Mechanism of Floater Formation in the Mold during Continuous Casting of Ti-Stabilized Austenitic Stainless Steels

Zhuo Chen, Min Li, Xufeng Wang, Shengping He and Qian Wang *

College of Materials Science and Engineering and Chongqing Key Laboratory of Vanadium-Titanium Metallurgy and Advanced Materials, Chongqing University, Chongqing 400044, China; chenzhuo@cqu.edu.cn (Z.C.); sjzlimin@cqu.edu.cn (M.L.); wangxufeng@cqu.edu.cn (X.W.); heshp@cqu.edu.cn (S.H.)
* Correspondence: q_wang@cqu.edu.cn; Tel.:+86-13983362315

Received: 7 May 2019; Accepted: 30 May 2019; Published: 31 May 2019

Abstract: During the continuous casting (CC) of Ti-bearing steel, a steel lump can solidify in the mold (i.e., floater steel) more easily than in the Ti-free steels. This causes severe surface defects or even a breakout. We have examined the mechanisms of floater formation during the CC of 321 stainless steel by analyzing the inclusions in the floater steel and in the 321 steel that was sampled from the mold. Additionally, we calculated the disregistry between the metallic phases and common inclusions. The mineralogy and morphology of the inclusions were examined while using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD). Thermodynamic calculations on the Ti$_x$O$_y$ inclusions at different oxygen potentials were performed while using FactSage 7.2. Using this approach, we determined that ferrite nucleates grow on TiN and MgO inclusions following solidification, which then form micro-aggregates as a result of dynamic collisions and alliances. Analysis of the mold slag from the metallurgy stage indicated that altering the basicity and properties of the mold flux systematically might minimize the reaction between the slag and steel, which would achieve a coordinated control over lubrication and heat transfer.

Keywords: continuous casting; floater; steel-slag reaction; inclusions; Ti-stabilized stainless steel

1. Introduction

Austenitic, Ti-stabilized 321 stainless steel exhibits a remarkable resistance to intergranular corrosion over an extended temperature range. Therefore, it is commonly used in applications, such as exhaust manifolds and expansion joints. The addition of titanium in 321 stainless steel (5(C + N), ~0.70 mass% Ti), in combination with an appropriate heat treatment, stabilizes the alloy against sensitization to intergranular corrosion. However, the addition of titanium can cause a number of problems during the continuous casting (CC) of high Ti-bearing alloy steels. One problem is the clogging, which adheres to the inner-wall of submerged entry nozzle (SEN) and involves the deposition of titanium oxide, nitride inclusions, Al$_2$O$_3$ or MgO inclusions, and frozen steel droplets [1–4]. The other is the formation of mold floater, known as a solidified lump of steel floating in a mold [2,4]. The severity of nozzle clogging and mold floaters in the case of Ti-bearing steels is significantly higher than that in the Ti-free steels. This is primarily because of heterogeneous nucleation of TiN on either Al$_2$O$_3$ or Al$_2$O$_3$-MgO spinel inclusions and the invariable and fast reaction with the alumina-graphite refractory of the SEN [5]. Furthermore, TiN is progressively oxidized to TiO$_x$, which can exist as a binary TiO$_x$-Al$_2$O$_3$ phase in the clogging [1,2,6]. The TiO$_x$-Al$_2$O$_3$ inclusions are reported to be more easily wetted by the liquid steel, when compared with the pure Al$_2$O$_3$ inclusions [7]. These inclusions have a tendency to adhere to the surface of the nozzle when it is immersed due to a combination of
turbulent flow, rough erosion of the nozzle walls, and the poor wettability between Al₂O₃ inclusions and the steel melt.

In contrast to the ferrite steels, the austenitic steels tend to suffer less from clogging, but more from mold floaters, because they have a lower liquidus temperature and both [N] and [O] are more soluble in steels [6]. Floaters that consist of a solidified steel buildup floating in the mold during the CC of 321 stainless steel have been reported previously [4,6,8]. These floaters primarily consist of a steel matrix that contains gas holes, TiN inclusions, and mold slag, which is likely trapped by an initial shell that solidifies and leads to breakout by sticking and surface defects. Therefore, TiN inclusions in the molten steel appear to accelerate the heterogeneous nucleation of ferrite, which then acts as an effective nucleating agent. Furthermore, TiN can react with the oxides in a mold powder or be entrapped air in the melt to form gas blowholes. Clogging and floaters can both deteriorate the castability of a metal by causing an asymmetric flow field of liquid steel in the mold, which increases the probability of mold flux inclusion in the cast products and surface defects.

The CC of Ti-bearing steels inevitably involves a reaction between the liquid steel and the molten mold flux in the casting mold, as shown in Figure 1. This involves following Equations (1)–(3) [9–12]:

\[
\text{(SiO}_2\text{)} + [\text{Ti}] = [\text{Si}] + (\text{TiO}_2) \quad (1)
\]

\[
\text{TiN} + \text{(SiO}_2\text{)} = [\text{Si}] + (\text{TiO}_2) + [\text{N}_2] \text{ (g)} \quad (2)
\]

\[
\text{TiN} + 2/3(\text{Fe}_2\text{O}_3) = 4/3[\text{Fe}] + (\text{TiO}_2) + 1/2[\text{N}_2] \text{ (g)} \quad (3)
\]

Figure 1. Schematic diagram of steel-slag reaction of Ti-bearing steel in the mold during the continuous casting (CC) process.

