Micro-structure Refinement in Low Carbon High Manganese Steels through Ti-deoxidation: Austenite Grain Growth and Decomposition

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This paper investigates the effect of de-oxidation inclusions on micro-structure evolution in low-carbon steels. Low carbon (0.07 wt%), high Mn (0.9 wt%) steel in a Al₂O₃ or MgO crucible was deoxidized by adding either aluminum (0.05 wt%) or titanium (0.05, 0.03 or 0.015 wt%) in a 400 g-scale vacuum furnace, and cast in a Cu mold at cooling rates between 2.0–6.0 K/s. These cast samples were re-melted and cooled at various cooling rates, 1 through 100 K/s in the hot-stage of a confocal laser scanning microscope (CSLM) in order to investigate the effect of cooling rate. Oxide inclusion sizes in all the Ti-killed steels were smaller and inclusion densities higher than those in the Al-killed steel. In Ti-killed steel, inclusion size and densities increased with increasing the oxygen content, inclusion size decreased and their densities increased with increasing the cooling rate. A Confocal Scanning Laser Microscope (CSLM) was used to study the differences in solid state micro-structural evolution between the Ti-killed and the Al-killed samples. The growth of austenite grains were studied under isothermal conditions and it was found that both grain-boundary mobility and final grain size were lower in the Ti-killed sample than for the others. With regards to austenite decomposition, during continuous cooling from a comparable austenite grain structure, the resulting austenite decomposition structure was finer for the Ti-killed sample due to a higher Widmanstätten lath density due to precipitation at. The inclusion size was found to have a significant effect on both austenite grain size and austenite decomposition structure. Different orientations of ferrite precipitates originating at inclusions were observed in the Ti-killed samples. The highest lath concentration was obtained for the sample that had the smallest average inclusion size rather than the sample with highest density of sub micro-meter inclusions.

KEY WORDS: low-carbon steel; de-oxidation; aluminum; titanium; inclusion; solidification microstructure; confocal-laser-scanning-microscopy; phase transformation; grain growth.

1. Introduction

Low-carbon (0.21 wt% maximum)–high manganese (2.5 wt% minimum) steels are used for ships and off-shore platform applications. To obtain the required strength and toughness, careful thermo-mechanical control processing (TMCP) is required to achieve a fine-grained micro-structure.¹⁻³ If these plates are to be produced through direct hot-charge rolling (DHCR), which is advantageous from energetic and productivity points of view, the ability to control micro-structure through TMCP is limited and the micro-structure resulting from continuous casting (solidification and secondary cooling) becomes more important for controlling the final micro-structure and properties. The cast micro-structure has two important features that are connected to one-another and that can potentially be controlled.⁴ Firstly, the solidification-microstructure itself is largely determined by the shapes and sizes of primary dendrites. Secondly, small (<1 mm) non-metallic inclusions (oxides, nitrides and sulfides) can precipitate as a result if solute segregation and these can affect the solid state evolution of the steel micro-structure resulting from austenite grain growth and decomposition.⁴⁻¹ If the small non-metallic inclusions are present during the early stage of solidification, then they may also influence the consecutive solidification micro-structure by providing nucleation points⁵ and/or control the growth of dendrites.⁷ In this study, the potential of Ti-oxides that precipitate during solidification of low-C (≈0.07 wt%), high-Mn (≈0.8 wt%) steel on the micro-structure evolution is being investigated. It was shown in earlier publications,⁸,⁹ that the ratio of sub-micrometer secondary-Ti oxide inclusions to larger Ti-oxide inclusions (resulting from primary melt de-oxidation) could be increased by increasing the solidification rate and by in-
creasing the starting Ti/O ratio in the melt. There was also evidence that the steel micro-structure became finer with increasing population of secondary Ti-oxides. This paper, investigates the effect of Ti-oxides on two important solid-state transformation processes subsequent to solidification, namely austenite grain growth and decomposition. Two types of thermal histories are investigated to simulate the micro-structure evolutions direct-hot charge rolling and conventional processing.

2. Materials and Methods

Melting of carbon steel (C/0.07 wt%, Mn/0.9 wt%) and de-oxidation was carried out in a vacuum-induction furnace, and the melt was subsequently cast in either a water-cooled copper or water-cooled stainless-steel mold. The resulting solidification structure was characterized through imaging in an optical microscope and the rate of solidification was estimated from the secondary dendrite arm spacing. Inclusion size, dispersion, chemistry are analyzed with SEM-EDX.

