, the CaO-SiO₂(-MgO) content in the average composition will be high, and Al₂O₃-TiO₂ will be low. On the other hand, when a small-sized deoxidization product is combined with small- or medium-sized CaO-SiO₂(-MgO) particles, the CaO-SiO₂(-MgO) content in the average composition will be relatively lower, and Al₂O₃-TiO₂ will be moderately higher. As a result, it can be concluded from Figure 5 that the CaO-Al₂O₃-SiO₂(-MgO)-TiO_x inclusion in LF originated from the reaction between CaO-SiO₂ from slag, MgO from refractory, and the deoxidization products Al₂O₃ and TiO_x.

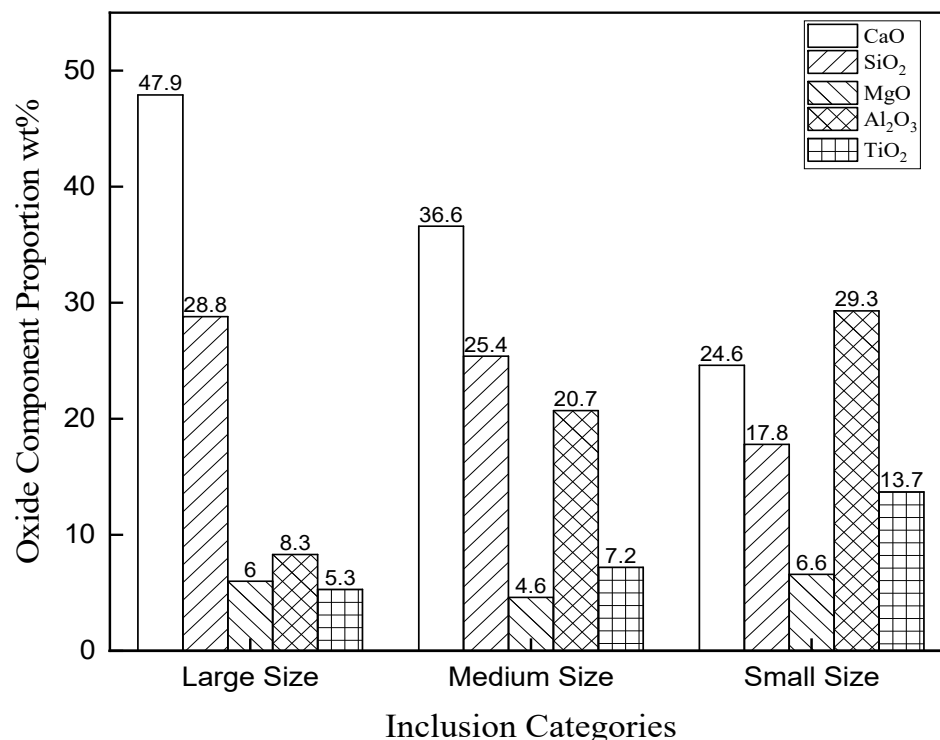


Figure 5. Oxide component proportion in different sized CaO-Al₂O₃-SiO₂(-MgO)-TiO_x inclusions.

The CaO-Al₂O₃-SiO₂-MgO-TiO_x inclusions' composition at different stages was projected into pseudo-ternary phase diagrams of CaO-Al₂O₃-TiO_x at fixed 20%SiO₂ (14.8–23.2% SiO₂) and 5%MgO (2.7–7.8%MgO), as shown in Figure 6. In Figure 6a, all the inclusions' composition is projected, and relatively dispersive. Accordingly, the average composition of each stage was calculated and is shown in Figure 6b. After the addition of Ti in the LF refining, the main inclusions are generally located in the regions of CaO-Al₂O₃-MgO and melilite, and with Ca addition in LF and following VD, the main inclusions are basically located in melilite and Ca₂SiO₄ regions, and the inclusion composition in final product is eventually located in the CaTiO₃ region.

The morphologies of CaO-Al₂O₃-SiO₂(-MgO)-TiO_x at different stages are shown in Figure 7. Generally, they were spherical. From the liquidus temperature in the pseudo-ternary phase diagram, the compositions of inclusions at different stages are located in the 1400–1500 °C liquidus region, which means they were in a liquid state in molten steel and thereby presented a sphere shape. The morphologies shown in Figure 7 indicate relatively fast cooling and the precipitation of different components; thus, the morphologies reflect the formation mechanism of inclusion. The component with a light grey colour is TiO₂, and the area proportion of TiO_x continuously increased with the refining process proceeding, which was in accordance with the TiO_x component trend shown in the phase diagram. During the early stage of LF refining after Ti addition, large amounts of Al-Ti-oxide particles started to gather around and stick to the CaO-SiO₂(-MgO) inclusion on its surface. Particularly, Al₂O₃ was from the oxidization of residual Al in the ferroalloys, and TiO_x was from the oxidization of Ti in the Ti-Fe alloy. These small deoxidization

products did not have enough time to dissolve into the inclusion from the refining slag, so they stayed on the surface. With the refining process proceeding, Ti-oxide continuously increased and had sufficient time to gradually dissolve into the inclusion from the refining slag and formed new inclusions as a whole. As can be seen in the phase diagrams shown in Figure 6, the liquidus of the average composition of the inclusions was in the range from 1400 to 1450 °C. So, these new inclusions were mainly liquid inclusions in molten steel. During the cooling of the sample-taking process, different phases precipitated and formed multiphase inclusions, as shown in Figure 7. As a result, the morphology after cooling presented, such as the Ti-oxide component, “entered” the inclusion and formed the core of the multiphase inclusions. Meanwhile, the Al_2O_3 and SiO_2 component generally decreased due to the reduction of Ca, so the average content of CaO showed an increasing trend when compared with that of Al_2O_3 and SiO_2 , as shown in Figure 6. The formation mechanism of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ is in accordance with that of the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)}$ inclusions in Si-Mn killed steel with a limited aluminum content [21].

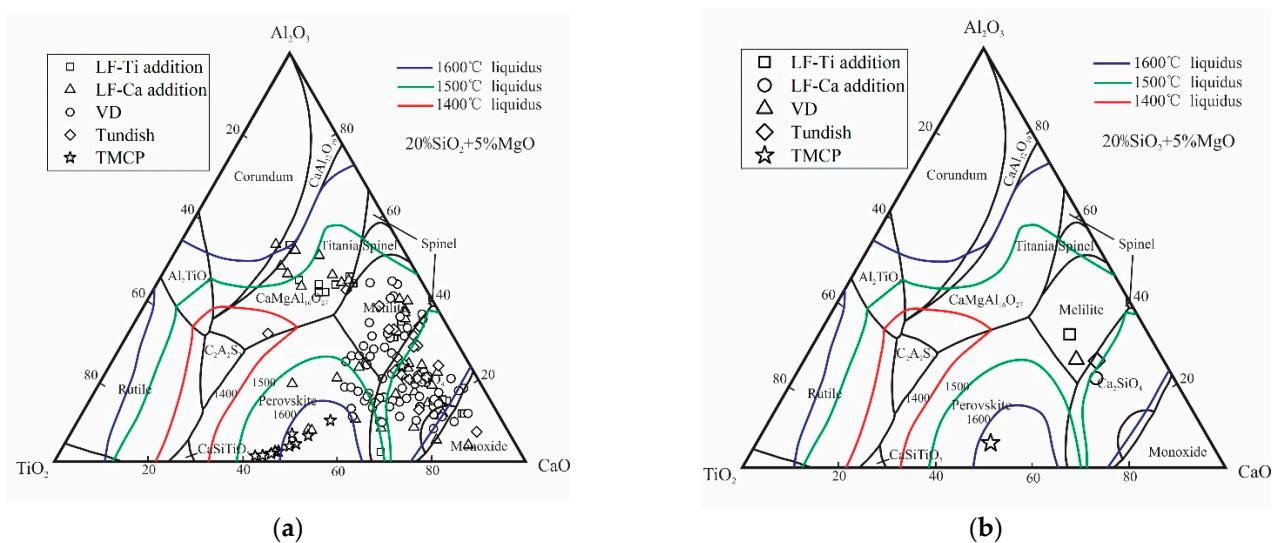


Figure 6. Pseudo-ternary phase diagrams $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2$ at fixed 20% SiO_2 (14.8–23.2% SiO_2) and 5% MgO (2.7–7.8% MgO); (a) experimental data; (b) average data.