A number of studies have focused on the effects of TiO₂ concentration on the properties of the mold flux when casting Ti-bearing steels, including viscosity, solidification temperature, crystallization behavior, and heat transfer [9,10,13–15]. Higher titanium levels promote the formation of a perovskite (CaTiO₃) at the expense of cuspidine. Moreover, the formation of TiN and Ti(C, N) adversely affects the quality of steel because of the reaction between TiO₂ with carbon and nitrogen [16]. Additionally,
the investigation on the structure of TiO$_2$-bearing mold flux system in the casting of Ti-stabilized stainless steel was reported by Li et al., showing that a small amount of Ti in the silicate network can act as the role of network formation, which enhances the degree of polymerization of the silicate network [17]. Raman spectral study on silicate glass indicated that Ti$^{4+}$ is in four-fold coordination and it forms discrete units in the structure of glasses, and four-fold titanium increases with increase of TiO$_2$ content [18–20].

However, there is little information relating to the mechanisms of floater formation when compared with the clogging of the Ti-bearing stainless steels. The research of the reaction performances of Ti-bearing steels between steel and slag is scarce in comparison to the high-Mn and high-Al steel. Therefore, we have focused on the generation of floaters at the steel-slag interface to clarify the limitations of sequence casting of Ti-bearing steels. In this paper, metallurgical observations of inclusions in different samples, in combination with analysis of thermodynamic analysis and the calculation of disregistry between inclusions and metallic phases, were used to improve the understanding of the impact of inclusions on the deterioration in the castability of 321 stainless steel. This allowed us to propose a mechanism for the formation of the floaters in high Ti-bearing alloy steels. Differences in the compositions and properties of mold slag, before and after the steel-slag reactions, were also studied by the steel-slag experiments.

2. Methodology

2.1. Characterization

The methodology used to examine the samples from the 321 stainless steel involved:

1. Collection of mold floater and 321 stainless steel samples from the mold metallurgy stage during CC.

2. Characterization of inclusions in the floater and steel samples while using scanning electron microscope (TESCAN, VEGA 3, Brno, Czech Republic) and energy dispersive spectroscopy (Oxford Instruments, Inca X-Max 50, Buckinghamshire, UK). The physical characteristics of the floaters were also visually examined. Heating the samples in a MoSi$_2$ furnace determined the densities of the floater and the alloy in the liquid phase. High purify argon gas (99.9999%) was passed over the sample (1 L/min) at atmospheric pressure during the measurement. The samples (20 g) were added to a MgO crucible that was placed in a graphite susceptor in a MoSi$_2$ furnace. The fluctuation of the melt temperature was controlled within ±5 °C. The vertical temperature distribution was maintained within 5 °C. Three samples of the 321 steel and the floater in the mold were examined.

3. The 321 steel and floater steel samples were cut, ground, and analyzed while using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-OES) (PerkinElmer, optima 8000, Waltham, MA, USA) to determine their chemical composition (as shown in Table 1). The inclusions within the samples from the mold metallurgy stage were analyzed by contrastive analysis using SEM and EDS. The molten mold fluxes were sampled by inserting a steel rod during the CC, which were then ground into powder for analysis. The content of CaO, SiO$_2$, Al$_2$O$_3$, MgO, Na$_2$O, and TiO$_2$ and mineralogical phase in the flux were determined using X-Ray Fluorescence spectroscopy (XRF) (Shimadzu, XRF-1800, Kyoto, Japan) and X-ray diffraction (XRD) (PANalytical, Empyreal, Almelo, the Netherlands), respectively.

2.2. Laboratory Investigations

1. To determine whether the small scale investigation of the floater formation mechanism was valid, the prepared steel sample (300 g) was added to a MgO crucible (OD 80 mm × ID 60 mm × H 100 mm) and melted in the MoSi$_2$ furnace at 1500 °C. The chamber was filled with high purity argon gas (99.9999%) at atmospheric pressure throughout the experiment. When the steel completely melted, pure iron pieces (60 g) or a mixture of pure iron pieces (60 g) and TiN (6 g) was added into the molten steel to obtain a composition that was similar to that of the floater from the mold. After homogenization
(30 min.), the temperature was decreased at a rate of 10 °C every 30 min. until it reached 1440 °C (nearly melting point of 321 steel). The floater steel that formed and collected during the cooling process was then quenched in cold water. The samples were ground, cut, and analyzed using SEM to determine the distribution of TiN within the steel samples.

(2) The reaction between the slag and the steel was conducted in an induction furnace. Approximately 5 kg of the steel sample was added to a MgO crucible (OD 80 mm × ID 60 mm × H 300 mm) and was heated between 1500 °C and 1530 °C. The atmosphere inside the furnace was high purity argon gas throughout the experiment. When the steel was completely melted, pre-fused mold slag (500 g) was added in the molten steel, followed by TiN (3 wt. % of the mold slag) to simulate the quality of TiN floating at the steel-slag interface during industrial production. The crust slag and liquid slag were sampled and then quenched in cold water. The crust slag samples were ground and analyzed while using XRF and SEM. The properties (viscosity at 1300 °C and melting point) of the liquid slags were measured through a rotating cylinder method and a melting point tester, with the flow of purified argon at 1 L/min. [21].

