Understanding Behavior of Ti in Ultralow-C Liquid Steel

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INTRODUCTION

IF (Interstitial-Free) steel is one of the steel products used for the outer panel of automotive. In order to make sure of high deformability, extremely low C and N contents are required. Such low C and N contents are obtained during the RH process via vacuum degassing. Therefore, it becomes Ultra-Low C (ULC) steel. Additional capture of these interstitial elements is additionally carried out by adding Ti into the liquid steel. Since Ti has an affinity to O, its addition follows Al deoxidation. During Al deoxidation, a considerable amount of alumina is generated, followed by decreasing soluble O content in the steel. The generated alumina is floated and removed to the RH slag by the circulation of the steel in the RH vessel. Therefore, the Ti addition aims at solely increasing dissolved Ti content in the steel, which later captures C and N. However, the ULC steelmaking process often undergoes troubles including severe nozzle clogging during continuous casting and surface defects after cold rolling. These troubles deteriorate as Ti content in the steel increases. It has been still unclear why Ti addition induces such troubles and some have suspected non-metallic inclusion evolution that contains Ti. However, the majority of the inclusions observed in the Ti-ULC steel are alumina, along with some portion of Ti content in the alumina. A complex oxide compound Al₂TiO₅ is often mentioned, and it appears in a number of inclusion stability diagrams. However, neither its existence nor its consequence to the troubles was clarified. In this article, the behavior of Ti in ULC steel is discussed by reviewing available research results including the present authors’ recent results. Most discussions will focus on coupled interaction between Ti and O in the steel.

FUNDAMENTAL INFORMATION REGARDING TI IN STEEL

1. Ti deoxidation in comparison with Al deoxidation

Contrary to the Al deoxidation equilibria in liquid steel, Ti deoxidation is somewhat complicated due to the stability of various oxides containing Ti. Within a reasonable range of content of each element in steel, Al deoxidation results in the generation of Al₂O₃ ([pct Al] varies from ~0.001 to ~0.1). On the other hand, Ti deoxidation results in the generation of Ti₅O₇ ([pct Ti] varies from ~0.001 to ~0.1), which forms a solid solution with FeTi₂O₅, called pseudobrookite (PB) solid solution. Fe content in the PB increases as Ti content in the steel ([pct Ti]) decreases: in the other words, O content in the steel [pct O] increases. Further decreasing [pct Ti] below 0.001 at 1600 °C (increasing [pct O]) results in the appearance of liquid oxide (FeO-TiO₂). In the case of the Al deoxidation equilibria, a liquid oxide (FeO-Al₂O₃) appears when [pct Al] is lower than ~0.00001.

2. Various Ti oxides and Al-Ti complex oxides

Contrary to the Al-O phase diagram where only one stable oxide is known (Al₂O₃), various Ti oxides are known including TiO, Ti₂O₃, Ti₃O₅, ..., TiO₂, in the Ti-O phase diagram, due to transition metal character of Ti (Ti²⁺, Ti³⁺, and Ti⁴⁺). As mentioned previously, Ti₅O₇ dissolves Fe to form the PB: (Ti, Fe)Ti₂O₅. This could happen when Ti₅O₇ exists in liquid Fe with considerable O content. In the Al-Ti-O phase diagram, “Al₂TiO₅” is known to exist in the temperature range relevant to steelmaking and casting. In order to keep this stoichiometry, Ti must be Ti⁴⁺, which is stable under oxidizing atmosphere. It has been reported that Al₂TiO₅ was not found in the Al-Ti-O phase diagram under strongly reducing conditions (under H₂ or C/CO equilibrium). This implies that “Al₂TiO₅” is unlikely to exist in liquid steel. This is why no one has reported any experimental evidence of the “Al₂TiO₅”, while it appears in the inclusion stability diagram several times. This requires a rigorous analysis of the stability of “Al₂TiO₅” or oxides composed of Al and Ti.
3. Types of inclusions in Ti-ULC steel
There have been a considerable number of experimental investigations regarding inclusion evolution in Ti-ULC steel, both in laboratories and in steel plants. Liquid steel samples were taken after Ti addition, and the composition of the inclusions in the steel samples was analyzed mostly using SEM-EDS. The majority of the inclusions were found to be alumina (almost pure Al2O3), and minor inclusions that contain a limited amount of Ti were reported (called “AT”-inclusion). For example, Dorrer et al. reported that Ti/Al mass ratio in “AT”-inclusions 3 minutes after FeTi addition to RH liquid steel was below 0.1 for approximately 70% of inclusions observed. Indeed, the inclusion composition plotted on the Al-Ti-O diagram spread over a wide range of compositions. This requires accurate information about the phase equilibria of the inclusion system.