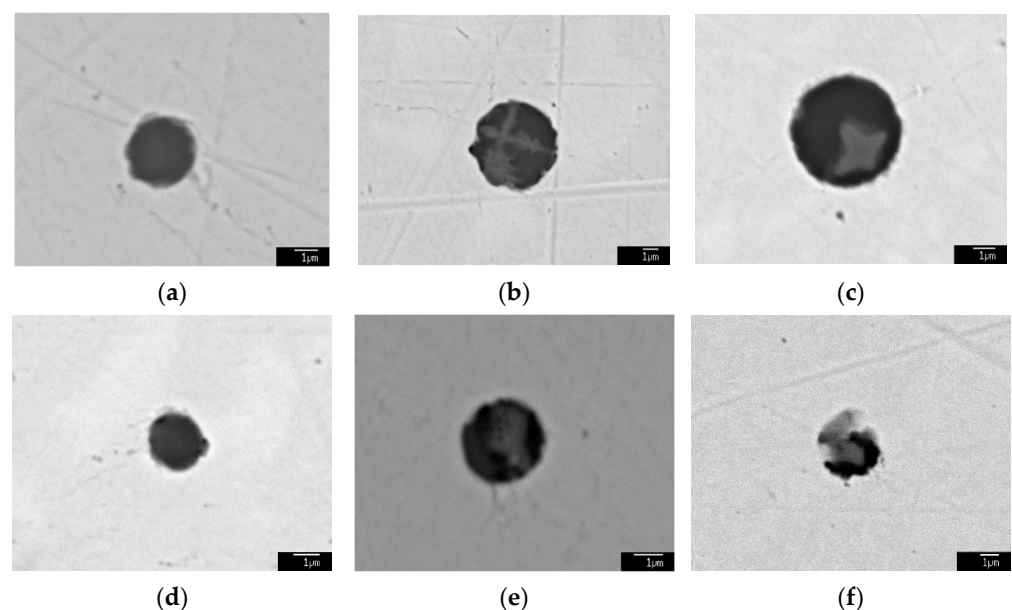


Figure 7. The morphologies of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ at different stages: (a) Ti addition; (b) Ca addition; (c) LF end; (d) VD; (e) Tundish; (f) product.

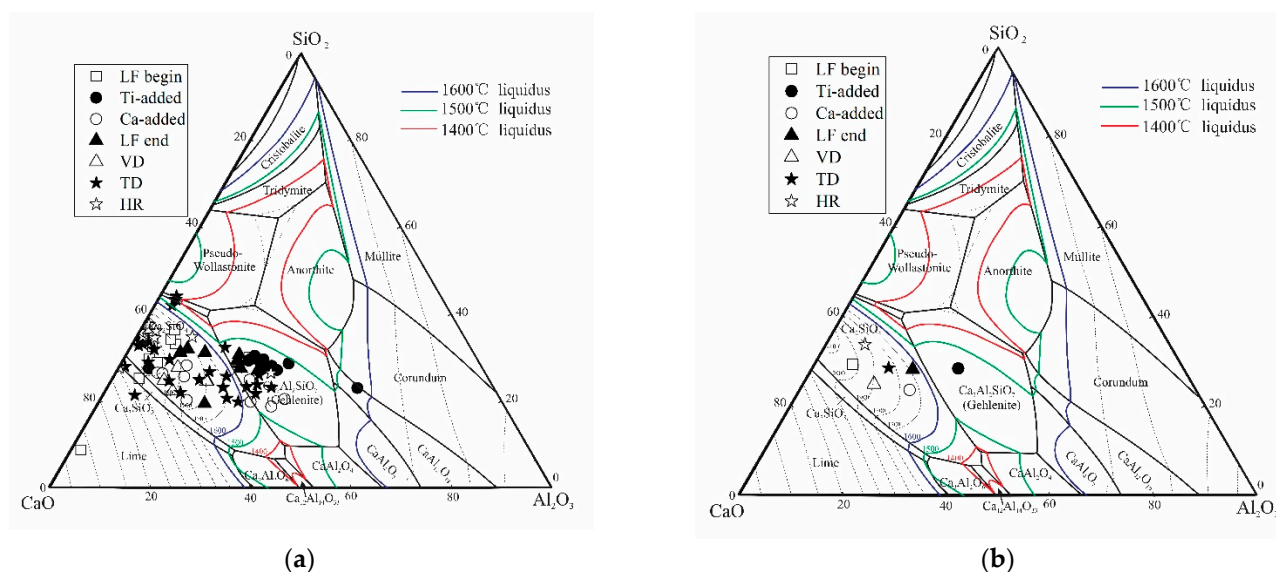
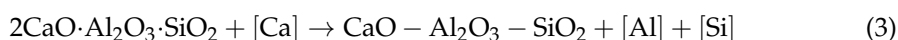
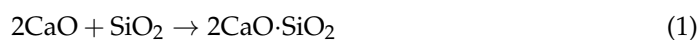


Figure 10. CaO-Al₂O₃-SiO₂ ternary phase diagrams.(a) experimental data, (b) average data.

The CaO-Al₂O₃-SiO₂ and CaO-SiO₂ inclusions' compositions at different stages were projected into ternary phase diagrams of CaO-Al₂O₃-SiO₂, as shown in Figure 10. Since the inclusion composition of the industrial sample is distributed dispersedly (Figure 10a), the average composition of inclusions during different stages is shown in Figure 10b. The initial composition of the LF entry is located in the 2CaO·SiO₂ region, and with the refining processing from LF→VD→TD→final products, the average composition moved from the 2CaO·SiO₂ region to the 2CaO·Al₂O₃·SiO₂ region (Gehlenite) and eventually returned to the 2CaO·SiO₂ region (Ca₂SiO₄). First, additive lime during the BOF tapping process brought CaO into molten steel, and it met the primary deoxidization product SiO₂ and formed 2CaO·SiO₂. When Ti-Fe alloy was added, residual Al entered the molten steel and formed the deoxidization product Al₂O₃. The combination of Al₂O₃ and Ca₂SiO₄ formed 2CaO·Al₂O₃·SiO₂, and significantly decreased the liquidus of inclusion. Then, Ca treatment led to the reduction of Al₂O₃ and SiO₂ in 2CaO·Al₂O₃·SiO₂, so the Al₂O₃ and SiO₂ content kept dropping while the CaO content gradually increased. When LF began, the average inclusion composition located in the 2CaO·SiO₂ region and the CaO/SiO₂ ratio was about 1.7–1.8, and its liquidus was around 2000 °C. After the Ti addition, the average inclusion composition was located in the Gehlenite region, and the liquidus significantly decreased to about 1500–1600 °C due to the increment of Al₂O₃. The inclusions after the Ti addition had a spherical and smooth shape because they remained liquid in molten steel. After Ca treatment, the CaO/SiO₂ ratio tended to be slightly higher than the initial CaO/SiO₂ ratio, and the average composition entered the Ca₂SiO₄ region, the liquidus of which was about 1700–1800 °C. As a result, the CaO-SiO₂ inclusions from VD, tundish, and the final product presented rough surfaces, which indicated that they remained in a solid state in molten steel as shown in Figure 11. The reactions during these processes can be described as Formula (1)–(3):