3. Results and Discussions

3.1. Characteristic of Floater and 321 Stainless Steel

The formation of floaters is typically observed at the steel-slag interface within the mold after casting for 15 min., and approximately one fifth of the floater was exposed to the air. The floaters that were formed had an average size of 80 × 40 × 20 mm³ and were coated with a thin enameled phase, as shown in Figure 2. Furthermore, the constituents of coated phase (CaO, SiO₂, Al₂O₃, TiO₂, MgO, and Na₂O) maintain a similar consistency of mold slag, as determined by microprobe analysis. The morphology of the steel-slag interface, as shown in Figure 3, was examined using SEM, which showed that it had a porous structure between the floater steel and the covered slag. This indicated that interfacial reactions between TiN and SiO₂ or Na₂O occurred in the floater matrix. The floaters that had higher porosity were 2.2% lighter than 321 steel in the determination of density by measuring the coefficient of linear expansion at 1450 °C (the interfacial temperature of steel-slag in mold). In addition, the melting temperature of the floater that was measured in the high temperature MoSi₂ furnace was 27 °C lower than that of the 321 steel. Table 1 shows the chemical compositions of the floater and the 321 steel. The iron content within the floater was 12 wt. % higher than that of the 321 steel, while the Cr and Ni content were lower than that in the 321 steel. However, titanium was only observed in 321 steel. Therefore, the differences in the physical properties can be explained by the differences in the composition, which were probably affected by the ability of TiN to nucleate δ-Fe for Ti stabilized steel.

| Samples   | Fe  | Ni  | Cr  | Ti  | Mn  | Si  | T_m ¹ (°C) | ρ₂₀ °C (g/cm³) | ρ₁₄₅₀ °C (g/cm³) |
|-----------|-----|-----|-----|-----|-----|-----|------------|----------------|------------------|
| 321 steel | 70.16 | 8.76 | 18.95 | 0.29 | 0.76 | 1.08 | 1441        | 7.92            | 6.98             |
| Floater   | 82.22 | 4.15 | 13.63 | -   | -   | -   | 1468        | 7.53            | 6.83             |

¹ Melting temperature.
which significantly minimizes the detrimental effects \[24\].

Thermodynamic calculations were performed to understand the precipitation of the inclusions at equilibrium. This was done while using FactSage 7.2 with FSmisc and FToxid databases \[22\]. The chemical composition of 321 stainless steel (100 g) in the ladle was taken and calculated to contain 71.216% Fe, 0.03% C, 17.31% Cr, 9.35% Ni, 0.31% Ti, 0.019% Al, 0.73% Si, 0.99% Mn, 0.0127% N, 0.028% P, and 0.003% S (wt. %). The oxygen content ([O\%]) was set as 0.006, 0.03, and 0.0015.

Figure 4 illustrates the evolution of inclusions as a function temperature at different production temperatures (Table 2) during the industrial process. As the steel cools, Ti$_2$O$_3$ starts to form at 1600 °C as the sole oxide inclusion under the equilibrium condition with [O\%] ≥ 0.002. We have previously examined the precipitation of TiN over the full duration of the casting sequence \[23\]. TiN was found to be one of the primary inclusions, with more than 80 wt. % TiN being precipitated before Period 3 (in the ladle and tundish). If countermeasures, such as a gas curtain and moderate argon injection into the nozzle before the SEN, are adopted, then the TiN inclusions are excluded and anti-oxidized, which significantly minimizes the detrimental effects \[24\].
3.2. Thermodynamic Analysis of Inclusions of 321 Stainless Steel

Thermodynamic calculations were performed to understand the precipitation of the inclusions at equilibrium. This was done while using FactSage 7.2 with FSmisc and FToxid databases [22]. The chemical composition of 321 stainless steel (100 g) in the ladle was taken and calculated to contain 71.216% Fe, 0.03% C, 17.31% Cr, 9.35% Ni, 0.31% Ti, 0.019% Al, 0.73% Si, 0.99% Mn, 0.0127% N, 0.028% P, and 0.003% S (wt. %). The oxygen content ([O%]) was set as 0.006, 0.03, and 0.0015.

Figure 4 illustrates the evolution of inclusions as a function of temperature at different production temperatures (Table 2) during the industrial process. As the steel cools, TiO2 starts to form at 1600 °C as the sole oxide inclusion under the equilibrium condition with [O%] ≥ 0.002. We have previously examined the precipitation of TiN over the full duration of the casting sequence [23]. TiN was found to be one of the primary inclusions, with more than 80 wt. % TiN being precipitated before Period 3 (in the ladle and tundish). If countermeasures, such as a gas curtain and moderate argon injection into the nozzle before the SEN, are adopted, then the TiN inclusions are excluded and anti-oxidized, which significantly minimizes the detrimental effects [24].

3.3. Calculation of Planar Disregistry

Grinder and Choné reported that TiN lowered the requirement of undercooling for the nucleation of δ-Fe in austenitic stainless steels [25]. The effectiveness of the nucleation catalysts can be explained using the disregistry between the lattice parameter of the substrate and the nucleating phase, since the disregistry can reflect the relative effectiveness of nucleating agents in promoting nucleation in liquid metals. The planar disregistry that is modified by Bramfitt can be calculated using Equation (4) [26]. In general, the nucleating agent is effective when the planar disregistry is below 6%, otherwise it will not effectively facilitate nucleation. Nunnington and Sutcliffe proposed that the formation of floaters is associated with the reaction of TiN inclusions with the mold flux, followed by solidification of δ-Fe [5]. However, there are no systematic studies that examine the effects of other common inclusions on nucleation.

\[
\delta_{(hkl)} = \sum_{i=1}^{3} \left( \frac{d_{[uvw]_s} \cos \theta - \left( \frac{d_{[uvw]_n}}{3} \right)}{d_{[uvw]_n}} \right) \times 100 
\]

where

- (hkl)s = a low-index plane of the substrate,
- [uvw]s = a low-index direction in (hkl)s,
- (hkl)n = a low-index plane in the nucleated solid,
- [uvw]n = a low-index direction in (hkl)n,
- \(d_{[uvw]}\) = the interatomic spacing along [uvw]s, and
- \(\theta\) = the angle between the [uvw]s and [uvw]n.

