1. Introduction

Various approaches for microstructure refinement of flat rolled steel products for improvement of mechanical properties have been explored. Thermo-Mechanical Control Process (TMCP) has been one of the common techniques where microstructure is controlled by introducing dislocations and influencing phase transformations. In TMCP, the microstructure of the steel slab is modified by tailoring the rolling pressure and cooling rate in a hot-rolling process. Recently, it was shown that the grain size of ferrite can be refined below 10 μm\(^2\) by appropriately designing this process. Processing methods such as Direct Hot Charge Rolling (DHCR), thin slab casting, strip casting and Cast Steel Products (CSP) such as near-net shape casting are becoming more widely used due to their energetic and economic advantages and these processes do not allow for conventional TMCP to be utilized to its fullest extent. As a result, inclusion control in the steelmaking and casting processes is becoming the pertinent tool for influencing the micro-structural evolution during solidification, subsequent cooling and hot-rolling.

In the past, micro-alloy addition for the precipitation of carbide or nitride was shown to be useful in achieving an equiaxed zone in ferritic stainless steels and electric silicon steels.\(^3\)\(^4\) A technical area named “Oxide metallurgy” was developed with the aim achieving microstructure control through appropriate tailoring of inclusions. This technique was adopted for various applications such as to control the microstructure during processes such as solidification, austenite grain growth and austenite decomposition. Heterogeneous nucleation of ferrite is important for micro-structure control during welding and heavy plate-steel manufacturing. Bainite and martensite formation in the heat affected zone (HAZ) of welding with high heat input (>5 MJ/m) cause embrittlement in steels and thus, refinement of ferrite grain have been an important topic of research for weld metals and heavy steel plates.\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^10\)\(^11\)\(^12\)\(^13\)\(^14\) The aim of these studies have been to promote the precipitation of acicular ferrite for which \(\mathrm{Al}_2\mathrm{O}_3\), \(\mathrm{TiO}_2\), \(\mathrm{TiN}\), VN, TiC, MnS were all found to provide heterogeneous nucleation points in weld metals. It was found that the particle size needs to be

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**Effect of Ti De-oxidation on Solidification and Post-solidification Microstructure in Low Carbon High Manganese Steel**

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This paper investigates the effect of de-oxidation inclusions on micro-structure in low-carbon steels. Low carbon (0.07 wt%), high Mn (0.9 wt%) steel in a \(\mathrm{Al}_2\mathrm{O}_3\) or \(\mathrm{MgO}\) 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. The oxide inclusions were identified as \(\mathrm{Al}_2\mathrm{O}_3\) (1–3 μm) in the Al-killed steel and Ti–\(\mathrm{Al}–(\mathrm{Mg})–\mathrm{O}\) (0.3–0.5 μm) in the Ti-killed steel. Oxide inclusion sizes in all the Ti-killed steels were smaller and inclusion densities higher than those in the Al-killed steel.

Solidification structure, defined as the density of primary dendrite arms within a defined region was finer with increasing inclusion density and as a result, the solidification structure of the Ti-killed steel was finer than that of the Al-killed steel.

A Confocal Scanning Laser Microscope (CSLM) and a Differential Scanning Calorimeter (DSC) were used to study the differences in solid state micro-structural evolution between the Ti-killed, Al-killed and the non-de-oxidized 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 particles in addition to grain boundaries.

KEY WORDS: low-carbon steel; de-oxidation; aluminum; titanium; inclusion; solidification microstructure; confocal-laser-scanning-microscopy; phase transformation; grain growth.
the smaller than 0.5 μm and the inclusion density higher than 10^3/mm^3 for achieving a successful grain refinement. As for the nucleation mechanism, it was suggested that the region of depletion of C (around carbide) and/or MnS (around the MnS) contributed primarily to the change in ferrite formation. The role of the oxides was not clarified but they were thought to provide locations for nucleation of other precipitates such as MnS. The resulting refined microstructure contributed to improved toughness and slower cleavage crack propagation compared with a bainitic structure. Similarly, in heavy plate steel (low carbon steel, C/0.05–0.15%, Mn/1.4–1.6%), REM(Ce), REM–B, REM–Ti(Nb), the following inclusions were utilized for the same purpose of controlling ferrite precipitation morphology, Al–Ti oxide, Ti–B, TiN, VN, AlO_x, MnS, V(C,N), TiO/MnS, BN, Fe_2(C,B)_6, REM(O,S), Ti_2O_5/MnS, Ti(O,N), Ti(O,S), Ti–Ca(O,S). It was found that the required particle size and inclusion density had to be 0.5–10 μm and >10^2–10^3/mm^3 respectively in order to adequately control the micro-structure. While it was reported that nonmetallic inclusions have a strong effect on the nucleation of ferrite, the mechanism behind this phenomenon was not established.