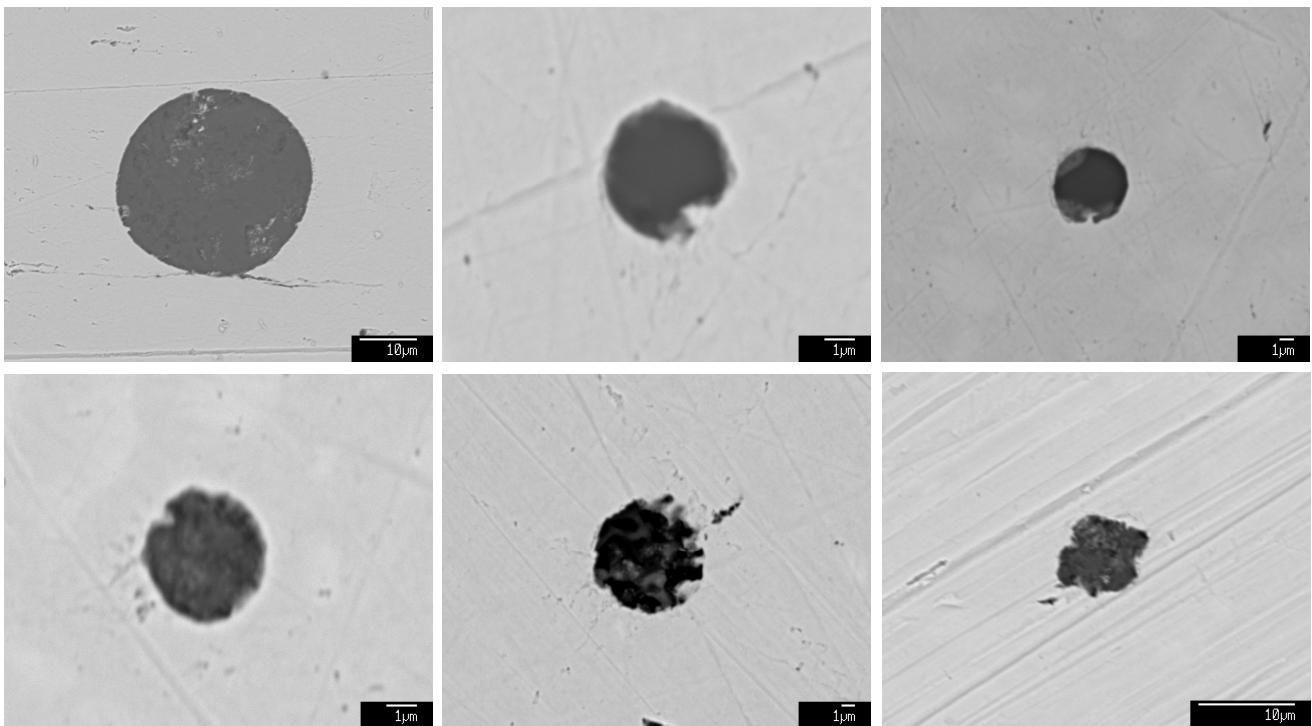


Figure 11. The morphologies of CaO-Al₂O₃-SiO₂ inclusions at different stages.

3.5. Effect of Inclusions on IAF Formation

As many researchers have reported, titanium oxide is the key part of “oxide metallurgy”. Generally, they perform as an effective and stable nucleation site for the induction of intragranular acicular ferrite (IAF). As discussed above, the main categories of inclusion in Ti-Ca industrial steel are CaO-Al₂O₃-SiO₂-(MgO)-TiO_x and CaO-Al₂O₃-SiO₂ (CaO-SiO₂ can be defined as one of CaO-Al₂O₃-SiO₂). However, CaO-Al₂O₃-SiO₂ may not be an effective inclusion for IAF promotion while CaO-Al₂O₃-SiO₂-(MgO)-TiO_x can be a potential nucleation site for IAF. As a result, the chemical composition of some typical inclusions was investigated using EDS mapping scanning of FE-SEM to clarify the element distribution in multiphase inclusions. Figure 12 shows the morphologies of typical Ti-oxide-containing inclusions in final products, and their chemical composition is shown in Table 4. They were generally CaO-Al₂O₃-(SiO₂-MgO)-TiO_x inclusions, with MnS precipitating around them.

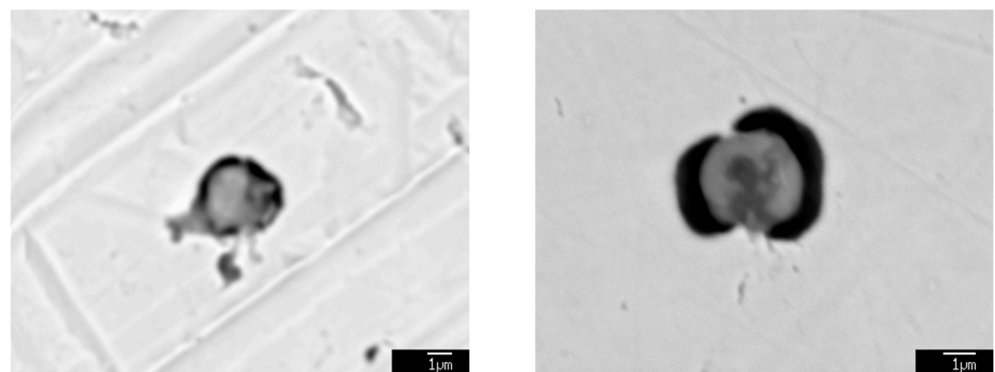
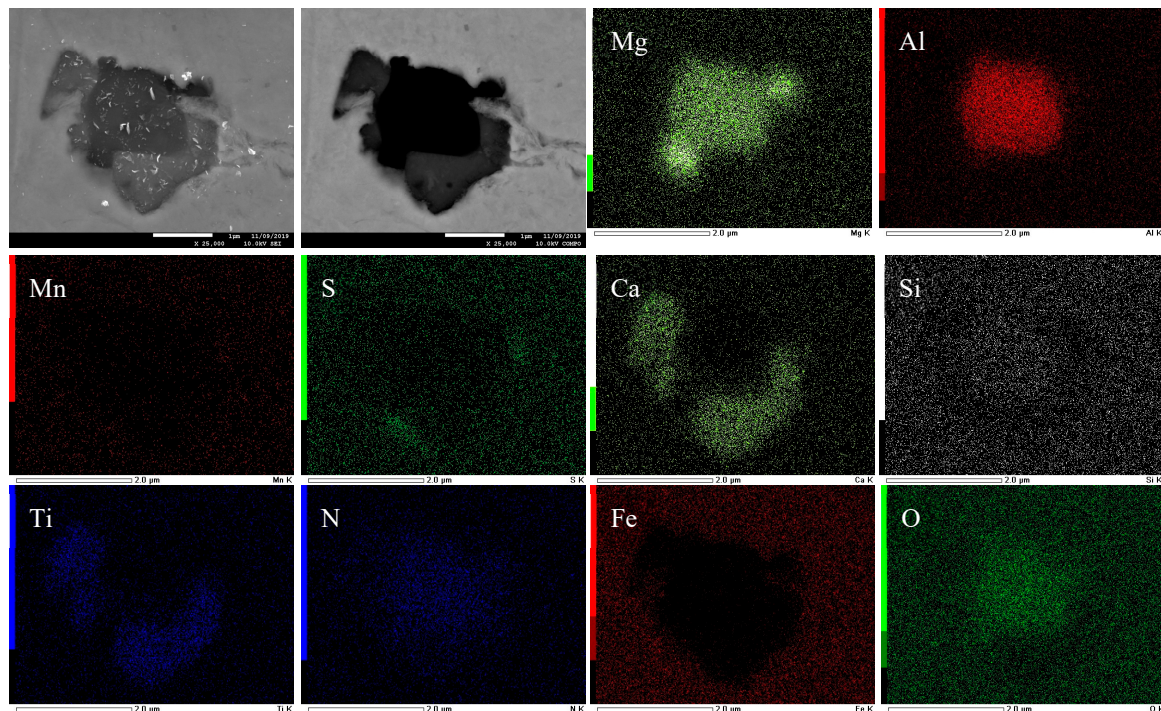


Figure 12. The morphologies of typical Ti-oxide-containing inclusions in the final products.