PHASE EQUILIBRIA

1. Al-Ti-O system
So far, only the phase diagram of the Al-Ti-O system was investigated under air (P<sub>O2</sub> = 0.21 atm) or under “strongly reducing” conditions (P<sub>O2</sub> = ~10<sup>-14</sup> to ~10<sup>-16</sup> atm). Since the stability of oxide containing Ti significantly depends not only on temperature and but also on oxygen potential in the system, a rigorous phase diagram analysis under various oxygen potentials is required. Park et al. recently reported the phase diagram of Al-Ti-O system which was experimentally determined in a wide range of T (1300 °C to 1600 °C) and P<sub>O2</sub> (10<sup>16.6</sup> to 10<sup>-8.0</sup> atm), using high-temperature equilibration under a controlled atmosphere, followed by quenching and XRD/EPMA. The most notable finding is that “Al<sub>2</sub>TiO<sub>5</sub>” is stable at its stoichiometric composition only at high P<sub>O2</sub>. Decreasing P<sub>O2</sub> resulted in the gradual dissolution of Ti (presumably Ti<sup>3+</sup>) and the rejection of Al. At a mid-range of P<sub>O2</sub> (e.g., 10<sup>-12</sup> to 10<sup>-11</sup> atm), Ti/Al molar ratio varies from ~1 to ~∞ (corresponding to Ti<sub>5</sub>O<sub>3</sub>). Therefore, a completely miscible PB solid solution between “Al<sub>i</sub>TiO<sub>3</sub>” and Ti<sub>5</sub>O<sub>3</sub> was confirmed at 1600 °C. No liquid oxide composed of Al-Ti-O was confirmed, which supports the present authors’ previous prediction of this ternary system. Figure 1 shows the assessed Al-Ti-O phase diagram at 1600 °C. It is seen in Fig. 1(a) that oxygen potential (P<sub>O2</sub>) is one of the very important variables in determining the existence and the evolution of stable phases. This implies that when the “AT”-inclusions are considered in Ti-ULC steel, the oxygen potential in the steel system, mostly controlled by O content in the steel should be taken into account.

At high O content, “AT”-inclusions with low Ti/Al mass ratio may be found, but at low O content, most of the inclusion should be either almost pure alumina or “AT”-inclusions (along with very few of high Ti/Al mass ratios), according to the phase diagram. It is clear that there is no “Al<sub>2</sub>TiO<sub>5</sub>” inclusion in Ti-ULC steel at equilibrium.

2. Dissolution of Fe into pseudobrookite solid solution (Fe-Al-Ti-O system)
However, this analysis is still to be amended by incorporating Fe into the consideration. Increasing O content in the Ti-ULC steel system causes oxidation of Fe, dissolving FeO into the PB solid solution, thereby forming (Ti, Al, Fe)Ti<sub>5</sub>O<sub>3</sub>. Once FeO dissolves into the PB solid solution, the melting temperature of the PB solid solution decreases due to the low melting temperature of FeO. Pesl and Eric reported phase equilibria in the Fe-Ti-O system that increasing oxygen potential in the system increases Fe content in (Ti,Fe)Ti<sub>5</sub>O<sub>3</sub> PB solid solution. At 1600 °C, the PB solid solution starts to melt to form liquid FeO-TiO<sub>2</sub> oxide when P<sub>O2</sub> is higher than ~10<sup>-10</sup> atm. A similar phenomenon is therefore expected in the Fe-Al-Ti-O system when a liquid Fe containing Al and Ti is exposed to oxidation. This situation may be regarded as reoxidation of Ti-ULC steel.
AGGLOMERATION BEHAVIOR OF INCLUSIONS ON THE SURFACE OF ULC STEEL