Particle pinning of austenite grain boundaries during grain growth is another important issue for refinement of microstructure of products and secondary particles such as oxides, carbides, nitrides and sulfides have been utilized for this purpose. Particle size and density are known to be significant parameters in Zener’s equation. Suito et al. evaluated the effect of Mg, Zr, Ce on the austenite grain growth in Fe–10mass%Ni steel, and showed that the particle size was required to be below 100 μm in order effectively pin the grains. The relative importance of the particle chemistry and morphology (crystal structure, size, shape, dispersion), physicochemical properties (i.e. interfacial energy and lattice miss-match with the matrix) and thermal expansion on the grain size have not been quantitatively established. As for the nucleation mechanism, it was suggested that secondary de-oxidation particles act not only as sites for nitride, sulfide and secondary precipitates such as MnS. The resulting refined solidification structure is characterized with predominantly primary de-oxidation inclusions which are expected to be larger. It is also proposed that the secondary de-oxidation particle morphology (in terms of size, chemistry, shape) and population (distribution and density) can be tailored by controlling the conditions in the solute rich interdendritic liquid during solidification through the choices of de-oxidation and alloy-additions in the ladle, oxygen concentration before and after de-oxidation and the cooling rate during solidification. The objective of this paper is to establish whether or not there is a notable difference in solidification micro-structure, austenite grain growth and austenite decomposition as a result of Ti de-oxidation compared to Al de-oxidation. Al is widely used as a de-oxidation agent in steelmaking process. Ti on the other hand is used primarily as an alloying element for binding the solutes C and N, but inevitable some amount of Ti-oxides are formed. Ti-precipitation products (oxides and nitrides etc.) are known to result in sites for heterogeneous nucleation. It is thus the aim of the current work to investigate how an intentional and controlled Ti-oxide precipitation can be used to control the subsequent micro-structure. The other pertinent conditions such as N and C levels, and solidification conditions are maintained same. Specific objectives are:

1. Cast under similar conditions low carbon steel samples de-oxidized with Al and Ti respectively.
2. Characterize the inclusion morphology and population.
3. Establish whether there is a notable difference in solidification structure.
4. Establish whether there are notable differences in the solid state micro-structural evolution subsequent to casting as a result of the inclusions.

2. Materials and Methods

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

The decomposition of austenite to ferrite and pearlite and austenite grain growth are investigated through in-situ observation with a Confocal Scanning Laser Microscope (CSLM). Differential Scanning Calorimetry (DSC) is used to measure austenite decomposition temperatures.

2.1. De-oxidation and Casting

De-oxidation tests were carried out inside a vacuum furnace which is shown in Fig. 1. The furnace chamber was evacuated and refilled with grade 5.6 Ar (99.9996%) before heating. The ingot sample was placed inside either a Al_2O_3 (ϕ 50–40×H=120 mm, TEP Ceramics, Al_2O_3/99 %) or a MgO (ϕ 50–40×H=120 mm, TEP Ceramics,

![Fig. 1. Experimental apparatus of vacuum furnace for de-oxidation tests.](image-url)
MgO/99%) crucible and heated to 1873 K and subsequently, de-oxidized by adding either aluminum (99.99%) or titanium (99.99%) addition. The oxygen contents before and after de-oxidation were measured through immersion of a custom-made oxygen sensor (Mo/Cr2O3//ZrO2 (CaO)/Fe–O/Fe supplied by Heraeus Electro-Nite). Finally, the molten de-oxidized steel was poured into a water-cooled copper mold (Inner size: 60×40×40 mm).

2.2. Material
A mother ingot (50 kg) was produced in a vacuum furnace with electrolytic iron (Wako Chemicals Fe/99.97%), graphite (Tokai carbon C/99.5%) and metallic Manganese (Wako Chemicals Mn/98%). The resulting chemical compositions of the mother ingot was C/0.10, Si/0.01, Mn/0.94, P/0.023, S/0.000, O/0.0273 wt%. This ingot was sectioned and machined into small pieces (400 g, φ 40×H = 30 mm) for the use in de-oxidation tests. Experimental conditions, target compositions of Al and Ti and dissolved oxygen activity (as measured by an oxygen sensor before each de-oxidation process are shown in Table 1.