Table 4. The chemical composition of typical Ti-oxide-containing inclusions in the final products.

No.	CaO	Al ₂ O ₃	SiO ₂	MgO	TiO ₂	MnO	FeO	S
1	22.7	15.7	0.7	6.6	15.3	16.1	12.1	11.0
2	27.7	19.2	6.9	9.2	22.8	2.8	6.6	4.7

Additionally, element mapping scanning was used to identify the chemical composition of different phases in multiphase inclusions. The element distribution of 2 typical multiphase inclusions is shown in Figures 13 and 14. The size of the inclusion in Figure 13 is about 2 μm . The shape of the inclusion shows different parts combined, and it mainly consists of two parts: MgO-Al₂O₃ spinel formed the core with two small MgO + MgS particles attached to it. The core was half surrounded by the CaO-TiO₂ layer, and the interface between the core and surrounding layer was relatively clear. The size of the inclusion in Figure 14 is about 1.5 μm . The shape looks like a whole, and it contains two phases: the left part is MgO-Al₂O₃ spinel, and the right part is CaO-TiO_x and (Ca, Mn) S. Generally, MgO-Al₂O₃ spinel is formed by the combination of [Mg], [Al], and [O] in molten steel and has a very high melting point. However, different mechanisms of the formation of MgO-Al₂O₃ spinel in Ti-Ca-treated industrial steel may exist. As for the multiphase inclusion in Figure 13, it is indicated that MgO-Al₂O₃ spinel was first formed when dissolved [Al] from ferroalloy combined with [Mg] from the refractory. Then, spinel acted as a heterogeneous nucleation site, and MgS and CaO-TiO_x started to precipitate around the core with the decreasing temperature of molten steel and the solidification process. As a result, clear interfaces between each phase existed. As for the multiphase inclusion in Figure 14, the explanation of its formation may be illustrated, as shown in Figure 8: liquid inclusion CaO-Al₂O₃-SiO₂-(MgO)-TiO_x was formed in the steel refining process, but with the decreasing temperature of molten steel and the solidification process, MgO-Al₂O₃ spinel firstly crystallized and precipitated due to its highest melting point, and then other phases, such as CaO-TiO_x and (Ca, Mn) S, precipitated in succession.

**Figure 13.** The element distribution of typical multiphase inclusion.

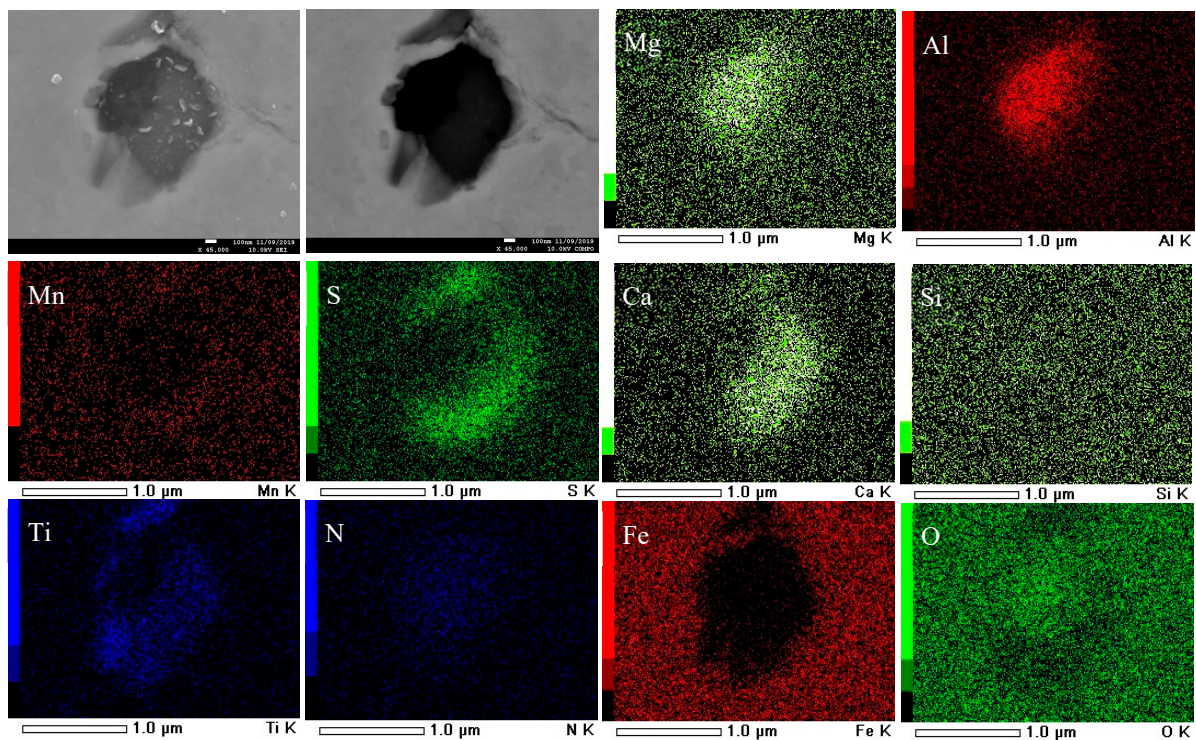


Figure 14. The element distribution of typical multiphase inclusion.

A large-sized multiphase inclusion is shown in Figure 15 and the results of EPMA analysis for each phase are listed in Table 5. The main body of this large-sized inclusion consisted of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ (red number 1) and CaO-TiO_x (red number 2). It seemed that this large-sized inclusion was crushed and separated into several parts composed of $(\text{Ca, Mn})\text{S}$ (red number 3), $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ (red number 4) and CaO-SiO_2 (red number 5) during the rolling process of TMCP, so it spread along the rolling direction.

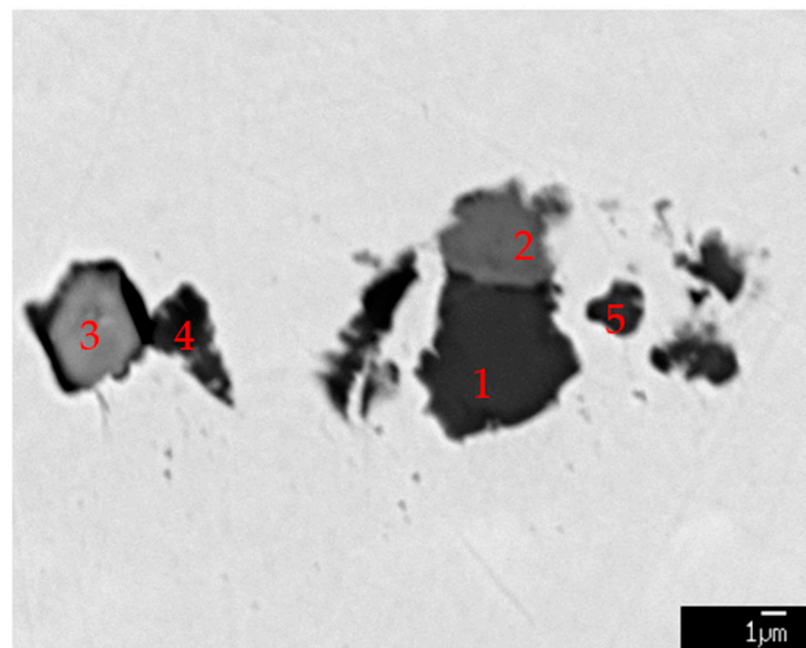
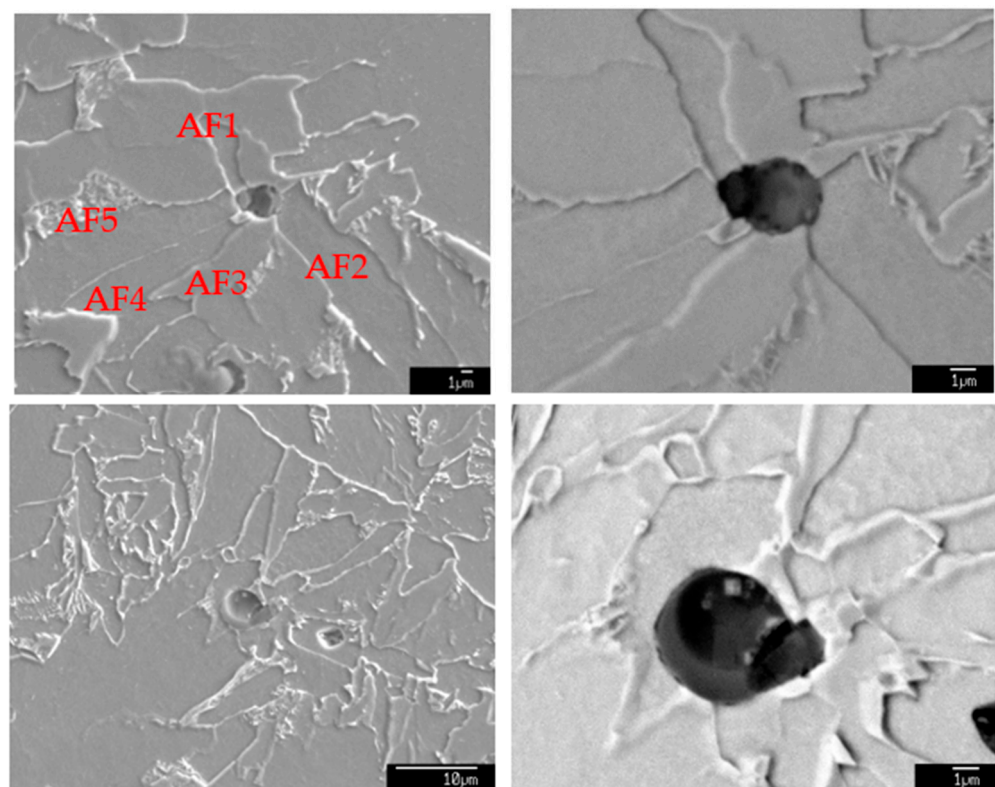


