Micro-structure Refinement in Low Carbon High Manganese Steels through Ti-deoxidation—Inclusion Precipitation and Solidification Structure

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(Received on January 7, 2008; accepted on May 7, 2008)

The substitution of Al by Ti as a de-oxidizing agent in a carbon (0.07 wt%) and Mn (0.9 wt%) containing steel was studied for two purposes. The first one was to establish whether inclusion precipitation during solidification (secondary de-oxidation) can be promoted. The second purpose was to investigate the influence of secondary inclusions on the subsequent evolution of the steel solidification-structure, varying initial oxygen and titanium contents along with cooling rate during solidification.

In the Ti-killed steel samples, the oxide inclusions were identified as MnO–TiO$_2$ (0.5–5 μm) and MnS (1–3 μm) in the samples with the higher initial oxygen contents (Total Oxygen (T.O)/H11005 50–80 ppm) while Ti–Al–(Mg)–O (0.3–1 μm) in the samples with the lower oxygen contents (T.O=7–10 ppm). Comparing with thermodynamic calculations, the latter inclusions are considered to be the result of solely secondary de-oxidation precipitated in the inter-dendrite regions. For the high initial oxygen content, the inclusions were found as a result of both primary and secondary de-oxidation. The influence of cooling rate during solidification was investigated by controlling the cooling rate between 3–10 K/s by using different molds in a vacuum induction furnace. In addition, cooling rates were controlled at 1.1, 14 and 84 K/s by re-melting the samples in a gold-image furnace attached to a Confocal Scanning Laser Microscope (CSLM). An increase in the cooling rate resulted in an increase in the inclusion density in the Ti-killed samples while such an effect was not observed in the Al-killed sample. The secondary particle sizes for the Ti-killed sample predicted by a solute segregation model during solidification agreed well with the observed average particle sizes.

In the Ti-killed samples, the solidification structure was finer with increasing density of inclusions below 1 μm, whereas such an effect was not observed in the Al-killed samples.

KEY WORDS: low-carbon steel; de-oxidation; titanium; cooling-rate; inclusion precipitation; solidification microstructure.

1. Introduction

Ferrite grain sizes below 1 μm$^{1-3}$ can be achieved by Thermo-Mechanical Control Process (TMCP) extensively applied for optimizing micro-structures of continuously cast steel products with high strain (up to 50%) at the low temperatures (500–700°C). However, for processes of direct hot-charging more widely used due to their economic and energetic advantages, TMCP is not effective enough. It is known that inclusion control, during steelmaking and casting, offers a possibility to influence the micro-structure. Therefore, the combination of TMCP and the control in steelmaking process, such as alloying, de-oxidation and solidification should be beneficial to refine micro-structure of continuously manufactured steel.

The area of “Oxide metallurgy”$^{4-13}$ was developed to control microstructure through appropriate tailoring of inclusions. Recently, Kojima has shown that small oxides and sulfides of Mg and Ca, which are more stable at high temperatures than TiN, have a role to pin the austenite grains in the heat affected zone during welding steel.$^{14}$ Moreover, TiN, Ti$_2$O$_3$, TiN–MnS have been shown to promote heterogeneous nucleation of inter-granular ferrite precipitation during the γ/α transformation. Ohkita showed that oxide particles, including TiO, could promote nucleation sites for acicular ferrite precipitation.$^{15}$ Several mechanisms for this phenomenon have since been suggested: 1) Influence on the interfacial energy between the particles and austenite,$^{16-18}$ 2) Influence on the crystal epitaxy between the particles and both of austenite and ferrite phases,$^{15,19}$ 3) Influence on the thermal expansion between the particles and austenite,$^{20}$ 4) Effect of the depletion of Mn around the particles associated with MnS precipitation at a oxide particle as a nucleation site.$^{21,22}$ In welding steels, it was confirmed that TiN, VN and MnS particles, smaller than 0.5 μm with population higher than 10$^5$/mm$^3$, could refine grains.$^{23}$

While Ti-oxides might be efficient for micro-structure control, a technology to control inclusion precipitation has
not been fully developed. To control precipitate size to be as small as possible, primary de-oxidation in the melt needs to be avoided. On the other hand, an appreciable amount of precipitation cannot be expected in the solid state before hot-rolling or during the direct hot-charging. The reason is that oxide precipitation will be limited by solid-state diffusion. Thus, precipitation through secondary de-oxidation during solidification remains as the best option. The current study focuses on this behavior.