2.3. Confocal Scanning Laser Microscope (CSLM)
The *in-situ* observations of phase transformation and migration of grains were carried out with confocal scanning laser microscope (CSLM). Details on the CSLM and its capabilities can be found in the pioneering work by Emi and co-workers.27–30 The CSLM used in this study is attached to a high temperature stage that consists of a gold-plated, ellipsoid-shaped furnace.27) Radiation from a halogen lamp is concentrated on the sample, which is located at the upper focus of the ellipsoid. Because the laser radiation used to form the image is much more intense than thermal radiation from the sample, a clear image of the surface can be obtained. The temperature is measured by a thermocouple placed near the surface of the sample. This thermocouple reading is also used to control the intensity of the heating lamp, and the temperature profile during an experiment can be programmed as desired. After polishing the surface, the steel sample to be investigated was placed in a Al2O3 crucible (Ozark ceramics 99.5%, φ 5–4 mm×5 mm) which was placed inside the sample holder. A vacuum pump and gas delivery system are used in tandem to evacuate the furnace of undesired gases before an experiment and provide a constant atmosphere of desired composition during an experiment.

The furnace chamber was repeatedly evacuated and refilled with grade 5.6 Ar, which was subsequently allowed to flow for 1 h. The oxygen potential was measured in the inlet and outlet gas streams by a ceramic oxygen sensor in order to ensure that appreciable oxygen leaks were not present. Generally a constant PO2 of less than 5×10–9 atm was maintained. The sample was then subjected to a programmed thermal profile while an image of the surface was continuously recorded in video recorder at a rate of 30 frames per second. The thermal profiles used for each sample are shown in Fig. 2(a) along with the thermodynamically calculated temperatures for the various phase transformations (this was carried out by using Thermo-Calc©*1).

A temperature calibration (for sample holder) was carried out by comparing the thermocouple response temperature to the observed melting points of pure silver (Alfa Aesar, casting grain, 99.99%) and pure copper (Alfa Aesar, turnings, 99.9%) and the observed ferrite to austenite transformation in pure iron (PURETRONIC, rod, 99.995%). Based on this procedure, a linear fit between the measured temperature, Tm and the expected temperature, Tm, for three calibration points yielded a relation: Tm = 0.989×Te with R2 = 0.974.

2.4. Differential Scanning Calorimetry (DSC)
Differential Scanning Calorimetry (Netzsch STA 449C Jupiter©*31,32) was carried out to find the phase transformations temperature. Al2O3 powder was used as a reference. Ar gas atmosphere was controlled to low oxygen partial pressure (P02 < 10–14 atm) with an oxygen getter furnaces.33) The thermal profile employed in the DSC experiments is shown in Fig. 2(b).

2.5. Characterization
The chemical composition of the cast samples were measured through infrared absorbometric method after combustion in the current oxygen for the element of carbon and sulfur, inert gas carrier melting thermo-conductometric method for total N, inert gas carrier melting infrared absorbometric method for total O and ICP-OES (Inductively coupled plasma optical emission spectrometric method) for all other elements. In the case of sol. Ti and sol. Al, these were analyzed using the residual dross after the analysis of total Ti and total Al. The dross was melted by pyro-potassium sulfate, and then, filtrated with hydrochloric acid as a specimen for ICP-OES.

Inclusions and solidification microstructure of the de-oxidized samples were evaluated. Two sections were selected in each cast sample. One section is close to the water-cooled copper mold (bottom), the other section is far from the mold (top). Each part was sectioned into ~2 mm thick slices, and cut into ~4×4 mm squares. The samples were polished, using a Struers TegraSystem™ automatic polisher, by a sequence consisting of: 320 SiC paper disc; 9μm 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

*1 Thermo-Calc© is a trademark of Thermo-Calc Software, Stockholm, Sweden.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deoxidation agent</th>
<th>[%Al] aim</th>
<th>[%Ti] aim</th>
<th>Crucible</th>
<th>α/ppm before deoxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al</td>
<td>0.050</td>
<td>-</td>
<td>Al2O3</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>Ti</td>
<td>-</td>
<td>0.050</td>
<td>Al2O3</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>Ti</td>
<td>-</td>
<td>0.015</td>
<td>MgO</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>Ti</td>
<td>-</td>
<td>0.030</td>
<td>MgO</td>
<td>21</td>
</tr>
<tr>
<td>5</td>
<td>No addition</td>
<td>-</td>
<td>-</td>
<td>MgO</td>
<td>31</td>
</tr>
</tbody>
</table>

Table 1. Experimental conditions of de-oxidation test (wt%).
polishing cloth, and 1/4 μm diamond suspension on a synthetic short-nap velvet polishing cloth. Polished samples were thoroughly cleaned between polishing steps using a precision, non-abrasive, residue-free detergent solution.