Figure 15. The morphology of a large-sized multiphase inclusion.

Table 5. The chemical composition of each part of the large-sized multiphase inclusion.

No.	CaO	Al ₂ O ₃	SiO ₂	MgO	TiO ₂	MnO	FeO	S	Composition
1	40.5	29.2	24.9	3.0	0.3	0.1	2.4	0.0	CaO-Al ₂ O ₃ -SiO ₂
2	40.3	1.4	0.5	0.3	54.7	0.0	2.9	0.0	CaO-TiO _x
3	53.4	0.1	0.0	0.3	0.0	6.7	9.1	30.3	(Ca, Mn) S
4	15.1	46.2	3.2	19.6	0.9	2.8	8.1	3.6	CaO-Al ₂ O ₃ -MgO
5	53.4	0.2	27.6	1.9	0.1	0.5	16.4	0.1	CaO-SiO ₂

After welding simulation, the inclusions and microstructure were investigated, and some typical inclusions that can effectively induce IAFs were observed and detected using EPMA. The morphologies and chemical composition of typical inclusions are shown in Figure 16 and Table 6, respectively. The induced IAFs are marked in red (AF1–AF6, AF1–AF3) in Figure 16. It can be confirmed that only TiO₂ containing inclusions were effective for IAF promotion while CaO-Al₂O₃-SiO₂ inclusions were not found to be the nucleation site of IAF formation. These effective IAF inclusions were generally multiphase, and their size ranged from 2 to 5 µm and consisted of CaO-Al₂O₃-(SiO₂-MgO)-TiO_x. This indicates that CaO-Al₂O₃-(SiO₂-MgO)-TiO_x was essential for inducing IAFs in Ti-Ca-treated offshore structural steel. Particularly, it can be found that the concentration of Ti-oxide in these effective IAF inclusions (20–30%wt) was significantly higher than the average concentration of Ti-oxide in all inclusions, as shown in Figure 13, which was about 15%wt. The higher concentration of Ti-oxide is generally considered to increase the possibility of IAF formation, thereby enhancing the mechanical property of steel. As a result, how to increase the proportion of CaO-Al₂O₃-(SiO₂-MgO)-TiO_x and how to increase the concentration of Ti-oxide can be a potential and meaningful research direction, and more work is yet to be done in the future.

**Figure 16.** Cont.

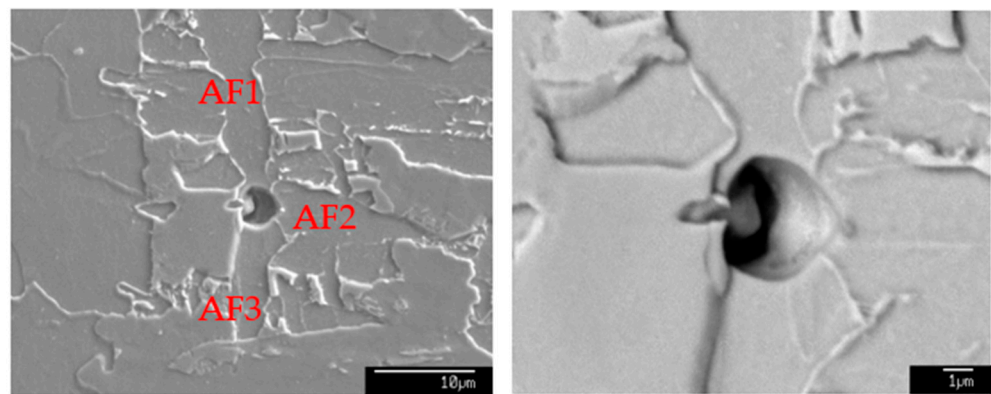


Figure 16. The morphologies of three typical inclusions after welding simulation.

Table 6. The chemical composition of typical inclusions after welding simulation.

No.	CaO	Al ₂ O ₃	SiO ₂	MgO	TiO ₂	MnO	FeO	S
1	13.4	29.3	8.0	24.8	19.1	1.6	10.6	0.1
2	11.7	16.5	16.3	20.8	30.1	1.7	3.3	0.2
3	3.7	18.2	0.3	3.8	36.1	3.2	37.3	1.0

To clearly identify different phases in these multi-phased inclusions and thoroughly clarify the formation mechanisms, mapping scanning of FE-SEM was used for detecting the elementary distribution of effective inclusions that induced IAFs (inclusion A, B, and C). The results are shown in Figures 17–19.