In a recent publication, the difference between Al and Ti-killed steel was clarified in the view of inclusion, solidification microstructure, phase transformation and grain growth. The differences in evolution of micro-structure during and after solidification was confirmed when Ti was used in place of Al. While the difference between Al and Ti killing was noted, the occurrence of secondary precipitation could not be unambiguously quantified due to the high Ti levels, which lowered the oxygen content in the melts through de-oxidation before solidification. The role of any secondary Ti de-oxidation inclusions could therefore not be determined. To fully understand the effect of secondary inclusions on micro-structure, primary Ti de-oxidation products have to be prevented.

The objective of this study is firstly to elucidate whether inclusions in the case of Ti de-oxidation are indeed generated during solidification. The potential to influence this process through control of Ti- and O-contents will be established controlling primary de-oxidation thermodynamically. Furthermore a wider range of cooling rates are investigated in order to quantify the extent of secondary de-oxidation. We also aim to determine the extent to which solidification micro-structure can be refined through Ti de-oxidation. To clearly see this extent, efforts were made to separate the effects of cooling rate and inclusion population on solidification structure.

De-oxidation tests were carried out with a vacuum induction furnace. Solidification tests were performed in molds and with an IR-furnace in order to examine how a variation in secondary oxide population (for the case of Ti de-oxidation) affects steel microstructure evolution during solidification at different cooling rates.

2. Experimental

2.1. De-oxidation and Casting

Details of the procedure have been described in a previous publication. A mother ingot (50 kg) whose composition was C/0.10, Si/0.01, Mn/0.94, P/0.024, S/0.001 and T.O/0.0273 wt% was produced with a vacuum furnace. Iron oxide was added before killing to obtain the higher oxygen content Ti-killed sample. Target compositions of Ti and dissolved oxygen activity (\(a_O\)) after de-oxidation process were 0.01 mass% and 50 ppm respectively. The ingot was sectioned into small pieces (400 g, \(\phi 40 \times H=30\) mm) for de-oxidation tests. De-oxidation tests were carried out inside a vacuum furnace with the same manner as the previous study. The furnace chamber was evacuated and refilled with grade 5.6 Ar (99.9996%) before heating. The ingot sample was melted in a MgO (\(\phi 50-40 \times H=120\) mm, TEP Ceramics, MgO/99%) crucible at 1873 K and subsequently, de-oxidized by titanium (99.99%) addition. An oxygen sensor (Mo/Cr_2O_3/ZrO_2(CaO)/Fe–O/Fe supplied by Heraeus Electro-Nite) was used to measure the oxygen contents before and after de-oxidation. Finally, the molten de-oxidized steel was poured into a water-cooled copper and stainless steel mold (Inner size: \(60 \times 40 \times 40\) mm). The cooling rate obtained by the stainless steel mold was expected to be 1/24 of that in the copper mold. Estimated cooling rate with the stainless steel mold is 0.275 K/s compared with the actual cooling rate, 6.6 K/s, with the copper mold. The Al-killed sample and a sample with no material added for de-oxidation that were investigated in a previous study were used in this study for comparison.

2.2. Confocal Laser Scanning Microscope (CSLM)

The experiments of rapid cooling from molten steels were carried out with confocal scanning laser microscope (CSLM) developed by Emi and co-workers. The samples solidified at a low cooling rate in the vacuum-furnace were chosen for the CSLM because they contained the smallest amount of secondary de-oxidation inclusions. The sample was heated to 1873 K at a rate of 10 K/s after which the molten sample was maintained for 1 min. Subsequently it was cooled to a room temperature at the cooling rates aimed at 1, 10 and 100 K/s in the range from 1873 to 1673 K as shown in Fig. 1. During heating and melting, Ar gas (0.8 NL/min) was flown followed by solidification under either Ar or a He-gas jet (0.8 NL/min). Cooling rates attained 100 K/s with the latter.

2.3. Analysis and Observation

Carbon, sulfur, nitrogen and total oxygen contents were measured. For soluble Ti and Al, the residual dross after the analysis of total Ti and total Al was melted by pyo-potassium sulfate, and then, filtrated with hydrochloric acid as a specimen for ICP-OES.