Table 3 provides the crystallographic properties of the effective compounds, which are calculated from the room temperature, \(a_0\) is calculated from the room temperature value by taking the linear thermal
coefficient of expansion of the compound between room temperature and 1450 °C (the interfacial temperature of steel-slag in mold) into account. In this study, δ-Fe and γ-Fe were considered as the primary nucleating phases during the solidification of the Ti-stabilized stainless steel and some common inclusions (SiO$_2$, MgO, MnO, Al$_2$O$_3$, TiN, Ti$_2$O$_3$, TiO$_2$) were used as the substrates. The disregistry values (Table 4) indicated that titanium nitride, titanium carbide, and magnesium oxide were highly effective nucleation agents of the δ-Fe phase, but they were ineffective for the nucleation of the γ-Fe phase. In contrast, silicon dioxide, aluminum oxide, and titanium dioxide did facilitate the nucleation of the γ-Fe phase, but not the δ-Fe phase. However, manganous oxide could not act as a nucleating agent for both phases.

### Table 3. Crystallographic data for the effective nucleating agent and matrix metal.

| Compound | Crystal System | Room Temperature, Lattice Parameter (Å) | 1450 °C, Lattice Parameter (Å) | Ref. |
|----------|----------------|----------------------------------------|---------------------------------|-----|
| γ-Fe     | BCC            | -                                      | -                               | -   |
| δ-Fe     | FCC            | -                                      | -                               | -   |
| MgO      | NaCl           | 4.2112                                 | -                               | -   |
| MnO      | NaCl           | 4.4457                                 | -                               | -   |
| TiN      | NaCl           | 4.246                                  | -                               | -   |
| SiO$_2$  | β-cristobalite | -                                      | -                               | -   |
| Al$_2$O$_3$ | α-Al$_2$O$_3$ | 4.7589                                 | 12.991                          | -   |
| TiO$_2$  | rutile         | 4.5937                                 | 2.9587                          | 4.6529 3.0063 |
| Ti$_2$O$_3$ | α-Ti$_2$O$_3$ | -                                      | -                               | 5.1251 - |

### Table 4. Planar distregistry between substrates and metallic phase, %.

| Metallic Phase | MgO  | MnO  | TiC  | TiN  | SiO$_2$ | Al$_2$O$_3$ | TiO$_2$ | Ti$_2$O$_3$ |
|----------------|------|------|------|------|---------|-------------|---------|-------------|
| δ-Fe           | 3.52 | 9.42 | 5.53 | 3.55 | 14.02   | 7.86        | 7.69    | 6.86        |
| γ-Fe           | 16.49| 11.73| 14.87| 16.47| 1.9     | 0.51        | 7.71    | 0.51        |

3.4. Characteristics of Inclusions in Floater and 321 Stainless Steel

Figure 5 shows the typical SEM images of TiN clusters that were observed in the gas holes within the floaters. The size of cube-shaped TiN particles ranged from 1 to 10 µm. The difference in the average number density of TiN within the floaters and the 321 steel were determined by examining 15 different SEM images; Figure 6 presents the typical images. The inclusions in all samples examined were highly heterogeneous. The average number density of TiN in the floaters was estimated to be as much as 1.7 times greater than that in the 321 steel. In addition, the TiN clusters in floaters (2–6 µm) were larger than those in 321 steel (1–4 µm), which suggested that the formation of TiN in the floaters is the solubility that produced inclusions forming in the ladle process. Additionally, a range of nonmetallic inclusions acted as potential nuclei for TiN (Figure 7a,c). Independent of the inclusion category, magnesium oxide and spinel (MgO-α-Al$_2$O$_3$) were found in most of the investigated nuclei; oxides are partially combined with CaO, also sporadically with TiO$_2$. Wavy and irregularly shaped inclusions that had high amounts of MgO, TiN, and traces of TiO$_2$ were observed in the 321 steel and the floater, as shown in Figure 7b,d.
Michelic et al. reported that heterogeneous nucleation is important in the formation of TiN, especially for continuous process times, as shown in Figure 8 [35]. The author summarizes the formation mechanisms of TiN during the production process, as well as the effect of heterogeneous nucleation and the influence of layer formation around TiN. Therefore, different nonmetallic inclusions could act as potential nuclei for TiN. Based on the calculations of the oxide-inclusions that were discussed in the previous section, the first Ti$_2$O$_3$ and TiN precipitation occurred with a high driving force, because the system conditions were significantly above the equilibrium at an early stage of secondary metallurgy.

High SiO$_2$ and Na$_2$O content within the mold flux can oxidize Al and Ti that are dissolved in liquid steel and their contact with Ti-bearing steels generates the secondary inclusions (Al$_2$O$_3$ and TiO$_2$). A consequence of these secondary inclusions is the formation of CaO-TiO$_2$, which results in the accelerated growth of TiN because of heterogeneous nucleation. In this work, the primary heterogeneous nuclei for TiN were magnesium-based inclusions (MgO or spinel), which resulted from the refractory material, slag, or impurities in the alloying elements.
aggregation will appear in the mold. The floater with the higher melting temperature and lower density as macroscopic aggregation can occasionally cause dynamic collisions and alliances following the liquid flow release of liquid metallic droplets into slag and the emulsification of micro-aggregates. These reactions between TiN and SiO$_2$ or Fe$_2$O$_3$, etc., which originate from the mold flux. The interfacial reactions can start as soon as the melt temperature drops below the liquidus temperature. TiN inclusion, as the most major inclusion in 321 steel, will bring about an evident increase in the iron content due to the preferential nucleation of δ-Fe on TiN and MgO or MgO·Al$_2$O$_3$ inclusions that were investigated by examining both the composition of floater and 321 steel. The nickel that can act as the austenizer in 321 steel sharply decreases, while the chromium inconspicuously decreased, owing to the overwhelming increase in Fe, 4.76% Cr, 11.96% Ni) that is shown in Figure 9 had a slightly higher percentage of Fe, but lower percentages of Cr and Ni when compared with the composition of floater collected from 321 steel heat, because the TiN was added during the experiment (Figure 9). The composition of the metallic phase (83.28% Ni) was attributed to the preferential nucleation of δ-Fe on the TiN inclusions. The difference in the composition of floater and 321 steel was likely to involve the formation of Ti or Al-oxides and TiN in the ladle following Al or Ti (TiFe alloy) additions, which continue to precipitate and aggregate as the temperature drops and the accelerated growth of TiN because of heterogeneous nucleation. In this work, the primary heterogeneous nuclei for TiN were magnesium-based inclusions (MgO or spinel), which resulted from the refractory material, slag, or impurities in the alloying elements.