The samples were etched with 2% Nital solution and picric acid saturated aqueous solution to reveal the initial microstructures. Etched sample microstructure were observed with a optical microscope (Nikon Eclipse ME600). Inclusions in each sample were observed with a Phillips XL-30FEG Scanning Electron Microscope at three specific areas, each of a size of 0.25 mm².

3. Results and Discussions

3.1. Cast Microstructure and Chemistries

Chemical compositions of the samples obtained after the de-oxidation tests are listed in Table 2. 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. Thus, the thermodynamic soluble oxygen in the case of sample 1 was estimated by assuming $a_{\text{Al}_2\text{O}_3}=1\), and in the case of samples 2–4 that $a_{\text{Ti}_3\text{O}_5}=1\). Activity coefficients were calculated with the interaction coefficients of Al–O, Al–Al, O–Al, O–O and O–Mn\(^{36}\) for Al-killed steel, and Ti–O, Ti–Ti, Ti–Mn, O–Ti, O–O \(^{35}\) for Ti-killed steel. Similarly nitrogen was in the case of sample 1 computed by assuming $a_{\text{AlN}}=1\), and in the case of samples 2–4, $a_{\text{TiN}}=1\). Activity coefficients were calculated with the interaction coefficients of Al–N, Al–Al, N–N and N–Al\(^{36}\) for Al-killed steel, and Ti–N, Ti–Ti, N–N and N–Ti\(^{36}\) for Ti-killed steel. The free energy of formation for the oxides and nitrides were obtained from literature. Yoshikawa et al. reported the thermodynamics of TiO\(_{1.5}\) which is stable in lower titanium content ([mass% Ti] < 0.2). In the case of TiN two values are reported in Refs. 36) and 37) respectively. From these, the results reported by Matsuda and Okamura\(^{37}\) are selected since chemical compositions is nearly same in terms of carbon and manganese ([C]=0.05–0.06 wt%, [Mn]=1.6–1.8 wt%) as that of the samples used in this work. Calculated soluble oxygen contents based on a unit activity of Ti oxide are higher than the analyzed ones. In Ti-killed steel, complex oxide, such as Ti–Al–(Mg)–O was mainly observed with SEM-EDX analysis. Therefore the actual activity of Ti oxide would be expected to be lower than unity.

Representative examples of inclusions are shown in Fig. 3. In the Al killed steel (sample 1), Al\(_2\text{O}_3\) (1–3 μm) was found predominantly in form of clusters. In the non de-oxidized sample (sample 5), Al–Mg–O inclusions of sizes between 0.5–1 μm were found. The sources of Al and Mg in these inclusions are not clear but most likely they result from unintentional interactions with the crucible material. In the Ti de-oxidized samples (samples 2–4) Ti–Al–(Mg)–O (0.3–0.5 μm) inclusions and TiN (0.5–1 μm) were found. The latter could be found by themselves (Fig. 3(b)) but were most often found with an oxide in their core (Fig. 3(c)). Inclusion size distributions in each sample are listed in Table 3.

In the Ti-killed steel, the total nitrogen contents were compared with calculated solubilities assuming the equilibration with TiN at 1 600°C\(^{36,37}\) and 1 300°C,\(^{37}\) and the results are shown in Fig. 4. Observed total nitrogen content
agreed with calculated equilibrium value at 1 600°C. It is estimated that the remaining nitrogen precipitates as TiN, as the temperature decreases.

Solidification microstructures of samples 1, 2, 4 and 5 (from the bottom of the mold) are shown in Fig. 4 and it can be seen that a dendritic structure is present. Macroscopic microstructures of the top part in the sample were observed to be the same as the bottom part. The microstructure of Ti-killed samples is finer than the Al-killed or the un-deoxidized sample. The dendrite densities were obtained by counting the number of primary dendrite arms in the whole surface of the samples.

Cooling rate was estimated by measuring the dendritic secondary arm spacing of each sample etched by picric acid saturated aqueous solution and Eq. (1)\[\lambda_2=688\cdot R_c^{-0.36}\]

where, \(\lambda_2\) is secondary dendritic arm spacing (micron), \(R_c\) is cooling rate (K/min).