The solidification tests with various cooling rate were carried out in either a mold in the induction furnace or in a IR-furnace attached to a Confocal Scanning Laser Microscope (CSLM).

2.1. Material

A mother ingot (50 kg) was produced in a vacuum furnace by melting electrolytic iron (Wako Chemicals Fe/99.97%), graphite (Tokai carbon C/99.5%) and metallic manganese (Wako Chemicals Mn/98%). The resulting chemical composition of the mother ingot was C/0.10 wt%, Si/0.01 wt%, Mn/0.94 wt%, P/0.024 wt%, S/0.001 wt% and T.O/0.0273 wt%. The ingot was sectioned and machined into small pieces (400 g, 40×40×40 mm) for the use in de-oxidation tests. Iron oxide was added before killing to obtain the Ti-killed sample with higher oxygen content. The dissolved Ti content after de-oxidation was measured to be 0.01 wt% and the oxygen activity at this point was 50 ppm.

2.2. De-oxidation and Casting

De-oxidation tests were carried out inside a vacuum furnace. The furnace chamber was evacuated and refilled with grade 5.6 Ar (99.9996%) before heating. The ingot sample was placed inside a MgO (φ50–40×H=120 mm, TEP Ceramics, MgO/99%) crucible and heated to 1 873 K and subsequently, de-oxidized by titanium (99.99%) addition. The oxygen contents before and after de-oxidation were measured through immersion of a custom-made oxygen sensor (Mo/Cr+Cr2O3/ZrO2(CaO)//Fe–O/Fe supplied by Heraeus Electro-Nite). Finally, the molten de-oxidized steel was poured into a water-cooled copper and stainless steel mold (inner size: 60×40×40 mm). An Al killed sample was used for comparison with the Ti-killed samples investigated in this study.

2.3. Confocal Laser Scanning Microscope (CSLM)

The experiments of rapid cooling of the steels from the molten state were carried out with the gold-image-hot-stage attached to a confocal scanning laser microscope (CSLM). Details on the CSLM and its capabilities can be found in the pioneering work by Emi and co-workers, and the CSLM used in this study can be shown in the previous paper. The three thermal profiles shown in Fig. 1 were adopted in this study. The purpose of these experiments was to assess how and if the secondary inclusion population generated as a result of varying cooling and solidification rate influences austenite grain growth and decomposition. Heating and melting was carried out under flowing Ar gas (0.8 NL/min) and solidification was carried out under either Ar or a He-gas jet (0.8 NL/min). The latter resulted in cooling rates approaching 100 K/s. The samples chosen for these experiments were such that they were solidified at a low rate in the vacuum-furnace such that they contained a minimum amount of secondary de-oxidation inclusions at the start of the CSLM experiment.

The first is shown in Fig. 1(a) and is intended to simulate continuous cooling from the melt during conventional continuous casting. The sample was heated to 1 873 K at a rate of 10 K/s after which the molten sample was maintained for 1 min, and subsequently cooled to room temperature at the aimed cooling rate. The cooling rates were aimed at 1, 10 and 100 K/s in the range from 1 873 to 1 673 K.

The second thermal profile is shown in Fig. 1(b), and is intended to simulate the thermal history during direct hot-charge rolling. In this case samples are melted in Ar gas atmosphere at 1 873 K, cooled to 1 573 K at cooling rates of 1 and 10 K/s, then the temperature is maintained at 1 573 K for 20 min, finally, cooled down to 373 K at the cooling rate of 13 K/s.

In the two aforementioned cases, the austenite grain growth could not be imaged well due to that the solidified sample did not result in a sufficiently flat surface for adequate imaging. Therefore CSLM was also used for the in-situ observation of austenite grain growth during iso-thermal holding at 1 573 K. This corresponds to the third thermal profile adopted in this study, which is shown in Fig. 1(c). Heating and cooling were carried out under Ar gas atmosphere (0.8 NL/min). Heating and cooling rate were 5

![Fig. 1. Thermal profiles used in CSLM experiments (a) solidification, (b) hot charge rolling simulation, (c) austenite grain growth and ferrite precipitation).](image-url)
and 13 K/s respectively. After cooling, ferrite precipitations were observed with optical microscope (Nikon Eclipse ME600).