Nozzle clogging during continuous casting of ULC steel and surface defect of the cold-rolled sheet of IF steel have been discussed in view of inclusion clustering in the steel. While direct observation is not possible, agglomeration of the inclusions on the surface of liquid steel has been investigated many times, thanks to the development of Confocal Scanning Laser Microscopy (CSLM). Kim et al. recently reported the agglomeration behavior of the inclusions on the surface of ULC steel, in particular to elucidate the roles of Ti and O in the steel. Details of the experimental setup and the procedure can be found elsewhere. Oxygen potential exerted on the surface of ULC steel was controlled by capturing a trace of O in a well deoxidized Ar gas by various metal foils (Ti, Ta, and Nb).

1. Role of Ti on the agglomeration behavior of oxide inclusions on the surface of Ti-ULC steel

In the previous investigations, the inclusion agglomeration was interpreted due to capillary force, which is controlled by the mass of the inclusion as a particle, densities of the inclusion and the steel, the surface tension of the steel, and the contact angle between the inclusion and the steel. Since [pct Ti] in Ti-ULC steel does not exceed 0.1 at most, the addition of Ti would affect mostly the surface tension of the steel. However, according to the experimental study about the surface tension by Lee et al., adding such a small portion of Ti to a liquid Fe hardly changes the surface tension. In the CSLM study in the present authors’ laboratory, which was carried out at very low P(O2) (10^-22 atm) by using Ti-foil, the addition of the Ti to ULC steel ([pct Ti] = 0.0735) hardly changed the agglomeration behavior. The agglomeration behavior was quantitatively described using the acceleration of the agglomeration (force divided by the effective mass of two inclusion particles). Figure 2 shows the acceleration of the agglomeration in two different steels: Ti-free ULC steel and Ti-ULC steel. While unavoidable scatters are seen, the measured acceleration in the two cases is hardly distinguishable. This implies that the addition of Ti up to 0.0735 pct has no noticeable effect on the agglomeration behavior.

![Figure 2. Acceleration of the agglomeration between two inclusions on liquid steel surface (Ti-added (red) and Ti-free (blue)): Case 1 (Ti foil installed). Average of each acceleration and upper range of 95 pct. confidence interval.](image)

2. Simultaneous roles of Ti and O on the agglomeration behavior

On the other hand, two similar measurements were followed under slightly oxidizing conditions using Ta and Nb foils, which captured the trace of O in the Ar gas less than Ti foil. The estimated P(O2) was ~10^-15 atm. Figure 3 shows the measured acceleration (on average with an upper confidence interval of 95%) of two steels (Ti-free ULC and Ti-ULC) under different oxygen potentials. In the case of Ti-free steel, increasing oxygen potential did not show a noticeable change in the acceleration. On the other hand, in the case of Ti-ULC steel, increasing oxygen potential decreased the acceleration. Therefore, Ti-containing steel exhibits somewhat different behavior regarding the inclusion agglomeration, only when oxygen potential is relatively high. It is thus concluded that Ti itself did not cause a difference in the agglomeration behavior, but Ti and O simultaneously affect the agglomeration behavior.