Inclusions and solidification microstructure were evaluated for the de-oxidized samples prepared in the vacuum induction furnace and the samples obtained by re-melting and solidification in the CSLM hot-stage. As for the de-oxidized sample, in order to obtain samples solidified at different cooling rates, two sections were selected in the cast samples obtained by vacuum induction furnace. In the case of the vacuum furnace experiments, they were the positions close to the water-cooled copper mold (bottom), and far from the mold (top). Each part was sectioned into ~2 mm thick slices, and cut into \(\sim 4 \times 4\) mm squares followed by a mirror polish.

The samples were etched with picric acid saturated aqueous solution to reveal the initial microstructures and estimates of the thermal profiles used in the CSLM.
mate the cooling rate during solidification. Micro-structures were observed with an optical microscope (Nikon Eclipse ME600). Inclusions of each sample were characterized with a Phillips XL-30FEG Scanning Electron Microscope (SEM). Inclusions of each sample were observed at five specific areas (0.25 mm²/each area). Inclusions were counted within a specific area (0.5 mm²) observed in an SEM to obtain density. Particles below 10–30 nm could not be accurately resolved. Inclusion size was defined as the average radius of inclusions in the area.

3. Results and Discussions

3.1. Chemistries and Inclusions

Chemical compositions of samples obtained through the de-oxidation tests are listed in Table 1 in which samples 1–5 are the same as in the previous study.24) Samples 2–4 and 6–9 are Ti-killed samples with various oxygen contents according to the Ti contents. Al-killed (1) and no-addition (5) experiments were used for comparison. Experimental conditions, during the molten-stage processing, of samples 6 and 7 were the same. But a water-cooled copper mold was used for sample 7 resulting in a cooling rate of 6.6 K/s (bottom). A water-cooled stainless steel mold resulting in a cooling rate of 5.2 K/s (bottom) was used for sample 6. No significant difference of the cooling rate was confirmed between the two kinds of molds differing from the expectation mentioned above. Particles below 10–30 nm could not be accurately resolved. Inclusion size was defined as the average radius of inclusions in the area.

Representative examples of inclusions in the samples 1, 2 and 6, containing the lower and higher oxygen contents respectively, are shown in Fig. 2. In sample 7 resulting in a cooling rate of 6.6 K/s (bottom). A water-cooled stainless steel mold resulting in a cooling rate of 5.2 K/s (bottom) was used for sample 6. No significant difference of the cooling rate was confirmed between the two kinds of molds differing from the expectation mentioned above. 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 the soluble Ti and Al contents ignoring the impurity oxides from crucibles and other sources with the assumption that equilibrium was attained during de-oxidation at 1 873 K.24) The Ti contents all lie below this minimum. In Fig. 2(b), the oxide phases in the inclusions appear to be a mixture of several inclusions. Therefore the activity of Ti₂O₃ would be lower than unity. The high oxygen samples (6, 7 and 9) on the other hand, would have Ti₂O₅ as de-oxidation products since the two plots out of three fall near the unit-activity curve. Inclusion-size distributions of Ti-killed samples 2, 6 and 9 are shown in Fig. 4. Inclusion becomes denser and larger with increasing starting oxygen content. Inclusion size distributions of the other low-oxygen Ti-killed samples 3 and 4 were similar to the sample 2. Although the high-oxygen samples, 6 and 7 were poured into the different molds with different cooling rates, inclusion size and density was found to be quite similar. It should be noted that samples 2 and 6 were cooled at similar rates with low and

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<td>0.0011</td>
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<td>0.01</td>
<td>0.88</td>
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<td>0.0010</td>
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<td>0.0009</td>
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<tr>
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<td></td>
<td>0.075</td>
<td>0.01</td>
<td>0.90</td>
<td>0.027</td>
<td>0.0010</td>
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<tr>
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<td>&lt;0.01</td>
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* LO: Low oxygen content sample, MO: Middle oxygen content sample, HO: High oxygen content sample

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Table 1. Composition of the steel samples after de-oxidation tests (wt%).
high amounts of oxygen content, respectively. In sample 5, small amounts of fine Al–Mg–O particles were observed as shown.

