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Effect of Alloy Addition on Inclusion Evolution in Stainless Steels
based on Three-Dimensional Investigation of Inclusions

Xue Yin, Yanhui Sun, Yindong Yang, Mansoor Barati, Alex McLean

Abstract:
The number, morphology, size, and composition of inclusions after deoxidation and alloying in Ti-stabilized stainless steel were investigated. This was carried out by electrolytic extraction of complete inclusions from steel matrix, followed by microscopic examination. It was found that after the addition of ferrosilicon and manganese, and later aluminum, the composition of inclusions changed from manganese silicate-rich inclusions to alumina-rich inclusions. After tapping and titanium wire feeding, three types of TiN inclusion morphologies were observed, single, twinned and clusters. Both the turbulence and Stoke’s collisions mechanisms play a considerable role in the formation of cluster TiN.

Key word: Deoxidizer, inclusion evolution, electrolytic extraction, three-dimensional investigations
1. Introduction

Non-metallic inclusions in steel can cause deterioration of mechanical properties, surface defects, initiation sites for corrosion-fatigue cracks, and hydrogen embrittlement, as well as operational complications such as clogging of the submerged entry nozzle (SEN) \cite{1-4}. However, complete removal of harmful inclusions from molten steel during the refining process is difficult. An alternative approach is to minimize the harmful effects of residual inclusions or to beneficially utilize these inclusions through proper control and modification.

Aluminum is one of the strongest deoxidizers \cite{14,15} for steel. However, due to the harmful effects of Al$_2$O$_3$-rich inclusions on steel quality and process, Si and Mn are often used as steel deoxidizers \cite{5,6}. After deoxidation by Si/Mn, the main constituents of inclusions are MnO and SiO$_2$. Al$_2$O$_3$ and CaO may also enter the steel through entrainment of the top slag. Titanium is another deoxidizer with beneficial effects in austenitic stainless steel, as it suppresses chromium carbide precipitation in the grain boundaries and reduces susceptibility to intergranular corrosion through the formation of very stable titanium carbide \cite{16}. However, the excessive Ti and N can form coarse TiN inclusions that grow to large particles \cite{17,18}. As one type of inherently brittle nonmetallic inclusion, they have often been reported to act as fracture initiation sites \cite{19-21} thus adversely affecting the fatigue life and toughness of the steel \cite{22-29}. Moreover, in titanium stabilized steels, TiN is found in the submerged entry nozzle (SEN) blockage materials. Hasegawa \cite{30} reported that the major deposited materials were made up of Al$_2$O$_3$ and TiN inclusions. Maddalena \cite{31} indicated that two distinct types of titanium nitride-based deposits were found after analysis of clogged nozzles from titanium treated stainless steel (types 321 and 409): pure TiN and TiN associated with a spinel phase. Gao \cite{32} reported that stainless steel with Ti content exceeding 0.15% increases the risk of clogging significantly.

The previous studies on TiN inclusions have concentrated on two dimensional (2D) investigation of inclusions by sectioning steel samples, limiting accurate chemical analysis of the inclusion surface and obtaining a full understanding of their 3D features \cite{33}. In the present study, electrolytic extraction (EE) was employed to extract intact inclusions from steel matrix, allowing three-dimensional investigations of inclusion characteristics (such as composition, size, number, and morphology) in steel samples taken after different deoxidizers additions. After separating the particles on the surface of film filter, the particle size distribution was determined for most of the major nonmetallic inclusion types found in the samples. The evolution of different inclusions and formation and growth mechanisms of TiN clusters were investigated and discussed.

2. Experimental Procedure

2.1 Sample preparation

In this study, inclusions formed in 17Cr austenitic stainless steel were investigated after deoxidation and Ti-stabilization. Steel scrap and alloys were initially melted in an intermediate frequency induction furnace, and the molten steel was subsequently decarburized, deoxidized, and desulfurized in an AOD furnace. After transfer to a ladle furnace, the composition and temperature of the steel were adjusted and argon injection was applied to enhance the removal of inclusions at the ladle treatment station. Table 1 presents the final composition of the steel before ingot casting.
Table I. Chemical composition of Ti-stabilized stainless steel (mass pct)

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Ti</th>
<th>Al</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.032</td>
<td>0.37</td>
<td>1.13</td>
<td>0.039</td>
<td>0.0017</td>
<td>17.14</td>
<td>9.06</td>
<td>0.307</td>
<td>0.026</td>
<td>0.025</td>
<td>0.0029</td>
</tr>
</tbody>
</table>

Steel samples for investigation of inclusions were obtained at various stages during the production process according to the scheme shown in Figure 1. The samples were taken after the addition of deoxidizing agents Si/Mn, followed by Al, after feeding titanium alloy wire and at the start of casting.