A series of post-mortem analyses for the inclusion composition was carried out using SEM-EDS. As seen in Figure 4 (please refer to the electronic version to distinguish different colors), most of the inclusions in Ti-free ULC steel were almost pure alumina, regardless of the oxygen potential on the steel surface. On the other hand, those in Ti-ULC steel were significantly oxidized to contain FeO. Since the SEM-EDS analysis was carried out in the same condition, the Fe content in the inclusions
was not due to the “background effect”. It clearly shows that the presence of Ti in the steel induces the oxidation of Fe along with Ti and Al, thereby forming complex oxides composed of FeO-Al₂O₃-TiOₓ. It was speculated that the decrease in the acceleration of the agglomeration was attributed to the formation of FeO-Al₂O₃-TiOₓ, which requires further rigorous analysis.

Figure 3. Summary of the agglomeration behavior in two different steels under three different O potentials: average of each acceleration and upper range of 95% confidence interval.¹

Figure 4. Composition of inclusions on surface of the steel samples solidified after the CSLM experiments (Ti-added (red) and Ti-free (blue)).⁹

**NOZZLE CLOGGING DURING CONTINUOUS CASTING**

The formation of FeO-Al₂O₃-TiOₓ was predicted by thermodynamic modeling and calculation.⁰⁻¹⁰,¹³,¹⁶ Figure 5 shows the oxide stability diagram of Fe-Al-Ti-O system (Ti-ULC steel system), showing the formation of FeO-Al₂O₃-TiOₓ at low Al and Ti contents.¹² Therefore, it is understood that reoxidation of the Ti-ULC steel could result in the formation of FeO-Al₂O₃-TiOₓ, which is liquid at the casting temperature (FAT).

1. **Nozzle clog deposits**

It is well known that increasing [pct Ti] in Ti-ULC steel increases the amount of clog deposits in SEN after a series of continuous casting.¹ Figure 6 shows an enlarged view of the deposits on the SEN after casting Ti-ULC steel containing 0.046 pct Ti, which was located between the SEN refractory and the skull of Fe. While Ca was initially present in the SEN refractory, thereby forming calcium aluminate in the deposits, even the distribution of Ti together with Ca and Al implies that Ti in the steel was oxidized and was deposited. An interesting finding was a number of big and small islands of Fe, which were metallic portions in the deposits. This cannot be explained by the “AT”-inclusions observed in the steel, whatever Ti/Al ratio was in

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the inclusion. This gives an idea that Ti was oxidized for some reason, but Fe and Al were involved in the oxidation simultaneously, according to the results shown in Figs. 4 and 5.

![Fe-Al-Ti-O diagram]

Figure 5. Oxide stability diagram of Fe–Al–Ti–O system at 1540 °C.\(^\text{12}\)

![Enlarged view of deposit]

Figure 6. Enlarged view of the deposit on the SEN used to cast ULC – 460Ti: (a) BSE image, EDS elemental mapping for (b) Al, (c) Ca, (d) Ti, and (e) Fe.\(^\text{1}\)

2. Mechanism of initial nozzle clog deposits formation for Ti-ULC steel casting
Probable reoxidation sources during the casting are air aspiration through slide gate, carbothermic reaction in SEN refractory, air entrapment due to tundish open eye, etc. Among these, the most direct cause seems the carbothermic reaction in the
refractory (SiO₂ (refractory) + 3C (refractory) = 2CO (gas) + SiC (s)). The present authors confirmed that various SEN refractories generate CO gas, and the CO gas oxidizes the surface of Ti-ULC steel.²⁴ As a result, a mixture of FAT (liquid) and alumina (solid) forms. The FAT plays a rapid erosion of SEN refractory, and Fe₃O in the FAT is reduced by Al or Ti in the liquid steel, leaving Fe islands as seen in Fig. 5. This observation is unique in the case of Ti-ULC steel. When Ti content was negligible, this phenomenon is not seen. Therefore, it was concluded that oxidation of Ti in the Ti-ULC steel causes the formation of Fe₃O-containing liquid oxide, which is a probable source of the troubles observed in Ti-ULC steel refining and casting. Regarding the nozzle clog deposits, the FAT formation is responsible for the initial nozzle clog deposits formation, similar to the formation of “network alumina” formation in typical Al-killed steel. The subsequent build-up of the clog deposits was due to suspending alumina inclusions, as proposed by Barati et al.⁵ Therefore, suppression of the reoxidation looks essential. One of the possible ways to suppress the reoxidation of Ti-ULS steel is to suppress the reaction between the CO gas and the Ti-ULC liquid steel. Lee et al. proposed to use CO absorbers in the SEN, which was shown to be effective.²⁶