Based on the calculations that were performed, the mechanism that caused the nucleation of the first Ti$_2$O$_3$ and TiN precipitation occurred with a high driving force, because the system conditions were significantly above the equilibrium at an early stage of secondary metallurgy. High SiO$_2$ and Na$_2$O content within the mold flux can oxidize Al and Ti that are dissolved in liquid steel and their contact with Ti-bearing steels generates the secondary inclusions (Al$_2$O$_3$ and TiO$_2$). Other large exogenous inclusions, such as refractories and refining or mold slags, will be entrapped during tapping or interfacial reactions. As TiN can easily nucleate on spinel, the clusters are normally composed of complex inclusions. Subsequently, ferrite from the refractory material, slag, or impurities in the alloying elements.

The effects of TiN inclusions on the nucleation of δ-Fe were investigated by examining both the properties of the TiN inclusions and the composition of the floater that was collected from...
the verification experiment. SEM-EDS analysis showed that the TiN in the floater from the verification experiment was more concentrated and larger than that in the floater from the 321 steel heat, because the TiN was added during the experiment (Figure 9). The composition of the metallic phase (83.28% Fe, 4.76% Cr, 11.96% Ni) that is shown in Figure 9 had a slightly higher percentage of Fe, but lower percentages of Cr and Ni when compared with the composition of floater collected from 321 steel heat. Therefore, the dominant factor that determined the composition of floaters was likely the nucleation of δ-Fe on the TiN inclusions. The difference in the composition of floater and 321 steel was attributed to the preferential nucleation of δ-Fe on TiN and MgO or MgO·Al2O3 inclusions that starts as soon as the melt temperature drops below the liquidus temperature. TiN inclusion, as the most major inclusion in 321 steel, will bring about an evident increase in the iron content due to the preferential nucleation of δ-Fe. The nickel that can act as the austenizer in 321 steel sharply decreased, while the chromium inconspicuously decreased, owing to the overwhelming increase in iron content, despite chromium being able to promote the formation of δ-Fe.

Based on the calculations that were performed, the mechanism that caused the nucleation of the inclusions was likely to involve the formation of Ti or Al-oxides and TiN in the ladle following Al or Ti (TiFe alloy) additions, which continue to precipitate and aggregate as the temperature drops and the unexpected air leakage continues. Other large exogenous inclusions, such as refractories and refining or mold slags, will be entrapped during tapping or interfacial reactions. As TiN can easily nucleate on spinel, the clusters are normally composed of complex inclusions. Subsequently, ferrite nucleates grow on TiN and MgO or MgO·Al2O3 inclusions, accompanied by the interfacial reactions between TiN and SiO2 or Fe2O3, etc., which originate from the mold flux. The interfacial reactions cannot lead to the evolution of N2 gas bubbles and lower the interfacial tension, which accelerates the release of liquid metallic droplets into slag and the emulsification of micro-aggregates. These micro-aggregates can occasionally cause dynamic collisions and alliances following the liquid flow in the mold. The floater with the higher melting temperature and lower density as macroscopic aggregation will appear in the mold.

Figure 9. SEM analysis of floater steel collected from verification experiment.

3.5. Reaction Performances of Steel-Slag

A semi-solid crust slag emerged from the mold 10 min. after the start of reaction, as shown in Figure 10a,b. Table 5 provides the composition of the mold flux. The interfacial features of a floater that was sampled from the 321 steel heat are shown in Figure 11. Spots 1, 2, and 3 highlight the perovskite, steel, and nepheline phases, respectively. The perovskite exhibited equiaxed crystals (light gray) that appeared to co-crystallize with the nepheline (dark gray) along the steel boundary, as shown in Figure 11. Both the perovskite and nepheline phases have high melting temperatures and they are detrimental to the crystallization behavior of the molten flux. As a comparison, the morphology of
the crust slag that was collected from the experimental furnace was observed using SEM-EDS, as shown in Figure 12. Following quenching with water, the CaO-TiO\textsubscript{2} phase precipitated as a dendritic crystal, while the amount of entrapped steel that was frozen inside the slag was ascribed to interfacial reactions, which caused the interfacial tension to decrease further.

![Figure 12](image)

**Figure 12.** SEM identification for semi-crust slag sampled from experiment and 1 represents steel phase, 2 represents CaO-TiO\textsubscript{2}, and 3 represents slag phase.

**Figure 11.** SEM identification for floater sampled from a 321 steel heat and 1 represents CaO-TiO\textsubscript{2}, 2 represents steel phase, and 3 represents Na\textsubscript{2}O\cdot\text{SiO}_2\cdot\text{Al}_2\text{O}_3.

**Figure 10.** Condition of the mold slag in field test. (a) Early period; and, (b) ten minutes after the start of casting.
Chung and Cramb reported that the interfacial tension between steel and slag in Ti-bearing steel significantly drops from a fairly high value, which leads to the spontaneous emulsification of the steel into the slag [36]. The emulsification and reaction of the steel-slag and the precipitation of CaTiO$_3$ causes variations in the viscosity of the slag and the melting temperature near the interface deteriorates the absorption of inclusions and lubrication.