2.5. Characterization

The chemical composition of the cast samples were measured through infrared absorptiometric method after combustion in oxygen for the elements of carbon and sulfur inert-gas-carrier melting thermo-conductimetric method was used to evaluate total N and inert-gas-carrier melting-infrared absorptiometric method was used for evaluating the total O. ICP-OES (inductively coupled plasma optical emission spectrometric method) was used for all other elements. In the case of soluble Ti and Al, these were analyzed using the residual dross after the analysis of total Ti and total Al. The dross was melted by pyo-potassium sulfate, and then, filtrated with hydrochloric acid as a specimen for ICP-OES.

Inclusions of de-oxidized samples prepared in the vacuum induction furnace and samples obtained by re-melting and solidification in the CSLM hot-stage were evaluated. The samples were polished, using a Struers TegraSystem™ automatic polisher, by a sequence consisting of: 320 SiC paper disc, 9 μm diamond suspension on a fine grinding disc, 3 μm diamond suspension on a stain-woven acetate polishing cloth, 1 μm diamond suspension on a synthetic short-nap velvet polishing cloth. Polished samples were thoroughly cleaned between polishing steps using precision, non-abrasive, residue-free detergent solution.

The samples were etched with picric acid saturated aqueous solution to reveal the initial microstructures and estimate the cooling rate during solidification. Etched sample micro-structures were observed with an optical microscope (Nikon Eclipse ME600). Inclusions in each sample were characterized with a Phillips XL-30FEG Scanning Electron Microscope. Inclusions of each sample were observed at three specific areas (0.25 mm²/each area). The cooling rates during solidification were estimated by measuring the secondary dendrite arm spacing in the samples which were etched by a picric acid solution.

In order to further analyze the structures an EBSD system was used after the CSLM experiments to characterize the transformed micro-structures. The motivation was to identify whether orientation of ferrite grains that interface a given non-metallic inclusions appeared to be oriented differently from one-another.

The sub-micro meter oxides in the Ti-killed sample (sample 2) were evaluated through microanalysis with the use of Field Emission–Transmission Electron Microscope (FE-TEM) and Energy Dispersive X-ray spectrometer (EDX). The sample preparation for TEM was based a typical 2-step extraction replica method, in which precipitates were fixed in Carbon evaporated film and its film was scooped on Al grid.

3. Results and Discussions

3.1. Chemistries and Inclusions

Chemical compositions of samples obtained through the de-oxidation tests are listed in Table 1. Samples 2–6 are Ti-killed samples with various oxygen and Ti contents, corresponding to different Ti/O ratios. Sample 1 is an Al-killed sample that was used for comparison. Experimental conditions, during the molten-stage processing, of samples 3 and 4 were same, but a water-cooled copper mold was used for sample 3 resulting in a cooling rate of 6.6 K/s (bottom), and a water-cooled stainless steel mold resulting in a cooling rate of 5.2 K/s (bottom) was used for sample 4. Included in this table are also the estimated values for soluble oxygen and nitrogen, denoted as [O]e and [N]e respectively. These were computed by using the soluble Ti and Al contents and ignoring the impurity oxides from crucibles and other sources and assuming equilibrium was reached at 1 873 K during de-oxidation. Equilibrium values were calculated with available thermodynamic data at 1 873 and 1 573 K. The details of these calculations were provided in a previous paper.

In sample 3, inclusions were found to be complex oxides, such as MnO–(SiO₂)–TiOₓ and MnS. These are larger than the typical inclusions that were found in the low oxygen (7–10 ppm) sample 2, such as Ti–Al–(Mg)–O (0.3–1 μm), TiN (0.5–2 μm). The latter could be found by themselves but were most often found with an oxide in their core. TiN was not found in the present samples were dissolved oxygen levels were high. In the Al-killed sample (sample 1), Al₂O₃ was as expected found.