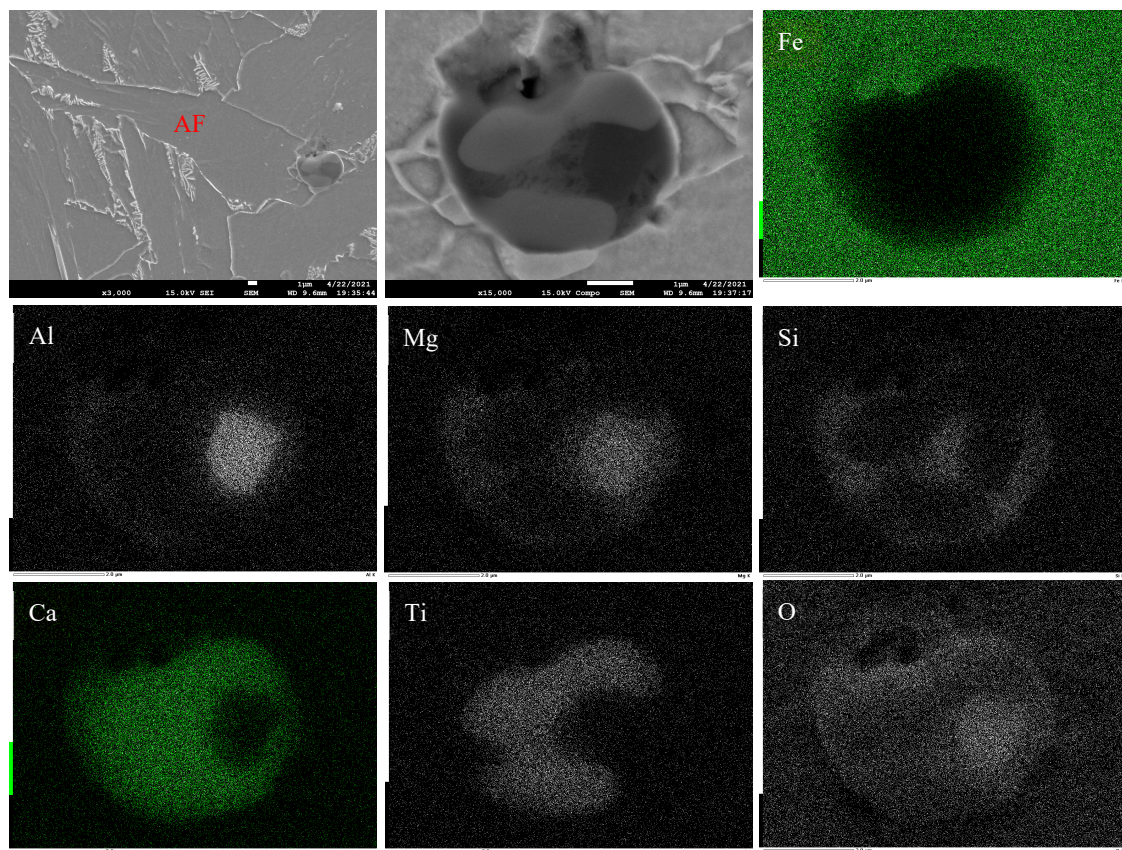


Figure 17. EDS mapping analysis of one typical inclusion A effective for IAF nucleation in Ti-Ca deoxidized steel.

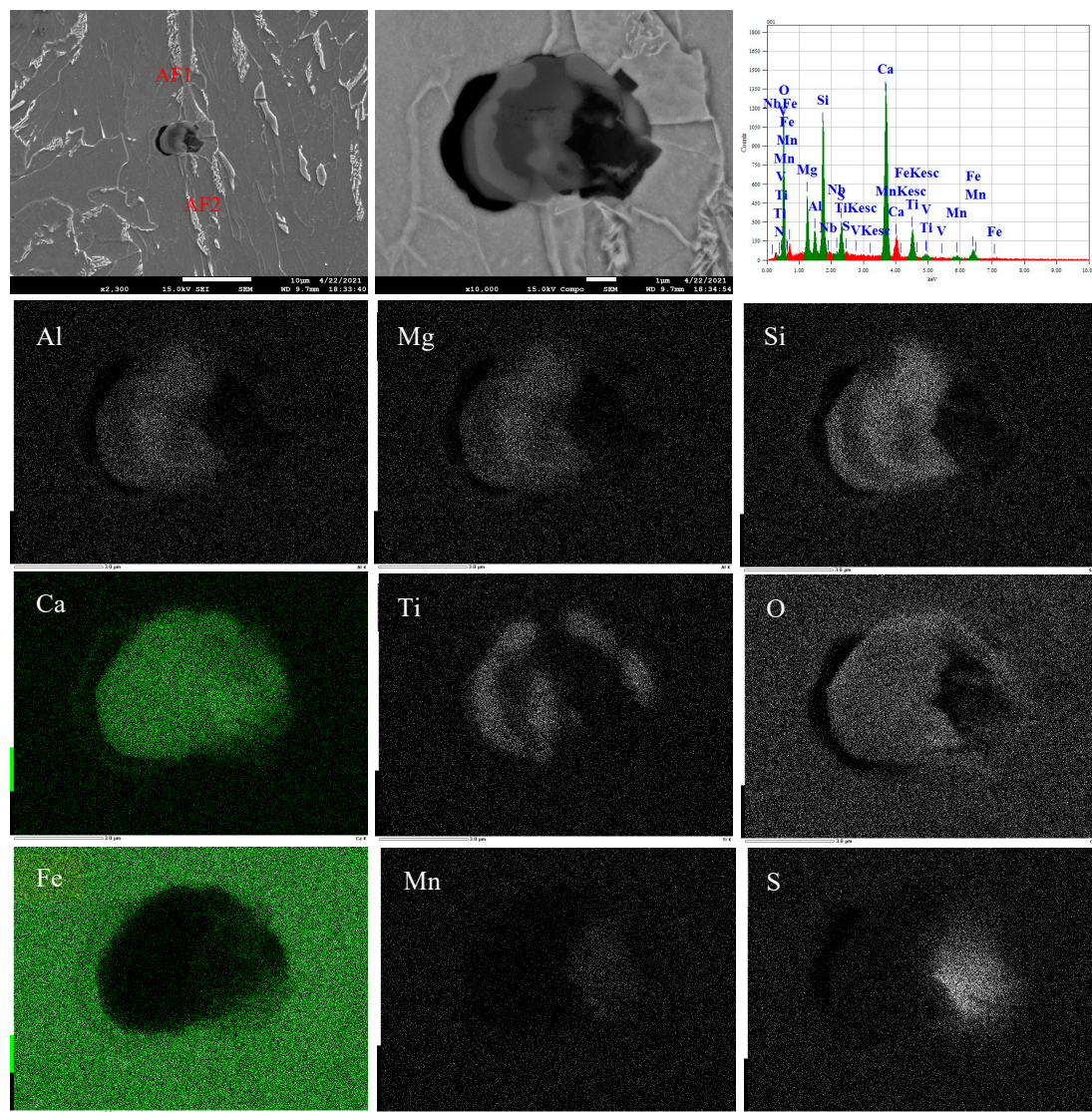


Figure 18. EDS mapping analysis of one typical inclusion B effective for IAF nucleation in Ti-Ca deoxidized steel.

As can be seen in Figure 17, the equivalent diameter of inclusion A is about 5.1 μm and one piece of acicular ferrite lath is induced by this inclusion. The morphology of the multi-phased inclusion has a spherical shape. This is a typical $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO-TiO}_x$ inclusion, and its main body consists of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$, $\text{Al}_2\text{O}_3\text{-MgO}$, and CaO-TiO_x , respectively. Particularly, $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ is the main content of secondary refining slag and has a low liquidus, thereby presenting a liquid state in molten steel. An $\text{Al}_2\text{O}_3\text{-MgO}$ spinel particle 1.2 μm in size is embedded into the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ liquid inclusion, and it has a very high liquidus temperature. CaO-TiO_2 also has a higher liquidus temperature than that of molten steel except for the condition when $\text{TiO}_2 = 80\%$. As a result, it can be concluded that the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO-TiO}_x$ liquid inclusion was formed in molten steel as described in Figure 8. Then, $\text{Al}_2\text{O}_3\text{-MgO}$ spinel and CaO-TiO_x perovskite precipitated in order during the cooling process.

As shown in Figure 18, inclusion B also shows the spherical shape, and two pieces of acicular ferrite laths are induced by this inclusion. It consists of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$, $(\text{Ca, Mn})\text{S}$, and CaO-TiO_x . Particularly, the left part of the main body is $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$, and the right part of the main body is $(\text{Ca, Mn})\text{S}$ while CaO-TiO_x perovskite precipitates along the edge of the above two phases.