Based on the thermodynamic stability of inclusions (Fig. 3), in the high-oxygen samples 6 and 7, the observed inclusions explained above are considered to result from both primary and secondary de-oxidation. The former ones are expected to be larger in size because they would have precipitated in the melt. Figure 5 shows the inclusion size distribution for the samples of the same melt chemistry (low oxygen) with the various cooling rates in the CSLM. The average inclusion size decreases as a result of cooling rate. The cooling rate was estimated by the following equation with the measured secondary-dendrite-arm spacing.32)

\[
\lambda_2 = 688 \cdot R_c^{0.36}
\]

where, \(\lambda_2\) is secondary-dendrite-arm spacing (\(\mu m\)), \(R_c\) is cooling rate (K/min). These values are shown in Table 2. Note that the calculated cooling rate was converted to K/s in unit. Inclusion densities and the amount of finer particles can be seen to increase with increasing cooling rate. (It should be noted that because the samples in Fig. 5 were remelted and solidified in the CSLM, they do contain the inclusions that were present after the first solidification in the vacuum furnace.)

The relationship between the cooling rate and the oxide inclusion density is shown in Fig. 6 including the results for Ti, Al, and no de-oxidation samples. Figure 6(a) shows the samples 1–5 and 9 (low oxygen content samples) and that obtained by CLSM quench tests. With increasing the cooling rate, oxide inclusion density becomes higher only for the Ti-killed steel samples. This implies that inclusions in Ti-killed are considered as secondary de-oxidation products precipitated during solidification. This is further supported
by the two earlier stated facts that (i) thermodynamically TiO was found not to be stable in the melt and (ii) inclusion sizes were small. No significant difference was observed between the Cu mold and stainless steel mold albeit the small difference in cooling rate (6.6 for Cu and 5.2 K/s for stainless steel).

Figure 6(b) shows the influence of high starting oxygen content from samples 6, 7 and 9 on the inclusion density dependence on cooling rate. A mathematical model of secondary particle precipitation was proposed by Goto et al.11–13 According to the model, the parameters of the secondary particles that precipitate are estimated to be below 1 mm. In Fig. 6(b), the inclusion densities with taking the ones below 1 mm into account are plotted with solid mark. Both plots have roughly the same linear correlation indicated by a dotted line at the cooling rates lower than 10 K/s. This suggests that the inclusions larger than 1 mm are not influenced by cooling rate. At the cooling rates higher than 10 K/s, inclusion densities are smaller than the extrapolation of the linear correlation. When applying the hot stage attached to a CSLM for achieving the high cooling rate, inclusions would be expected to readily float to the surface of the small (below 2 mm depth) crucible during re-melting. Yin et al.25 reported that primary de-oxidation inclusions, such as single particles below 1 mm and small aggregates of Al2O3 around 2 mm floated to the molten Al-killed steel surface within a few seconds in the same size crucible as this work.

Figure 7 shows the relationship between the cooling rate and average inclusion size.

### Table 2. Summarized results of inclusion and microstructure.

<table>
<thead>
<tr>
<th>Killing condition</th>
<th>Dendrite density N/mm²</th>
<th>Secondary arm spacing (μm)</th>
<th>Cooling rate (K/s)</th>
<th>Inclusion size (μm)</th>
<th>Oxide density (N/mm²)</th>
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<tr>
<td>1-T</td>
<td>1.8</td>
<td>123.4</td>
<td>2.0</td>
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<td>1-B</td>
<td>2.1</td>
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* LO: Low oxygen content sample, MO: Middle oxygen content sample, HO: High oxygen content sample

![Fig. 6](image_url) Relation between cooling rate and inclusion density. (a) Ti-killed, Al-killed and no-addition samples with low starting oxygen content. (b) Ti-killed samples with high starting oxygen content.

![Fig. 7](image_url) Relation between cooling rate and average inclusion size.
starting oxygen content. It can be seen that the inclusion size decreases with increasing cooling rate for the Ti-killed sample differing from the Al-killed and no-addition samples. As explained in Fig. 5, the particles in sample 2 are secondary de-oxidation particles, that are influenced by solidification conditions. The differences in inclusion sizes cannot be accounted for by solid state growth, which should be negligible even at the lower cooling rates.

3.2. Solidification Structure

Solidification structures of samples 2 and 7 (bottom and top of the mold) are shown in Fig. 8 showing that dendritic structure is prevalent. The structures of the top part were quite similar to the bottom part. The microstructures of sample 6 are finer than that of sample 2. The dendrite densities were obtained by counting the number of primary dendrite arms in the whole surface of the samples. Figure 9 shows the solidification structures for the samples cooled in the CSLM at different rates. These are the same samples as those for which inclusion distributions are shown in Fig. 5. The dendrite density remarkably increased with increasing cooling rate.