![Fig. 1 Schematic illustration of sampling locations.](image)

### 2.2 Inclusion Characterization

Electrolytic extraction (EE) method was applied for extraction of inclusion particles. The method involves dissolution of steel matrix under an applied potential, leaving intact particles behind. Steel sample (15 × 15 × 4 mm) were subjected to EE in a 10% AA (10 v/v% acetylacetone-1 wt/v% tetramethylammonium chloride-methanol) electrolyte. The current density was set at 40-50 mA cm⁻² during the extraction. The weight of dissolved metal during electrolytic extraction was 0.12-0.2 g with the EE time at about 2.5-3 hours. After extraction, the solution containing inclusions was filtrated through a polytetrafluoroethylene (PTFE) membrane with an open pore size of 0.2 µm. After coating the membrane filter with gold under vacuum conditions, the characteristics (morphology, size and composition) of extracted inclusions were investigated using the SEM equipped with EDS. The number of inclusions per unit volume \( N_v \) was calculated as follows:

\[
N_v = n \cdot \frac{A_{\text{filter}}}{A_{\text{observed}}} \cdot \frac{\rho_{\text{metal}}}{W_{\text{dissolved}}}
\]  

where \( n \) is the number of inclusions in the appropriate size interval, \( A_{\text{filter}} \) is the area of the film filter, \( A_{\text{observed}} \) is the total observed area, \( \rho_{\text{metal}} \) is the density of the steel matrix and \( W_{\text{dissolved}} \) is the dissolved weight of the steel during extraction.

### 3. Result and Discussion

#### 3.1 Morphology and size Changes of inclusions

Inclusions typically found after Si/Mn deoxidation are shown in Figure 2. The non-metallic inclusions were classified into two different categories based on their composition and morphology: manganese silicates (Figure 2 (a) ~ (c)) and inclusions containing both oxide and manganese sulfide (Figure 2 (d) ~ (f)). Most of the manganese silicate inclusions are spherical in shape (a) due to the fact that these inclusions are liquid at steelmaking temperature. It can be seen from (d) ~ (f) that MnS patches are present at the surface of oxide inclusions. Kim et al. [34] and Wakoh et al. [35]
reported that MnS phase could precipitate by S diffusion from the matrix to the oxide due to segregation during cooling. Such kind of MnS has often been found in the inclusions after Si/Mn deoxidation \cite{35-37}. As the temperature is reduced, an appreciable amount of sulfur has to diffuse into the liquid (Si, Mn)-rich oxide as the solubility of sulfur in solid steel is very low. As a result, the (Si,Mn)-rich oxide is enriched in sulfur especially at the outer layer of inclusions and will be supersaturated with sulfur on further cooling. This sulfur is eventually precipitated as MnS phase on the inclusion surface.

![Fig. 2 Three-dimensional morphologies of inclusions extracted from steel samples after Si/Mn](image)

After Al addition, the silicate based inclusions are generally transformed into alumina-rich inclusions according to Reactions [2] and [3] due to the higher affinity between Al and O. The total oxygen was about 110 ppm after Si/Mn deoxidation and decreased to 39 ppm after Al addition. Inclusions typically observed after Al additions are shown in Figure 3. These inclusions are irregular in shape with a rough surface, pointing to their presence in steel as solid phases, due to their high melting temperature.

\begin{align*}
4[Al] + 3(SiO_2)_{\text{inclusion}} & = 2(Al_2O_3)_{\text{inclusion}} + 3[Si] \quad [2] \\
2[Al] + 3(MnO)_{\text{inclusion}} & = (Al_2O_3)_{\text{inclusion}} + 3[Mn] \quad [3]
\end{align*}

![Fig. 3 Three-dimensional morphologies of inclusions extracted from steel samples after Al addition](image)

The particle size distributions of inclusions are shown in Figure 4. Most of the inclusions were observed to be < 4 µm in size with majority being around 1.5 µm and 1.0 µm after Si/Mn and Al
additions respectively. Further, the number density of inclusions is much higher after Si/Mn addition than that of Al addition. Noting that no obvious coarsening is happening during Al addition, based on the size distributions, it is concluded that some inclusion have been removed during the refining process.