For comparison, Table 5 provides the composition and properties of the slags that were obtained in our experiments, and these showed similar values (note that the titanium oxide is reported as TiO$_2$, even though it is expected to be a mixture of tetravalent and trivalent oxides. Moreover, TiN is converted into TiO$_2$ because of the indetermination of nitrogen by XRF). The TiO$_2$ content varied between the initial, liquid, and crust slags in this study, with larger amounts in the crust slags. The crust slags also had higher melting temperatures and viscosities than the liquid slags (note that the viscosity of Slag 5 was not measured because of the insufficiency quantity). Meanwhile, a liquid slag with the addition of 7–8% TiO$_2$ and lower basicity than the crust slags was also investigated, and this resulted in a reasonable elevation in properties.

Previous studies have shown that TiO$_2$ plays an important role in the properties of the slag that affect both the physical and thermodynamic behavior of slags. TiO$_2$, containing the Ti$^{4+}$ cation, is generally classified an amphoteric oxide, although Ti$^{4+}$ is preferentially regarded as a network forming ion and it has demonstrated glass forming properties. [37–39] The addition of 10% TiO$_2$ results in a decreased viscosity and crystallization ratio in a mold flux with a CaO/SiO$_2$ ratio > 1, while the viscosity of slags with CaO/SiO$_2$ ratios < 1 and TiO$_2$ > 10% increases with the increased TiO$_2$ content [8,13,35] and the precipitation of solid CaTiO$_3$ or CaSiTiO$_5$ phases increases the non-uniform heat transfer performance and precipitation temperature. [9–11,13] The amount of TiO$_2$ within slags 2, 3, and 4 in this study was significantly greater than 7%, and this would have significantly accelerated the precipitation of CaTiO$_3$. The main mineralogical phases in the crust slag that was collected from the mold were perovskite, nepheline, and small amounts of TiN (Figure 13), which was similar to the phases of the interfacial slag that are shown in Figure 11.

Only small increases in the Al$_2$O$_3$ content were observed (0.93–1.16%) that were caused by the oxidation of metal or extraneous inclusions. The reduction of SiO$_2$ by Ti or [TiN] in the initial slag increased the CaO/SiO$_2$ ratio, which ranged between 1.01 and 1.15. The Na$_2$O content also decreased by more than 3.0%, which most probably arose from the steel-slag reactions during casting, as described by Equations (5) and (6).

\[(\text{Na}_2\text{O}) + [\text{Ti}] = [\text{Na}] (g) + (\text{TiO}_2) \]  
\[(\text{Na}_2\text{O}) + \text{TiN} = [\text{Na}] (g) + (\text{TiO}_2) + [\text{N}_2] (g)\]  

Figure 13. XRD analysis of crust slag from mold.
Table 5. Main compositions (wt. %) and properties of slags following steel-slag reaction.

| No. | Status       | Basicity | SiO$_2$ | CaO  | Al$_2$O$_3$ | MgO  | Na$_2$O | TiO$_2$ | $T_m$ (°C) | $n_{1300}$°C (Pa·s) |
|-----|--------------|----------|---------|------|-------------|------|---------|---------|------------|------------------------|
| 1   | Initial slag | 0.78     | 30.79   | 23.87 | 6.7         | 3.18 | 11.57   | 0.18    | 1049       | 0.131                  |
| 2   | Liquid slag  | 0.97     | 24.51   | 23.69 | 7.63        | 3.21 | 8.18    | 7.4     | 1036       | 0.185                  |
| 3   | Crust slag   | 1.15     | 21.26   | 23.68 | 7.86        | 3.25 | 7.18    | 9.1     | 1270       | >2.0                   |
| 4   | Exp. Liquid slag | 0.91 | 25.73   | 23.37 | 7.69        | 3.58 | 9.18    | 8.2     | 1054       | 0.24                   |
| 5   | Exp. Crust slag | 1.1  | 21.47   | 23.7  | 9.62        | 3.4  | 11.49   | 9.6     | 1258       | -                      |

$^1$ Exp. Liquid slag and Exp. Crust slag were collected from the laboratory-scale experiment.

Todoroki et al. reported that a crystalline flux film with a basicity of 1.03 stiiffly adhered to the sides of the mold because of the solid and moderate heat flux of flux film toward the mold to bring uniform shell [9]. However, the chemistry of slags that include SiO$_2$, TiO$_2$, and Al$_2$O$_3$ are continually changing throughout the casting process, primarily because of the oxidation of TiN and [Ti]. Furthermore, the perovskite will precipitate at the steel-slag interface, which causes the slag that feeds into the gap between the solidifying shell and the mold inner wall to exhibit non-uniform physical properties, including increasing basicity. This leads to non-stable thermal and lubrication conditions and ultimately results in surface quality problems [40]. We have previously examined the reactivity of slags with different basicity and SiO$_2$ content and found that CaO-Al$_2$O$_3$ slags with a low SiO$_2$ content are preferable, as they are less reactive towards steel [11]. In future work, the systematic analysis and explanations on the reaction performances in terms of the thermodynamics and kinetics of Ti-bearing steels will be performed.

4. Conclusions

We have investigated the mechanisms for the formation of floaters in molds during the casting of a Ti-stabilized stainless steel while using a combination of thermodynamic calculations, experimental investigations, and calculations of the planar disregistry between the inclusions and metallic phases. The following key results were determined:

1. The densities of the floaters at ambient temperature and 1450 °C were 7.53 g/cm$^3$ and 6.83 g/cm$^3$, respectively. These values were lower than the 321 steel. The liquidus temperature of the floater was 27 °C higher than the 321 steel, because of the differences in alloys composition.