Dendrite densities were obtained by counting the number of primary dendrite arms within a specific area (2.5×2.5 mm²). The relation between the cooling rate and dendrite density is shown in Fig. 10. Obvious is the most marked increase with cooling rate for the Ti-killed samples comparing to the other samples. It is noteworthy that this result coincides with the trends in Figs. 6 and 7 where the number of finer inclusions increases with increasing cooling rate only for the Ti-killed samples. This implies that the Ti de-oxidation influences the solidification structure. This could be due to solidification being influences by the presence of secondary Ti de-oxidation particles or that thermophysical properties such as viscosity or interfacial tension is influenced by soluble Ti.

The relation between the inclusion density and dendrite density is shown in Figs. 11(a)–11(c) for all the samples. In the Ti-killed samples, dendrite densities at low cooling rates (filled circles) can be seen to have a lower dependence on inclusion density when the inclusion density exceeds (approximately) 100 N/m². When identifying the experimental points it was found that they are limited to the high oxygen content Ti-killed samples, and therefore include many large primary inclusions. The relation between the density of only large inclusions up to 1 mm and dendrite density is shown in Fig. 11(b). No apparent relation is found and a lack of influence of larger inclusions on solidi-

![Fig. 8.](image1)

![Fig. 9.](image2)
Solidification structure appears to be the case. In Fig. 11(c), inclusion densities when only the smaller inclusions (<1 μm) are considered and it can be seen that dendrite density increases with increasing inclusion density and the trend for both low and high oxygen content samples seem to overlap. It is noteworthy that this overlap in trends occurs despite the differences in inclusion chemistries (discussed in Fig. 2) between the high and low oxygen content samples.

The present results indicate that the densities of both dendrites and secondary inclusions increase with increased cooling rate. It is expected that inclusion density would increase with increased segregation due to faster solidification at higher cooling rates. This is in support of the observed results. However, the other question of interest in the current study is whether the increased inclusion precipitation in turn contributes to an increased dendrite density. From Fig. 10, the effect of cooling rate in the Al-killed and no addition samples is not appreciable. On the other hand, it is significant in the Ti-killed samples since the inclusion density of inclusions of sizes below 1 μm was notable. Thus, it appears that dendrite density is indeed influenced and enhanced by the presence of the secondary Ti de-oxidation inclusions. Ohta et al.33) reported that de-oxidation particles, such as Ce₂O₃, ZrO₂, MgO have an effect on the solidification microstructure. The extent of equiaxed crystallization for a given particle type was explained by the lattice misfit parameter between austenite and delta-ferrite.

If the dendrite structure is refined by soluble Ti, rather than the inclusions, solidification structure would be finer for the low oxygen content Ti-killed sample. Comparison of dendrite densities between low and high oxygen content Ti-killed sample is shown in Fig. 12. Dendrite densities in the high oxygen content sample are higher than those in the low oxygen content sample and the results are thus not consistent with the expected effect of refined solidification structure resulting from soluble Ti. D. Ness et al.34) reported that carbide particles within the mushy zone restrain the permeability of the liquid into the inter-dendritic region during solidification of Ni-base super alloys. The authors calculated the permeability corresponding to the carbide volume density, 0.00235–1.940%. It was shown that the permeability decreased with increasing the carbide density.

In this study, Ti oxide volume densities were 0.0021–0.025%, which is at the lower end of their study.34) If the influence was enough in the current system, secondary particle precipitation could restrain the dendrite growth leading to finer dendrite structure.

Dendrite structures were observed with SEM-EDS as shown in Fig. 13. In the low oxygen, high cooling rate sample (Fig. 13(a)), fine dendrite arms can be observed. It can be seen that in the low oxygen content samples, segregated Ti contents are higher than those in the high oxygen samples in the inter-dendritic regions. The segregated regions and dendrite structures became finer with increasing the cooling rate in both the high and low starting oxygen content samples. These regions with higher Ti content would be expected to have an increased potential for oxide precipitation during solidification. Small Ti oxide particles were found in these regions as shown in Fig. 14. The precipitation of particles in the inter-dendritic areas may restrict the flow of the enriched melt as suggested by Ness et al.34) and thereby influence the dendrite growth.