For Ti-killed steels, the total nitrogen and oxygen contents were compared with calculated solubility limits as-

| Sample | Killing condition* | Mold | C  | Si | Mn | P  | S  | sol.Al | Ti | sol. Ti | T[O] | T[N] | [O]e | [N]e |
|--------|--------------------|------|----|----|----|----|----|--------|----|--------|------|------|------|------|
| 1      | Al                 | Cu   | 0.074 | 0.004 | 0.87 | 0.026 | 0.0011 | 0.062 | 0.001 | 0.001 | 0.0008 | 0.0014 | 0.0005 | 0.0158 |
| 2      | TiOLO              | Cu   | 0.090 | 0.004 | 0.89 | 0.030 | 0.0010 | 0.009 | 0.009 | 0.087 | 0.0007 | 0.0019 | 0.0016 | 0.0016 |
| 3      | Ti/HO              | Cu   | 0.084 | <0.01 | 0.79 | 0.022 | 0.0020 | 0.001 | 0.007 | 0.006 | 0.0081 | 0.0033 | 0.0062 | 0.0195 |
| 4      | Ti/HO              | SUS  | 0.081 | <0.01 | 0.78 | 0.021 | 0.0024 | 0.001 | 0.009 | 0.005 | 0.0056 | 0.0029 | 0.0054 | 0.0194 |
| 5      | TiOLO              | Cu   | 0.068 | <0.008 | 0.85 | 0.021 | 0.002 | 0.003 | 0.003 | 0.064 | -      | 0.0009 | 0.0022 | 0.0013 | 0.0021 |
| 6      | Ti/MO              | Cu   | 0.078 | <0.008 | 0.83 | 0.021 | 0.002 | 0.002 | 0.002 | 0.010 | -      | 0.0023 | 0.0025 | 0.0042 | 0.0134 |

* LO: Low oxygen content sample, MO: Middle oxygen content sample, HO: High oxygen content sample
summing the equilibration with TiN\(^{17}\) and Ti\(_3\)O\(_5\) at 1 873 K\(^{16}\) and 1 573 K.\(^{18}\) In Ti-killed steel, the stable Ti-oxide is expected to be Ti\(_3\)O\(_5\) in case of \[%Ti\]/H\(_{1021}\).\(^{16}\) TiN is stable in the melt for the low oxygen samples whereas in the high oxygen samples (sample 3 and 4), it should not precipitate until temperatures reach 1 573 K and below.\(^{8}\) In Ti-killed steel, inclusion size and density increased with increasing the starting oxygen content.\(^{6}\) In low starting oxygen content sample below 10 ppm, inclusion size decreased and inclusion density increased with increasing the cooling rate during solidification only in Ti-killed steel.\(^{8}\) With this result, inclusions in low starting oxygen content sample below 10 ppm, inclusion size decreased and inclusion density increased with increasing the cooling rate during solidification only in Ti-killed steel.\(^{39}\) With this result, inclusions in low starting oxygen content Ti-killed steel are considered to be secondary inclusions. In previous paper,\(^{8}\) solidified micro-structure was dependent on the small inclusion density smaller than 1 \(\mu m\) in Ti-killed steel. The effects of Ti/O and cooling rate on the density of submicrometer inclusions are shown in Fig. 2(a). Figure 2(b) shows the average inclusion size as function of cooling rate for the same samples. CLSM results with the conditions in Fig. 1(a) together with the results of the previous cast samples (with water-cooled copper mold)\(^{8}\) are shown in Figs. 2(a) and 2(b). The cooling rates of the cast samples are 2–6 K/s. In Figs. 2(a) and 2(b), vertical lines are inserted to represent the cooling rates during solidification which are employed in this study (shown in Fig. 1(a)). The intersection of these lines with the curves representing inclusion density in Fig. 1(a) would indicate the inclusion density which would be present at the end of solidification.\(^{8}\) It should be noted that the inclusion population analysis did not consider inclusions smaller than 0.03 \(\mu m\). Inclusions were evaluated in the samples, which were obtained with CLSM at 3 cooling rates 1, 10 and 80 K/s as shown in Fig. 1(a) and the previous cast samples.\(^{8}\)

### 3.2. Austenite Grain Growth

The cast samples and CSLM samples (cooled at 80 K/s during solidification) were chosen for the evaluation of austenite grain growth and ferrite precipitation. Observed data concerning austenite grain size and ferrite precipitation are shown in Table 2. Examples of the austenite grain sizes at the end of isothermal treatments are shown in Fig. 3 for samples 1, 2 obtained by the experiment in Fig. 1(c). During the isothermal treatment, the surface grain size delineated by the grain boundary traces intersecting the surface did not appear to change after a period of ten minutes. At that point, the structures appeared shown in Fig. 3. It is clear that the Ti killed samples result in a significantly finer austenite size than the Al-killed ones. This is consistent