2. Both the size and number density of TiN cluster and other inclusions in the floaters were larger than that in the 321 steel, which lead to the preferential nucleation of discrepant precipitates. The formation of floaters occurred during the casting of the 321 steel, which solidified with a preferential and primary precipitation of $\delta$-Fe.

3. Calculations of the planar disregistry between the inclusions and the metallic phases showed that magnesium oxide, titanium carbide, and titanium nitride were very effective as nucleating agents for the $\delta$-Fe phase, but inferior for the $\gamma$-Fe phase. In contrast, silicon dioxide, aluminum oxide and titanium dioxide were reasonably effective at nucleating $\gamma$-Fe but were poor at nucleating the $\delta$-Fe phases. However, manganous oxide could not act as a nucleating agent for both phases.

4. The high-reactivity between slag and steel leads to variations in the SiO$_2$, Al$_2$O$_3$, TiO$_2$, and Na$_2$O contents. Therefore, the basicity, melting temperature, and viscosity of the crust slag were higher than that of the liquid slag because of the high-reactivity with steel.

Author Contributions: Z.C. contributed to the calculation of disregistry, collected samples from steel mill, preformed data analysis, and wrote the paper; M.L. and X.W. mainly focused on thermodynamic calculation and performed the experiments, material characterization; S.H. contributed to the design of the experiment; Q.W. revised the paper and refined the language.

Funding: This research was funded by the Key Program of National Natural Science Foundation of China (No. U1660204).

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

1. Hasegawa, M.; Maruhashi, S.; Kamidate, Y.; Muranaka, Y.; Hoshi, F. Tundish nozzle constriction in continuous casting of titanium bearing stainless steel slabs. *Tetsu-to-Hagane* 1984, 70, 1704–1711. [CrossRef]

2. Basu, S.; Choudhary, S.K.; Girase, N.U. Nozzle clogging behaviour of Ti-bearing Al-killed ultra low carbon steel. *ISIJ Int.* 2004, 44, 1653–1660. [CrossRef]

3. Cui, H.; Bao, Y.; Wang, M.; Wu, W. Clogging behavior of submerged entry nozzles for Ti-bearing IF steel. *Int. J. Miner. Metall. Mater.* 2010, 17, 154–158. [CrossRef]

4. Bergman, A. On the Formation of Crusts During Continuous Casting of Titanium-Stabilized Stainless Steel. *Scand. J. Met.* 1983, 12, 232–234.

5. Nunnington, R.C.; Sutcliffe, N. The steelmaking and casting of Ti Stabilized Stainless Steels. In Proceedings of the 59th Electric Furnace Conference and 19th Process Technology Conference, Phoenix, AZ, USA, 11–14 November 2001.

6. Ruby-meyer, F.; Lehmann, J.; Gaye, H. Thermodynamic analysis of inclusions in Ti-deoxidised steels. *Scand. J. Met.* 2000, 29, 206–212. [CrossRef]

7. Ogibayashi, S. Mechanism and countermeasure of alumina buildup on submerged nozzle in continuous casting. *Taikabutsu Overseas* 1995, 15, 3–14.

8. Hasegawa, M.; Maruhashi, S.; Muranaka, Y.; Hoshi, F. Mechanism of formation of surface defects in continuously cast stainless steel slabs containing titanium. *Tetsu-to-Hagane* 1987, 73, 505–512. [CrossRef]

9. Todoroki, H.; Ishii, T.; Mizuno, K.; Hongo, A. Effect of crystallization behavior of mold flux on slab surface quality of a Ti-bearing Fe-Cr-Ni super alloy cast by means of continuous casting process. *Mater. Sci. Eng.* A 2000, 293, 121–128. [CrossRef]

10. Mukongo, T.; Pistorius, P.C.; Garbers-Craig, A.M. Viscosity effect of titanium pickup by mould fluxes for stainless steel. *Ironmak. Steelmak.* 2004, 31, 135–143. [CrossRef]

11. Chen, Z.; Xu, K.; He, S.; Wang, Q. Thermodynamic Calculation on the Reactivity Between Slag and Ti-Stabilized Stainless Steel. In Proceedings of the 8th International Symposium on High-Temperature Metallurgical Processing, San Diego, CA, USA, 26 February–2 March 2017; pp. 169–176.

12. Skoczylas, G.; Dasgupta, A.; Bommaramu, R. Characterization of the Chemical Interactions During the Casting of High-Titanium Low Carbon Enameling Steels. In Proceedings of the Steelmaking Conference Proceedings, Warrendale, PA, USA, 14–17 April 1991; pp. 707–717.

13. Bothma, J.A.; Pistorius, P.C. Heat transfer through mould flux with titanium oxide additions. *Ironmak. Steelmak.* 2007, 34, 513–520. [CrossRef]

14. Wang, Z.; Shu, Q.F.; Hou, X.M.; Chou, K.C. Effect of substituting SiO$_2$ with TiO$_2$ on viscosity and crystallisation of mould flux for casting titanium stabilised stainless steel. *Ironmak. Steelmak.* 2012, 39, 210–215. [CrossRef]

15. Shu, Q.; Wang, Z.; Klug, J.L.; Chou, K.; Scheller, P.R. Effects of B$_2$O$_3$ and TiO$_2$ on Crystallization Behavior of Slags in Al$_2$O$_3$-CaO-MgO-Na$_2$O-SiO$_2$ System. *Steel Res. Int.* 2013, 84, 1138–1145. [CrossRef]

16. Wang, Q.; Lu, Y.J.; He, S.P.; Mills, K.C.; Li, Z.S. Formation of TiN and Ti (C, N) in TiO$_2$ containing, fluoride free, mould fluxes at high temperature. *Ironmak. Steelmak.* 2011, 38, 297–301. [CrossRef]

17. Li, J.; Shu, Q.; Chou, K. Structural Study of Glassy CaO-SiO$_2$-CaF$_2$-TiO$_2$ Slags by Raman Spectroscopy and MAS-NMR. *ISIJ Int.* 2014, 54, 721–727. [CrossRef]

18. Mysen, B.O.; Ryerson, F.J.; Virgo, D. The influence of TiO$_2$ on the structure and derivative properties of silicate melts. *Am. Mineral.* 1980, 65, 1150–1165.