3.3. Secondary Inclusion Size Prediction

A mathematical model of secondary particle generation in Ti-killed steel has been proposed by Goto et al.11–13) based on a micro-segregation model developed by Ohnaka.35) It is assumed that all the rejected oxygen forms oxides which grow during solidification. Growth should be dependent only on the availability of oxygen during solidification. Growth should be dependent on the availability of oxygen during solidification of Ni-base super alloys. The authors calculated the permeability corresponding to the carbide volume density, 0.00235–1.940%. It was shown that the permeability decreased with increasing the carbide density. In this study, Ti oxide volume densities were 0.0021–0.025%, which is at the lower end of their study.34) If the influence was enough in the current system, secondary particle precipitation could restrain the dendrite growth leading to finer dendrite structure.
tent is required, which is considered as a local solidification time in this model. The measured size of secondary particles was compared with that calculated by this model. The concentration of solute oxygen, \( i \) at time \( t \) during solidification from liquidus \( (T_L) \) to solidus temperature \( (T_S) \) can be calculated by the following Eqs. (2)–(4).

\[
[w_{\text{O}}](t) = \left[ w_{\text{O}} \right]_0 \cdot \left[ 1 - \left( 1 - \beta k_o/(1 + \beta) \right) \right] - f_s(t) \frac{k_o}{1 + k_o} \frac{1}{1/k_o + 1} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 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where, \( r \) (cm): radius of oxide, \( \rho_{\text{ox}} \) (g/cm³): density of steel and oxide, \( M_s, M_{\text{ox}} \) (g/mol): molar weight of oxide and steel, \( D_{\text{OM}} \) (cm²/s): diffusion coefficient of oxygen in the mushy region, \( D_{\text{OL}} \) (cm²/s): diffusion coefficient of oxygen in molten steel, \( C_{\text{OL}} \) (mass%): oxygen content in steel, \( C_{\text{OE}} \) (mass%): oxygen content in equilibrium with oxide.

The oxygen mass balance during solidifications is indicated as the Eqs. (9)–(12).

\[
\frac{4\pi}{3} l^3 \cdot \rho_l \cdot \frac{C_{\text{OL}}(0)}{100} = \frac{4\pi}{3} r(t)^3 \cdot \rho_{\text{ox}} \cdot \frac{C_{\text{ox}}(t)}{100} + \frac{4\pi}{3} \left( l^3 - r(t)^3 \right) \cdot \rho_{\text{Fe}} \cdot \frac{C_{\text{Fe}}(t)}{100} \quad \cdots \quad (9)
\]

where, \( l \) is the radius of unit molten steel sphere (in cm), \( r(t) \) is the oxide radius at time \( t \) (in cm), \( C_{\text{OL}}(0) \) is the initial oxygen content in the molten steel (in mass%), \( C_{\text{ox}}(t) \) is the oxygen content in molten steel (in mass%), \( C_{\text{Fe}}(t) \) is the oxygen content in the oxide (in mass%) and \( \rho_{\text{ox}} \) is the density of oxides (g/cm³).

\[
\frac{4\pi}{3} l^3 \cdot N_v = 1 \quad \cdots \quad (10)
\]

\[
N_v = \frac{2}{\pi} N_A \cdot \frac{1}{d^*} \quad \cdots \quad (11)
\]

\[
\frac{1}{d^*} = \frac{1}{n} \sum \frac{1}{d^*} \quad \cdots \quad (12)
\]

In Eqs. (10)–(12), \( N_A \) is the observed number of oxide per unit area (N/cm²) and \( N_v \) is the observed number of oxides per unit volume (N/cm³), \( d^* \) is the observed average oxide diameter of oxide particles (cm) and \( n \) is the observed number of oxides.

Oxide generation and growth are calculated with the following steps.