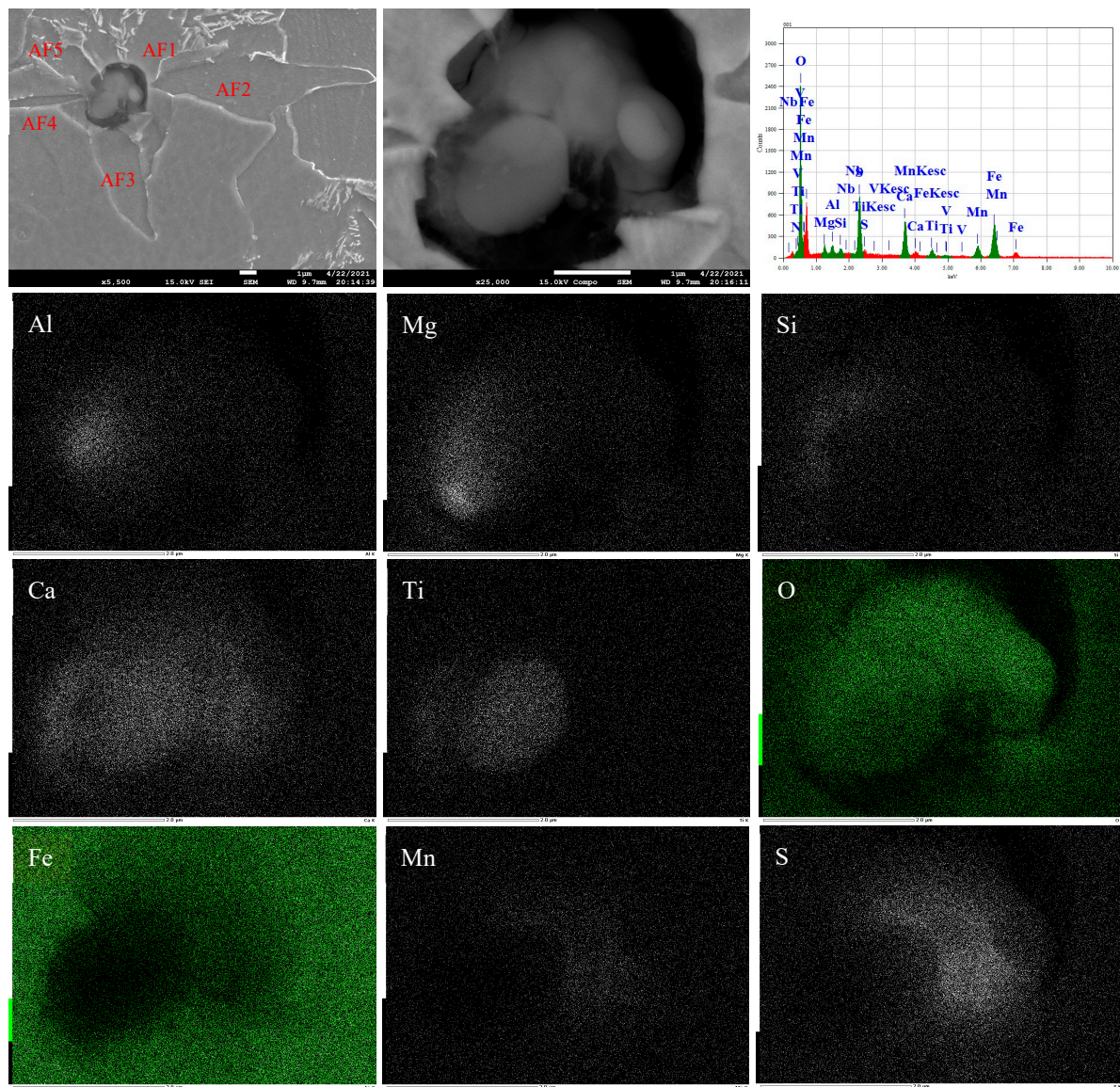


Figure 19. EDS mapping analysis of one typical inclusion C effective for IAF nucleation in Ti-Ca deoxidized steel.

In Figure 19, five pieces of acicular ferrite laths are induced by inclusion C. Different from the above two inclusions, the morphology reveals that it is formed due to the coalescence of several particles: $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$, $(\text{Ca}, \text{Mn})\text{S}$, and CaO-TiO_x . During the secondary refining process, phases with a higher liquidus temperature, such as $(\text{Ca}, \text{Mn})\text{S}$ and CaO-TiO_x , are “captured” by liquid-phase $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$. These particles do not melt and form a new liquid inclusion but mechanically coalesce together.

Almost all the detected inclusions effective at inducing IAFs are found to be $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO-TiO}_x$ -based inclusions. It can be confirmed that $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO-TiO}_x$ -based inclusions are effective nucleation sites for IAF promotion while $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ -based inclusions are ineffective at inducing IAFs. The above three elementary distribution analyses also prove the formation mechanism of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO-TiO}_x$ -based inclusions due to the combination of particles from refining slag and deoxidization products. Then, different phases precipitate in order during the cooling process after secondary refining.

4. Conclusions

To clarify the formation mechanism and evolution of oxide inclusions in Ti-Ca-treated offshore structural steel, industrial sampling was conducted from LF, VD, and TD to final products. Continuous changes and correlations of various inclusions were explained by analysing the number density, morphology, and chemical composition using EPMA and FE-SEM. The primary findings are concluded as follows:

1. The evolution of inclusions during different stages in Ti-Ca-treated offshore structural steel is from primary deoxidization products ($\text{Al}_2\text{O}_3\text{-MnO}$, $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-MnO}$) and their combination with lime ($\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MnO}$ and CaO-SiO_2) $\rightarrow$ $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2 \rightarrow \text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$, $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, and secondary deoxidization products ($\text{Al}_2\text{O}_3\text{-MnO-TiO}_x$ and $\text{SiO}_2\text{-MnO}$) $\rightarrow$ $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. The number density of the inclusions in Ti-Ca-treated industrial steel generally dropped from LF, VD, and Tundish to the final product, except for the Ti-Fe and Si-Ca addition in the LF, the number density slightly increased. The total decrease in the inclusion number density was mainly due to the significantly decreasing number density of small inclusions ($<1\ \mu\text{m}$) during the refining process.
2. The formation mechanism of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ inclusion was due to $\text{CaO-SiO}_2\text{-(MgO)}$ from refining slag and refractory combining with the deoxidization product Al_2O_3 and TiO_x . With the refining process proceeding, Ti-oxide continuously increased and gradually “entered” the inclusion and formed the core of the multiphase inclusions while the Al_2O_3 component generally decreased due to the reduction of Ca, so the average content of CaO showed an adverse trend when compared with that of Al_2O_3 .
3. The formation mechanism of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ inclusions is the initial $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ inclusion came from the combination of CaO-SiO_2 particles in refining slag and the deoxidization product Al_2O_3 , and its liquidus was lower than that of molten steel, so it presented a liquid state in steel and had a smooth surface. After Ca addition, the initial $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ was gradually transferred to $2\text{CaO}\cdot\text{SiO}_2$ with Al_2O_3 continuously reduced by Ca. $2\text{CaO}\cdot\text{SiO}_2$ had a higher liquidus than that of molten steel, so it presented as a solid state in steel and had a rough surface.
4. In Ti-Ca-treated offshore structural steel, after welding simulation, $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ inclusions were not effective at inducing IAFs while $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ inclusions were proven to be effective nucleation sites for promoting IAFs. The $\text{Al}_2\text{O}_3\text{-MgO}$ spinel component in welding samples may have different formation mechanisms: one is that it formed directly in molten steel as a solid state, and other phases and inclusions, such as CaO-TiO_x and MnS , precipitated on $\text{Al}_2\text{O}_3\text{-MgO}$ spinel, so the interface between each phase was clear. Another is that $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-(MgO)-TiO}_x$ as a whole formed in molten steel as a liquid state, and $\text{Al}_2\text{O}_3\text{-MgO}$ spinel firstly precipitated due to its highest melting point and was followed by other phases, so the interface between each phase was not clear.