19. Mysen, B.; Neuville, D. Effect of temperature and TiO$_2$ content on the structure of Na$_2$Si$_2$O$_5$-Na$_2$Ti$_2$O$_5$ melts and glasses. *Geochim. Cosmochim. Acta* 1995, 59, 325–342. [CrossRef]

20. Bihuniaik, P.P.; Condrate, R.A. Structures, spectra and related properties of group IVB-doped vitreous silica. *J. Non. Cryst. Solids* 1981, 44, 331–343. [CrossRef]

21. Wu, T.; He, S.P.; Zhu, L.L.; Wang, Q. Study on reaction performances and applications of mold flux for high-aluminum steel. *Mater. Trans.* 2016, 57, 58–63. [CrossRef]

22. Bale, C.W.; Belisle, E.; Chartrand, P.; Decterov, S.A.; Eriksson, G.; Gheribi, A.E.; Hack, K.; Jung, I.-H.; Kang, Y.-B.; Melançon, J.; et al. FactSage thermochemical software and databases, 2010–2016. *Calphad* 2016, 54, 53–53. [CrossRef]

23. Chen, Z.; Zhang, Y.B.; He, S.P.; Li, Z.R.; Wang, Q. Reaction Performances of Mold Slags with Different SiO$_2$ Contents for 321 Stainless Steel. *Can. Metall. Q.* 2019, in press. [CrossRef]
24. Bai, H.; Thomas, B.G. Effects of clogging, argon injection, and continuous casting conditions on flow and air aspiration in submerged entry nozzles. *Metall. Mater. Trans. B* **2001**, *32*, 707–722. [CrossRef]

25. Grinder, D.; Choné, J. Formation of titanium nitride particles in continuously cast stainless steel products. *Contin. Cast.* **1995**, *1*, 173–195.

26. Bramfitt, B.L. The effect of carbide and nitride additions on the heterogeneous nucleation behavior of liquid iron. *Metall. Mater. Trans.* **1970**, *1*, 1987–1995. [CrossRef]

27. Kohlhaas, R.P.; Dünner, and N. Schmitz-Pranghe. *Z. Angew. Phys.* **1967**, *23*, 245.

28. Wyckoфф, R.W.G. *Crystal Structure*, 2nd ed.; Wiley: New York, NY, USA, 1963; Volume I, p. 85.

29. Morosin, B. Exchange striction effects in MnO and MnS. *Phys. Rev. B* **1970**, *1*, 236–243. [CrossRef]

30. Taylor, A.; Kagel, B.J. *Crystallographic Data on Metal and Alloy Structures*; Dover: New York, NY, USA, 1963.

31. Wright, A.F.; Leadbetter, A.J. The structures of the β-cristobalite phases of SiO₂ and AlPO₄. *Philos. Mag.* **1975**, *31*, 1391–1401. [CrossRef]

32. Newnham, E.E.; de Haan, Y.M. Refinement of the αAl₂O₃, Ti₂O₃, V₂O₃ and Cr₂O₃ structures. *Zeitschrift für Krist. Mater.* **1962**, *117*, 235–237. [CrossRef]

33. Abrahams, S.C.; Bernstein, J.L. Rutile: Normal probability plot analysis and accurate measurement of crystal structure. *J. Chem. Phys.* **1971**, *55*, 3206–3211. [CrossRef]

34. Rice, B.Y.C.E.; Robinson, W.R. High-Temperature Crystal Chemistry of Ti₂O₃: Structural Changes Accompanying the Semiconductor-Metal Transition. *Acta Cryst.* **1977**, *203*, 1342–1348. [CrossRef]

35. Michelic, S.K.; Loder, D.; Reip, T.; Barani, A.A.; Bernhard, C. Characterization of TiN, TiC and Ti(C, N) in titanium-alloyed ferritic chromium steels focusing on the significance of different particle morphologies. *Mater. Charact.* **2015**, *100*, 61–67. [CrossRef]

36. Chung, Y.; Cramb, A.W. Dynamic and Equilibrium Interfacial Phenomena in Liquid Steel-Slag Systems. *Metall. Mater. Trans.* **2000**, *31*, 957–971. [CrossRef]

37. Tranell, G.; Ostrovski, O.; Jahanshahi, S. The Equilibrium Partitioning of Titanium between Ti³⁺ and Ti⁴⁺ Valency States in CaO-SiO₂-TiOₓ Slags. *Metall. Mater. Trans. B* **2002**, *33*, 61–67. [CrossRef]

38. Furukawa, T.; White, W.B. Structure and crystallization of glasses in the Li[sub 2]Si[sub 2]O₅-TiO[sub 2] system determined by Raman spectroscopy. *Phys. Chem. Glasses* **1979**, *20*, 69–80.

39. Rao, B.V.J. Properties and Structure of Glasses in the Binary Systems Alkali-TiO₂. *J. Am. Ceram. Soc.* **1964**, *47*, 455–463. [CrossRef]

40. He, S.; Li, Z.; Chen, Z.; Wu, T.; Wang, Q. Review of Mold Fluxes for Continuous Casting of High-Alloy (Al, Mn, Ti) Steels. *Steel Res. Int.* **2019**, *90*, 1800424. [CrossRef]