1) Calculate the segregated content of oxygen during solidification with Eqs. (1)–(3): \( C_{\text{OL}} \)
2) \( C_{\text{OL}} \) and \( C_{\text{OE}} \) are substituted to Eq. (7)
3) Calculate \( r(t) \) through the integration of Eq. (7) during solidification
4) Compute the oxygen balance (Eq. (9))

The predicted evolutions of oxide radii are shown in Fig. 15. The comparison of oxide size between the calculated and observed is shown in Fig. 16. The observed values agreed relatively well with the calculated values. The observed values are bit smaller than those calculated for the inclusion sizes below 1 µm. It should be noted that nucleation kinetics was not considered in the present calculations. This assumption would be expected to restrict the growth time. In the low oxygen content Ti-killed sample (Figs. 15(a)–15(d)), oxide growth starts at \( f_s \) of 0.4 at which the solute content reach the saturation limit with respect to Ti₃O₅ precipitation. The oxide radius remained constant at \( f_s \) of 0.6–0.7 due to no oxygen supply. Growth rate and the final radius of secondary particle decreased with increasing the cooling rate during solidification. With increasing cooling rate, segregated solute content increases and the oxygen diffusion rate from bulk metal to oxide decreases. In these predictions, the effect of cooling rate contributes primarily to influencing the diffusion coefficient rather than the segregation in the low oxygen content Ti-killed steel. In the high oxygen content steels (Figs. 15(e) and 15(f)), oxide growth starts when \( f_s \) is close to zero, due to the high initial oxygen content causing saturation to be reached instantaneously as solidification starts. In this case, the effect of primary oxide generation on the oxygen content before solidification was ignored for simplicity.

Summarizing this study, for Ti-killed steels the oxide

\[
\sum \frac{N_v}{d^*} \quad \cdots \quad (13)
\]

where, \( N_v \) is the observed number of oxide per unit area (N/cm²) and \( N_v \) is the observed number of oxides per unit volume (N/cm³), \( d^* \) is the observed average oxide diameter of oxide particles (cm) and \( n \) is the observed number of oxides.

Fig. 15. Changes of oxide particle radius during solidification.

Fig. 16. Comparison between calculated and observed oxide diameter.

Fig. 17 Conditions of cooling rate and Ti/O for high secondary particle density.
particles below 1 μm are considered to precipitate during solidification resulting in higher dendrite density. The precise mechanism needs to be further investigated. Oxygen content should be controlled below the [Ti]–[O] equilibrium line (Fig. 3) to enhance the population of small Ti-oxides. The cooling rate during solidification should be as high as possible. Suzuki et al. evaluated the oxide growth during solidification in SUS 304 stainless steel, Si–Mn-killed steel. They proposed that the soluble oxygen content before solidification should be decreased to have smaller inclusion avoiding the Ostwald Rippening Growth of oxide particles during solidification.

Figure 17 shows the relation between the cooling rate, [%Ti]/[%O] and the ratio of inclusions below 1 μm to total number of inclusions. To obtain high density of secondary inclusions, [%Ti]/[%O] should be 100–1 000 in the case of continuous slab casting (cooling rates between 5–10 K/s). The ratio ranging 0.1–1.0 is desired for strip casting (cooling rates of 80 K/s).

4. Conclusions

Low carbon (0.07%) high Mn (0.9%) steel was deoxidized by aluminum and titanium in 400 g-scale vacuum furnace. The relationship between the inclusions and microstructure was investigated with a various oxygen contents and cooling rates.

(1) In terms of inclusion morphology MnO–SiO₂–Ti–O (0.5–5 μm) and MnS were typically observed in the high oxygen content (T.O=50–80 ppm) Ti-killed steel samples. Inclusion size and density of high oxygen content Ti-killed steel were higher than those of the low oxygen content (T.O=7 ppm) Ti-killed steel.

(2) Cooling rate during solidification (1.1–84 K/s) had a strong effect on the size and density of particles in Ti-killed steel samples. Particle size decreased and particle density increased with increasing cooling rate. Therefore the inclusions particles observed in the Ti-killed steel samples are considered to be found as a result of secondary deoxidation. A similar effect was not observed in the other samples.

(3) The behavior of secondary particle was estimated by Goto's model. The observed average values agreed well with the calculated one. Oxygen content before solidification should be controlled below the [Ti]–[O] equilibrium line in order to precipitate the small secondary inclusions. The cooling rate during solidification should be as high as possible.

(4) Solidification structure was finer with increasing inclusion density. As a result, solidification microstructure of high oxygen content Ti-killed steel was finer than that of the low oxygen content Ti-killed steel samples.

Acknowledgements

The authors would thank JFE Steel Corporation for the materials and chemical analysis.

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