![Fig. 4 Particle size distributions of inclusions (a): After Si/Mn addition (b): After Al addition](image)

### 3.2 Composition Change of inclusions

The inclusion compositions, determined from the SEM-EDS analysis of steel samples after Si/Mn and Al additions were plotted on the polythermal projection of the SiO₂–MnO–Al₂O₃ and SiO₂–Al₂O₃–MnO ternary diagram respectively as shown in Figure 5 calculated by FactSage 7.0. It should be mentioned that CaO was also detected in the inclusions due to the interaction between slag and steel; its effect on the phase diagram and inclusion composition was however ignored due to the low content (< 5%) and for simplification. As can be seen from Figure 5 (a), after Si/Mn addition, the inclusion compositions are concentrated close to the MnO-SiO₂ binary region, which is almost in liquid region due to its lower melting point than that of steel \(^{38}\). This explains the spherical shape of the inclusions in Figure 2. After Al addition, the composition shifts towards high-alumina phases near the Al₂O₃ corner with a higher melting point.

![Fig.5 Calculated polythermal projection, (a): After Si/Mn addition (b): After Al addition](image)

The effect of alumina content on the liquidus temperature and the primary crystalline phase of the inclusions were calculated by FactSage 7.0 with the FToxid database as shown in Figure 6. Increasing the concentration of alumina in the inclusions changed the primary phase in the following order SiO₂, MnSiO₃ (rhodonite), Mn₃Al₃Si₃O₁₂ (spessartite), MnAl₂O₄ (galaxite), and Al₂O₃. The
liquidus temperature of the inclusion first decreased with increasing alumina concentration up to about 7.5 mol %, followed by a rebound after this composition. In this study, the alumina concentration of the inclusions after Al addition was found to be over 60%, explaining their solid state in steelmaking temperatures and irregular morphologies, as seen in Figure 3.

![Diagram](image)

**Fig. 6** Calculated liquidus temperatures in the MnO-SiO$_2$-Al$_2$O$_3$ systems as a function of the concentration of Al$_2$O$_3$ when the ratio of mol pct MnO to mol pct SiO$_2$ is 0.75

### 3.3 Inclusion Characteristics after Ti addition

The TiN inclusion belongs to the cubic or triangular-shaped crystal phase system with a high melting temperature and hardness, making them difficult to deform during steel processing$^{[24]}$. Zhou et al. $^{[39]}$ reported that nitrides with the average size of 6 µm are equivalent to oxides with an average size of 25 µm in terms of the deterioration of fatigue life.

After Ti-core wire feeding, inclusions with three distinct morphologies were identified: single particles of titanium nitride (Figure 7 (a) - (d)), twinned particles of titanium nitride (Figure 7 (e) - (h) and clusters (Figure 7 (i) - (l)). Single TiN has a regular cubic structure, while the twinned TiN particles resembled two more cubic crystals colliding with each other. Maddalena et al. reported that this kind of TiN was caused only by growth of two nucleates $^{[31]}$. TiN clusters usually have a larger size, which may be broken up into smaller TiN particles as a stringer shape during rolling process$^{[40,16]}$. The microvoids in such stringers, when exposed to an aqueous solution, will act as sites for pitting corrosion or the initiation of stress corrosion cracking, negatively impacting the to the steel quality.

It should be pointed out that oxide particles were still observed in the steel samples after Ti addition. However, due to their very low content less than 1%, only TiN was discussed. The oxide inclusions can in fact act as the effective heterogeneous nuclei for TiN formation which was confirmed by two dimensional analysis on the cross-sections$^{[40,41-44]}$. 
Figure 8 gives the size distributions of the three types of TiN inclusions. In sample L1, the number densities of single and twinned TiN are dominant. In sample C1, the density of large clusters has increased due to agglomeration of single, twinned, or small clusters of TiN into bigger clusters. Clusters with the size more than 10 µm were also observed in sample C1 as shown in the upper right corner of Figure 8 (b). These larger clusters can easily adhere to the nozzle wall and cause nozzle clogging. Moreover, they can severely impact the steel quality if they appear in the final product.

3.4 Formation and Growth Mechanism of TiN Clusters

The formation and growth of TiN clusters in the liquid steel appears to take place in two steps: 1) formation of small clusters by collision of single or twinned inclusions, 2) growth of clusters by collision with single/twinned inclusion or with other clusters. There are three types of collision which can happen between inclusions: 1) Brownian collision due to the random movement of very small inclusions in molten steel, 2) Turbulence collision because of the turbulent flow of liquid steel which can cause the inclusion collision, 3) Stoke’s collision due to the density difference between steel and inclusions so that larger inclusions ascend faster than smaller ones and collide with them as they travel up. Each of the collision mechanisms makes a contribution to the total number of inclusion collisions.