Author Contributions: Conceptualization, Z.R. and X.M.; methodology, Z.R., B.Z. and X.M.; software, Z.R.; validation, B.Z., X.M. and G.W.; formal analysis, Z.R.; investigation, Z.R. and X.M.; resources, H.L., P.Z. and F.W.; data curation, H.L., P.Z. and F.W.; writing—original draft preparation, Z.R.; writing—review and editing, Z.R, F.T.; visualization, Z.R.; supervision, X.M.; project administration, B.Z., X.M. and G.W.; funding acquisition, B.Z. and X.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Hebei Iron and Steel Group (HBIS), grant number ICSS2017-02.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: Financial support for this research provided by Hebei Iron and Steel Group (HBIS) is greatly appreciated. The authors also acknowledge the facilities and the scientific and technical assistance of the Australian Microscopy & Microanalysis Research Facility at the Centre of Microscopy and Microanalysis at the University of Queensland.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wan, X.L.; Wu, K.M.; Wang, H.H.; Li, G.Q. Applications of Oxide Metallurgy on High Heat Input Welding Steel. *China Metall.* **2015**, *25*, 6–12.
2. Villegas, R.; Redjaimia, A.; Confente, M.; Perrot-Simonetta, M.T. Fractal Nature of Acicular Ferrite, and Fine Precipitation in Medium Carbon Micro-Alloyed Forging Steels. Proc. New Developments on Metallurgy and Applications of High Strength Steels. Ed. Asoc. Argentina de Materiales. Buenos Aires. 2008. Available online: https://www.researchgate.net/publication/301840861_Proc_of_New_Developments_on_Metallurgy_and_Applications_of_High_Strength_Steels_Conference_Minerals_Wiley_John_Sons_Incorporated (accessed on 15 February 2022).
3. Sarma, D.S.; Karasev, A.V.; Jönsson, P.G. On the Role of Non-metallic Inclusions in the Nucleation of Acicular Ferrite in Steels. *ISIJ Int.* **2009**, *49*, 1063–1074. [\[CrossRef\]](#)
4. wan Kim, J.; koo Kim, S.; sik Kim, D.; deuk Lee, Y.; keun Yang, P. Formation Mechanism of Ca-Si-Al-Mg-Ti-O Inclusions in Type 304 Stainless Steel. *ISIJ Int.* **1996**, *36*, 140–143. [\[CrossRef\]](#)
5. Kanazawa, S.; Nakashima, A.; Okamoto, K.; Kanaya, K. Improved Toughness of Weld Fusion Zone by Fine TiN Particles and Development of a Steel for Large Heat Input Welding. *Tetsu Hagané* **1975**, *61*, 2589–2603. [\[CrossRef\]](#)
6. Takamura, J.; Mizoguchi, S. Roles of Oxides in Steels Performance. In Proceedings of the 6th International Iron and Steel Congress, ISIJ, Nagoya, Japan, 21–26 October 1990; Volume I, pp. 591–597.
7. Mizoguchi, S.; Takamura, J. Control of Oxides as Inoculants-Metallurgy of Oxides in Steels. In Proceedings of the 6th International Iron and Steel Congress, ISIJ, Nagoya, Japan, 21–26 October 1990; Volume I, pp. 598–604.
8. Sawai, T.; Wakoh, M.; Ueshima, Y.; Mizoguchi, S. Effects of Zirconium on the Precipitation of MnS in Low Carbon Steels. In Proceedings of the 6th International Iron and Steel Congress, ISIJ, Nagoya, Japan, 21–26 October 1990; Volume I, pp. 605–611.
9. Ogiyayashi, S.; Yamaguchi, K.; Hirai, M.; Goto, H. The Features of Oxides in Ti-deoxidized Steel. In Proceedings of the 6th International Iron and Steel Congress, ISIJ, Nagoya, Japan, 21–26 October 1990; Volume I, pp. 612–617.
10. Kojima, A.; Yoshii, K.I.; Hada, T.; Saeki, O.; Ichikawa, K.; Yoshida, Y.; Shimura, Y.; Azuma, K. Development of High Toughness Steel Plates for Box Columns with High Heat Input Welding. *Shinnittetsu Giho.* **2004**, *90*, 39–44.
11. Kojima, A.; Kiyose, A.; Uemori, R.; Minagawa, M.; Hoshino, M.; Nakashima, T.; Ishida, K.; Yasui, H. Super High HAZ Toughness Technology with Fine Microstructure Imparted by Fine Particles. *Shinnittetsu Giho.* **2004**, *380*, 2–6.
12. Uemori, R. Analysis of the Crystallographic Direction of the Intra-granular Ferrite in Low Alloy Steel. *CAMP-ISIJ* **2001**, *14*, 1174.
13. Kojima, A.; Tomoya, K.; Noboru, H. Effect of Microstructure and Chemical Composition on Laser Weld Metal Toughness. Welded Structure Symposium 2002. *Collect. Lect. Pap.* **2002**, *11*, 327.
14. Kojima, A. High HAZ Toughness Steels with Fine Microstructure Imparted by Fine Particles. *CAMP-ISIJ* **2003**, *16*, 360.
15. Shigesato, G. Progress of High-Performance Steel Plates with Excellent HAZ Toughness. *Nippon. Steel Sumitomo Met. Tech. Rep.* **2018**, *119*, 22–25.
16. Ye, G.; Jönsson, P.; Lund, T. Thermodynamics and Kinetics of the Modification of Al₂O₃ Inclusions. *ISIJ Int.* **1996**, *36*, 105–108. [\[CrossRef\]](#)
17. Ito, Y.I.; Suda, M.; Kato, Y.; Nakato, H.; Sorimachi, K.I. Kinetics of Shape Control of Alumina Inclusions with Calcium Treatment in Line Pipe Steel for Sour Service. *ISIJ Int.* **1996**, *36*, S148–S150. [\[CrossRef\]](#)
18. Higuchi, Y.; Numata, M.; Fukagawa, S.; Shinme, K. Inclusion Modification by Calcium Treatment. *ISIJ Int.* **1996**, *36*, S151–S154. [\[CrossRef\]](#)
19. Kato, T.; Sato, S.; Ohta, H.; Shiwaku, T. Effects of Ca Addition on Formation Behavior of TiN Particles and HAZ Toughness in Large-Heat-Input-Welding. *Kobelco Technol. Rev.* **2011**, *30*, 76–79.
20. Wang, K.; Jiang, M.; Wang, X.; Wang, Y.; Zhao, H.; Cao, Z. Formation Mechanism of CaO-SiO₂-Al₂O₃-MgO Inclusions in Si-Mn-Killed Steel with Limited Aluminum Content during Low Basicity Slag Refining. *Metall. Mater. Trans. B* **2016**, *47*, 282–290. [\[CrossRef\]](#)
21. Wang, C.; Wang, X.; Kang, J.; Yuan, G.; Wang, G. Effect of Thermomechanical Treatment on Acicular Ferrite Formation in Ti-Ca Deoxidized Low Carbon Steel. *Metals* **2019**, *9*, 296. [\[CrossRef\]](#)
22. Wang, X.; Wang, C.; Kang, J.; Yuan, G.; Misra, R.D.K.; Wang, G. Improved Toughness of Double-pass Welding Heat Affected Zone by Fine Ti-Ca Oxide Inclusions for High-strength Low-alloy Steel. *Mater. Sci. Eng. A* **2020**, *780*, 139198. [\[CrossRef\]](#)
23. Yamamoto, K.; Hasegawa, T.; Takamura, J.I. Effect of Boron on Intra-granular Ferrite Formation in Ti-Oxide Bearing Steels. *ISIJ Int.* **1996**, *36*, 80–86. [\[CrossRef\]](#)

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24. Mabuchi, H.; Uemori, R.; Fujioka, M. The Role of Mn Depletion in Intra-Granular Ferrite Transformation in the Heat Affected Zone of Welded Joints with Large Heat Input in Structural Steels. *ISIJ Int.* **1996**, *36*, 1406–1412. [[CrossRef](#)]
 25. Fukunaga, K.; Chijiwa, R.; Watanabe, Y.; Kojima, A.; Nagai, Y.; Mamada, N.; Adachi, T.; Date, A.; Taniguchi, S.; Uemori, R.; et al. Advanced Titanium Oxide Steel with Excellent HAZ Toughness for Offshore Structures. In Proceedings of the ASME 2010 29th International Conference on Ocean, Offshore and Arctic Engineering OMAE2010, Shanghai, China, 6–11 June 2010; pp. 1–9.