![Fig. 2. Effects of cooling rate and Ti/O on (a) small inclusion density (<1 \(\mu m\)) and (b) inclusion size.](image)

| Sample | Killing condition | [O] | cooling rate | Inclusion size | Inclusion density | \(Z_p\) | \(\gamma\) grain size | RA | \(N_p\) | \(N_q\) | \(N_pq\) | \(R_q\) |
|--------|------------------|-----|--------------|----------------|------------------|-----|-------------------|----|--------|--------|----------|------|
| 1      | Al-killed        | 8   | 4.6          | 1.58           | 24               | 0.225 | 677               | 95 | 0.32   | 6.4    | 6.7      | 4.8   |
| 2      | Ti-killed        | 7   | 64.3         | 2.08           | 36               | 0.202 | 607               | 36 | 17.7   | 4.2    | 21.8     | 81.0  |
| 3      | Ti-killed        | 81  | 5.3          | 0.68           | 60               | 0.447 | 169               | 45 | 20.16  | 38.4   | 58.6     | 34.4  |
| 4      | Ti-killed        | 56  | 83.8         | 0.28           | 96               | 0.959 | 85                | 33 | 74.8   | 33.2   | 108.1    | 69.2  |
| 5      | Ti-killed        | 9   | 68.7         | 1.12           | 154              | 2.75  | 178               | 44 | 17.7   | 20.8   | 38.4     | 45.9  |
| 6      | Ti-killed        | 23  | 78.1         | 1.15           | 114              | 1.87  | 177               | 40 | 18.7   | 17.7   | 36.4     | 51.4  |

\(R_q\): Ratio of ferrite precipitation at inclusions
\(N_p\): Ferrite density precipitated both at inclusions and grains
\(N_{pq}\): Ferrite density precipitated at inclusions

Table 2. Summarized results of inclusion and microstructure.

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with the inclusion population shown in Fig. 2 were it is seen that the Ti-killed samples have consistently a higher density of sub-micrometer sized inclusions. The effect of cooling rate during solidification of the Ti-killed samples is however not quite as expectable. The smallest austenite grain size is achieved in Ti-killed sample 2 cooled at 84 K/s. In Fig. 2, it can be seen that this sample does not contain the highest density of sub-micron-sized inclusions (Fig. 2(a)). It does however contain the smallest average inclusion size (Fig. 2(b)). In the Ti-killed steel, inclusions were observed at the boundaries of smaller austenite grains, which are surrounded by circles as shown in Fig. 4. The Zener pinning force can be expressed by Eq. (1), where grain size is predicted by Zener's model (Eq. (3)) when grain size is predicted by the inclusions ability to pin grain boundaries by exerting a pulling force. The radius of a grain (\(r\)) is proportional to the radius of the pinning inclusion (\(r_p\)) and is inversely proportional to the inclusion volume fraction (\(f_v\)). The constant \(\beta\) depends on the geometry and force balance.

\[
R = \beta (r/f_v)...........................(3)
\]

Assuming that the pinning inclusions were oxides of the radius \(r\), Eq. (2) was modified by Nishizawa\(^{24}\) as Eq. (3a), where the constant \(\beta = 4/9\) instead of 3/4 which was originally proposed by Zener\(^{21}\) Mizoguchi\(^{25}\) adopted Eq. (3a) for his analysis. Here, the oxide inclusion has a stoichiometry, \(M_n\text{O}_m\), and therefore the radius of grain (\(R\)) is expressed by Eqs. (3a) and (3b), where \(f_o\) is volume fraction of oxide, \(d\) is a mean inclusion diameter (\(mm\)) and \(f_v\) calculated by Eq. (7) is a volume fraction of oxide inclusions. In the T-killed sample, both oxides and nitrides were originally present in the samples cast in the vacuum induction furnace. However, only the oxide inclusions were taken into account for \(d\) and \(f_v\), since the nitrides are not expected to present appreciably as a result of the thermal profile employed in the CSLM. In Eq. (2), \(n\) and \(m\) are the numbers of cation, \(M\), and oxygen respectively in oxide, \(M_{n\cdot m}\text{O}_{n\cdot m}\). \(\rho\) and \(\rho_o\) are the density of oxide and iron respectively, \(T[\text{O}]\) is analyzed total oxygen content. Figure 5 shows the relation between \(Z_p\) and austenite grain size after isothermal treatment for 20 min. The austenite grain size does not have any apparent correlation with \(Z_p\) but this could be due to that inclusions below 0.1 \(\mu m\) were not quantified.