The collision number of inclusions in the liquid steel per unit time (“collision rate”) can be
calculated by the following Equation [45]:

\[ \frac{dn_{ij}}{dt} = w_{ij} n_i n_j \]  \hspace{1cm} [4]

where \( w_{ij} \) is the collision volume \((\text{m}^3/\text{s})\) of a certain collision phenomenon, \( n_i \) and \( n_j \) are the number of inclusions within certain size ranges and \( t \) is time \((\text{s})\). The collision volume for Brownian collision \((w_{ij}^B)\), Turbulence collision \((w_{ij}^T)\) and Stoke’s collision \((w_{ij}^S)\) can be expressed as following respectively:

\[ w_{ij}^B = \frac{2kT}{3\mu} \left( \frac{1}{r_i} + \frac{1}{r_j} \right) (r_i + r_j) \]  \hspace{1cm} [5]

\[ w_{ij}^T = 1.3\alpha \sqrt{\pi \varepsilon \rho_{Fe} / \mu} (r_i + r_j)^3 \]  \hspace{1cm} [6]

\[ w_{ij}^S = \frac{2\pi g (\rho_{Fe} - \rho_i)}{9\mu} (r_i + r_j)^3 |r_i - r_j| \]  \hspace{1cm} [7]

In these equations, \( k \) is the Boltzmann constant \((\text{J/K})\), \( T \) is the absolute temperature \((\text{K})\), \( \mu \) is the dynamic viscosity of steel \((\text{kg/m} \cdot \text{s})\), \( \alpha \) is the collision efficiency, \( \varepsilon \) is the turbulent energy dissipation \((\text{m}^2/\text{s}^3)\), \( \rho_{Fe} \) and \( \rho_i \) are the densities of the steel and inclusion respectively \((\text{kg/m}^3)\), \( g \) is the gravitational acceleration \((\text{m/s}^2)\) and \( r_i \) and \( r_j \) are the radii of the two colliding inclusions \((\text{m})\).

Each of the different collision mechanism can make a contribution to the total number of collisions. Therefore, collision volume \( w_{ij} \) was calculated using the parameters given in Table 2 in order to determine the significance of the separate collision mechanisms. It should be pointed out that the calculation of collision volume was based on considering spherical inclusions in steel. Therefore, in this study, it was assumed that an irregular shape inclusion can rotate around its center due to the liquid steel flow, and can collide with other inclusions within the rotational region, whose maximum length equals to the inclusion diameter.

Figure 9 presents the calculated values of the collision volumes for an inclusion of 1.48\( \mu \text{m} \) (size with a highest content according to Figure 8 ) that collides with other inclusions of different sizes.

It can be seen from Figure 9 that Brownian collision volume \( w_{ij}^B \) is drastically smaller than that of Stoke’s and Turbulent collision volume in all studied ranges of \( r_i \), whose impact on inclusion growth can be neglected. Both Turbulence and Stoke’s collision mechanism have a much higher effect on the collision volume compared to the Brownian collision. They keep an increasing trend as a function of increased size (more than 1.48\( \mu \text{m} \)). Moreover, the effect of Turbulence collision is higher than Stokes and the difference between these two collisions is decreasing as the inclusion size increases within the the range studied here. Therefore, both Turbulence and Stoke’s mechanism are believed to play a considerable role in inclusion coarsening.

<table>
<thead>
<tr>
<th>( k ) ((\text{J/K}))</th>
<th>( T ) ((\text{K}))</th>
<th>( \mu ) ((\text{kg/m} \cdot \text{s}))</th>
<th>( \alpha ) ((\text{m}^2/\text{s}^3))</th>
<th>( \varepsilon ) ((\text{m}^2/\text{s}^3))</th>
<th>( \rho_{Fe} ) ((\text{kg/m}^3))</th>
<th>( \rho_i ) ((\text{kg/m}^3))</th>
<th>( g ) ((\text{m/s}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.38 \times 10^{-23} )</td>
<td>1873</td>
<td>0.005</td>
<td>0.3</td>
<td>0.0018</td>
<td>8000</td>
<td>5220</td>
<td>9.81</td>
</tr>
</tbody>
</table>
4. Conclusions

Inclusions characteristics (such as morphology, composition and size distribution) were analyzed in steel samples taken after different alloy additions using electrolytic extraction methods followed by SEM-EDS characterization. The following conclusions were drawn.

(1) After the addition of ferrosilicon alloy and electrolytic manganese, followed by aluminum, the composition of inclusions changed from manganese silicate-rich inclusions with spherical shapes to alumina-rich inclusions with irregular shapes.

(2) After Ti-stabilization, three TiN inclusion morphologies were found: single particle, swinned particles, and clusters.

(3) Both the Turbulence and Stoke’s collision mechanism are the effective in formation and coarsening of TiN clusters; the Brownian collision mechanism appeared to play a minor role.

5. Acknowledgments

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6. Reference