CONCLUSIONS

In order to understand some troubles caused by Ti addition to ULC steel better, various high-temperature phenomena occurring in Ti-ULC liquid steel refining and continuous casting processes were reviewed. One of the most frequently mentioned problems is the deterioration of SEN clogging. With regard to this, it was found that Ti-ULC steel systems are very prone to reoxidation. More specifically, the presence of Ti in ULC steel promotes simultaneous oxidation of Fe, Ti, and Al which yields Fe₃O-containing oxide (FAT). This kind of oxide has a low melting temperature, has high wettability to other phases, and is a carrier of O in the steel, thereby causing additional oxidation inside the steel. This is partly due to the transition metal character of Ti. Therefore, phases of the Ti oxide-containing system should be understood in a wide range of oxygen potential near the refining and casting temperature.

The phase diagram of the Al-Ti-O system was analyzed by using a recently reported by the present authors. It was found that the well-known Al₂TiO₅ is a part of a solid solution with Ti₅O₆ (a pseudobrookite solid solution). While Al₂TiO₅ has been often mentioned as possible inclusion in Ti-ULC steel, it cannot be stable under low oxygen potential pertaining to well deoxidized Ti-ULC liquid steel. The phase diagram showed that Al₂TiO₅ should decompose into Al-rich oxide (Al₂Ti₃O₇) and Ti-rich oxide (Ti₅Al)₂Ti₂O₈, where the latter would correspond to the “AT”-inclusions often mentioned in literature.⁴³ When the Al-Ti-O oxide inclusion exists inside liquid steel, Fe can dissolve into the oxide and form Fe₃O-Al₂O₃-TiO₇. This may be either (Fe,Ti,Al)Ti₂O₅ pseudobrookite s.s. or liquid oxide. While a related phase diagram study (both experiment and thermodynamic modeling) is in progress in the present author’s laboratory, the latter liquid oxide looks to play a very important role regarding the inclusion behavior and the nozzle clogging.

Agglomeration of oxide inclusions on the surface of ULC liquid steel was investigated using CSLM. It was found by post-mortem EDS analysis that the inclusions were almost alumina regardless of Ti content (up to 0.0735 pct), when oxygen potential on the surface of the steel was very low (P₀₂ = ~10⁻²² bar). The presence of Ti did not affect the agglomeration force between two oxide inclusions. On the other hand, when the oxygen potential was slightly high (P₀₂ = ~10⁻¹⁵ bar), the inclusions were found to be Fe₃O-Al₂O₃ (Ti-free ULC steel) and Fe₃O-Al₂O₃-TiO₇ (Ti-ULC steel). The presence of Ti decreased the agglomeration force between two oxide inclusions. This would influence inclusion removal from liquid steel.

Since the Ti-ULC steel is prone to reoxidation, oxidizing gas supply from SEN by a carbothermic reaction to liquid steel rapidly oxidizes the steel, thereby forming FAT liquid oxide. This oxide phase is easily wettable to SEN refractory and to steel, and corresponds to initial clog deposits. However, Fe₃O in the FAT is rapidly reduced by Al or Ti in the steel. Therefore, FAT is considered as a precursor of the initial clog deposit. Remaining Ti oxide and Al oxide are often found in final clog deposits in used SEN for continuous casting of Ti-ULC steel.

It was therefore concluded that coupled interaction between Ti and O in Ti-ULC steel causes those phenomena which were not seen in Ti-free steel. And reoxidation of Ti-ULC steel is recommended to suppress the troubles reported in the Ti-ULC steel refining and casting processes.

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REFERENCES


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