\[
Z_p = \frac{3 \cdot \sigma \cdot V \cdot f_v}{d}...........................(1)
\]

\[
f_v = \frac{(nO + mM)}{nO} \left(\frac{\rho_o}{\rho}\right) \cdot T[\text{O}]...........................(2)
\]

The finer grained structure observed in the Ti-killed samples are attributed to either of the following (i) the Ti-O having a grain-boundary pinning effect that is more effective than those of the alumina inclusions in the Al-killed sample or (ii) solute drag caused by soluble Ti in the Ti killed steels decrease the mobility of the boundaries. A relation utilizing inclusion size and the spatial distribution between inclusions to predict grain size proposed by Mizoguchi\(^{23}\) and this was used to investigate the plausible effect of grain-boundary pinning. The relation is based on Zener’s model (Eq. (3))\(^{21}\) where grain size is predicted by the inclusions ability to pin grain boundaries by exerting a pulling force. The radius of a grain (\(r\)) is proportional to the radius of the pinning inclusion (\(r_p\)) and is inversely proportional to the inclusion volume fraction (\(f_v\)). The constant \(\beta\) depends on the geometry and force balance.
The decomposition of the austenite grains into ferrite would depend on the aforementioned growth of austenite grains and the population of non-metallic inclusions. It was however shown that the austenite grain size is itself influences by the non-metallic inclusions and the latter can therefore have a dual role in refining the resulting decomposed ferrite micro-structure. In this work we chose to combine the two roles but investigate their relative importance in conventional vs. DHCR by simulating the thermal profiles as shown in Figs. 1(a) and 1(c) in the CSLM. In the DHCR process more time is allowed for austenite grain growth.

We will first discuss the structures resulting from the thermal profile shown in Fig. 1(a) (corresponding to conventional casting were samples are cooled continuously to room temperature). The small inclusion density depends on both Ti/O and cooling rate as shown in Fig. 2(b).

Figure 7 shows the comparison of the final decomposition structure in Ti-killed steels, which were cooled at the lower cooling rate (as cast, 5.3 K/s) and higher one (quenched, 84 K/s). In the Al-killed samples, the decomposition proceeded by coarse Widmanstätten plate forming independently of the inclusions. On the other hand, in the Ti-killed steel, Widmanstätten ferrite precipitated at inclusions as well as at grain boundaries. Widmanstätten ferrite precipitation was classified as precipitates at grain boundary and inclusions by counting the number of these in each sample. It should be noted that individual laths, especially when emanating from an austenite grain boundary might not be individual nuclei but rather perturbations from the same precipitate. The difference can be resolved if orientations differ between individual laths in which case they are likely separate precipitates. In this analysis however, it is assumed that each lath is an individual precipitate. Widmanstätten ferrite precipitations at inclusions are shown in Fig. 7, which are surrounded by the circles. The increased number of precipitated laths, result in a finer decomposed ferrite micro-structure. In this work we chose to investigate the effect of inclusions on the ferrite lath density. Figure 8 shows the relations between the density of ferrite precipitation and $Z_f$ (Fig. 8(a)), and inclusion size (Fig. 8(b)). No significant correlation was confirmed in Fig. 8(a). However, it was found that the ferrite density increased with decreasing the inclusion size shown in Fig. 8(b). By comparing the austenite grain size at the end of isothermal anneal treatment (Fig. 3), it is expected that the decomposition structure would be influenced by the starting austenite grain size and this is confirmed in Fig. 9(a). The number of Widmanstätten ferrite precipitated at both grain boundary and inclusion was counted in the specific area (2.5 mm×2.5 mm). The ratio of Widmanstätten ferrite precipitation at inclusions, $R_p$, was calculated as Eq. (6) with the number of
Fig. 7. Optical images of sample 2s (a), (c): cooled at 5.3 K/s during solidification, (b), (d): cooled at 84 K/s during solidification) after isothermal treatment (1300°C, 20 min, then cooled at 13 K/s).

Fig. 8. Relation between density of ferrite precipitates and (a) $Z_p$ and (b) inclusion size.

Fig. 9. Relation between (a) density of ferrite precipitates and austenite grain size, and (b) $R_p$ and inclusion size.

Fig. 10. Final microstructures in experiments (A: (a), (c), (e), B: (b), (d), (f) ) for DHCR simulation (Fig. 1(b)).
Widmanstätten ferrite at inclusions, where \( N_p \) (N/mm²) is the density of ferrite precipitated at particles (inclusions) and \( N_g \) (N/mm²) is the same at grain boundaries.

\[
R_p(\%) = \frac{N_p}{N_p+N_g} \times 100 \tag{6}
\]

The relation between \( R_p \) and inclusion size is shown in Fig. 9(b) and it can be seen that \( R_p \) is indeed influenced by the inclusion size. The obtained values are summarized in Table 2. Based on the in-situ observations, solidification structure, delta–ferrite to austenite transformation, austenite grain growth and decomposition are all influenced by the inclusion size.

The thermal history shown in Fig. 1(b) was employed out in order to simulate the DHCR or other CSP processes. Optical images of ferrite precipitation are shown in Fig. 10. Higher ferrite density can be observed in Ti-killed lower starting oxygen content and higher cooling rate. Comparison of ferrite density precipitated at inclusions is shown in Fig. 11. This is the sample for which the smallest average inclusion size was found. The highest ferrite density can be observed in Ti-killed low oxygen sample cooled at 10 K/s. The ferrite density was evaluated at inclusions, since in this case, austenite grains can’t be observed after experiments. The higher ferrite density was obtained in low oxygen content, high cooling rate (10 K/s) Ti-killed sample, whose inclusions were smallest in these conditions. Therefore, the results of ferrite precipitation in this experiment are considered to be the same as those with cast samples. The finer ferrite precipitation can be obtained by achieving smaller inclusions utilizing secondary inclusion generation in DHCR or other CSP processes. In this experiment, the cooling rate during solidification can’t be controlled more than 10 K/s. The higher cooling rate during solidification is needed for detail investigation on DHCR or other CSP processes.

Figures 12(a) and 12(b), show EBSD maps for the final microstructure. The results indicate that ferrite-grains with different orientations appear to exist near non-metallic inclusions (indicated by arrows) suggesting that the inclusion
could be an initiation point for ferrite precipitation.

The observation results with FE-TEM and EDX are shown in Figs. 13(a)–13(c) (1–10 indicated in Fig. 13 are the analysis points with EDX). Small Ti oxides, 0.3–1.5 μm were observed in the replica samples such as the points 1, 3, 5–7, 9 and 10. Their shapes were found to vary. In some
cases, Ti oxide inclusions contain Al, and Mn–S was observed at the outer layer (2, 3, 7, 9 and 10). It should be noted that Fe was frequently observed around the Ti oxide inclusions (1, 3, 5–7, 9 and 10), which are bar or needle shapes (8). C peaks were seen together with iron peaks in the EDX analysis (1, 4). It could be possible that the Fe and C peaks are caused by ferrite or Fe₃C precipitation. However, the C peak is likely a result of the C evaporated film. Therefore, the Fe observed around Ti oxide inclusions is considered to be the ferrite precipitations, since the ferrite precipitations were mainly observed at the Ti oxide inclusions in this work. Further investigation is needed, which can estimate the chemistries and crystal structures of secondary Ti oxide inclusions and their effect on microstructure.

The results in this study show that austenite grain size becomes smaller and ferrite lath density higher when the average size of non-metallic inclusion below 1 μm increases. The results in this study indicate that this can be obtained if Ti is used in place of Al in order to control the de-oxidation in such a manner that it occurs during casting, and thereby result in secondary inclusions. Practically, it appears that this can be achieved by maintaining a high Ti/O ratio in the melt before casting and maintaining an as high cooling rate as possible. The condition of both cooling rate and Ti/O has been proposed in the previous paper. Ti/O need to be 100 in the case of the cooling rate of 8 K/s, which is supposed to be the normal cooling rate in a continuous slab caster.

4. Conclusions

To summarize, the results presented in this paper indicate that the secondary Ti-oxides that have previously been shown to precipitate during solidification of low C, high Mn steel samples solidified under high cooling rate and a high starting Ti/O ratio, are indeed beneficial for solid-state micro-structure refinement. The micro-structure resulting from heat treatments corresponding to both DHCR and conventional casting, re-heating and hot-rolling were finer for Ti-killed samples compared to the Al-killed ones. The achieved densities of ferrite precipitation were the same level in DHCR and conventional heat treatments.

The finest micro-structure, resulting from both a finer austenite grain size and high ferrite precipitate density, is achieved when the average inclusion size is minimized.