Inclusion densities were obtained by counting the number of inclusions within a specific area (0.5 x 0.5 mm) observed in a SEM. Particles below 10–30 nm could not be accurately resolved. Inclusion size was defined as the average radius of inclusions in the area. These values are shown in Table 4 and it can be seen that inclusion sizes of Ti-killed samples were smaller and inclusion densities higher than in the Al-killed and no-addition samples. The relation between the cooling rate and the oxide inclusion density is shown in Fig. 6. The effect of the cooling rate on the inclusion density is only apparent in the Ti-killed steel and therefore inclusions observed in Ti-killed steel are speculated to be partly the result of secondary de-oxidation resulting from precipitation during solidification.

Yamamoto\[39\] investigated the nucleation mechanism of intergranular ferrite in Ti-killed steel. The de-oxidation product Ti2O3 was found to be a nucleation site for MnS and TiN or BN. A Mn depleted zone around MnS, was thought to assist the ferrite precipitation. TiN on the other hand, provides the nucleation site of ferrite because it has a lattice match with ferrite. In this work, the complex oxide (Ti–Al–Mg–O) particle is considered to be the nucleation site of TiN, and ferrite formation could be enhanced by their process.

The relation between the inclusion density and dendrite density is shown in Fig. 7. Points with a star-point mark indicate samples taken for the bottom part of the sample. From Fig. 7, it can be seen that dendrite density increases with increasing inclusion density. Mg contamination in inclusions was observed with using the MgO crucible, but that has no apparent effect on the solidification microstructure.

The relation between the inclusion density and dendrite density is shown in Fig. 7. Points with a star-point mark indicate samples taken for the bottom part of the sample. From Fig. 7, it can be seen that dendrite density increases with increasing inclusion density. Mg contamination in inclusions was observed with using the MgO crucible, but that has no apparent effect on the solidification microstructure.

It is noteworthy that in all the trends in Fig. 7 of the micro-structural feature variation with inclusion density overlap for Al and Ti killed samples, indicating a linear dependence. It is interesting to consider whether the refined solidification structure is a result of increased inclusion density or whether the increased inclusion density is caused by increased rate of solidification. When comparing the current results from Al and Ti killed samples, solidified
under the same cooling rates, the Ti killed samples have finer solidification structure. In Fig. 7, Al and Ti-killed samples obtained from the bottom part of the ingot, were solidified under the same cooling rate, but the dendrite densities in Ti-killed samples were higher than that of Al-killed sample. If the small amounts of dissolved Ti and Al are assumed not to influence the solidification conditions appreciable, then the observed effect appears to be that secondary inclusion precipitation does indeed influences solidification. The precise nature of the effect is at this stage difficult to establish quantitatively since secondary inclusion precipitation is caused by segregation due to solidification but at the same time the particles affect solidification. From Fig. 7, it can be summarized that there is a beneficial effect from achieving a high inclusion density in that it appears to result in a finer solidification structure. The final grain structure could depend partly on the solidification structure.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Killing condition</th>
<th>Crucible</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al-killed</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>2</td>
<td>Ti-killed</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>3</td>
<td>Ti-killed</td>
<td>MgO</td>
</tr>
<tr>
<td>4</td>
<td>Ti-killed</td>
<td>MgO</td>
</tr>
<tr>
<td>5</td>
<td>No addition</td>
<td>MgO</td>
</tr>
</tbody>
</table>

Table 4. Summarized results of microstructure and inclusions in de-oxidation tests.

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Fig. 6. Relation between cooling rate and oxide inclusion density.

Fig. 7. Relation between dendrite density and inclusion density.
but also, on independent effects of the inclusions on the processes in the solid state. To investigate this further, the effects of de-oxidation treatment on the following micro-structural evolutions were investigated for samples 1, 2 and 5: (i) delta-ferrite to austenite, (ii) austenite grain growth and (iii) austenite decomposition. The approach was to start with a controlled micro-structure and observe the differences in evolution.

3.2. Precipitation Temperatures during Phase Transformations

Phase transformations were observed during a thermal cycle denoted as B in Fig. 2(a) in the CSLM. The precipitation temperatures obtained by CSLM and DSC are shown in Table 5. In CSLM, the approximate starting temperatures of phase transformation were determined by identifying in the digitalized screen images at which precipitation was observable, and in the DSC, these were decided by analyzing the obtained thermal response with a software. Temperatures obtained by CSLM are in accordance with the temperatures obtained by DSC within ±20 degrees. Neither method suggested any appreciable difference in the transformation temperature between the samples.

3.3. Austenite Grain Growth

The austenite grain sizes at the end of isothermal treatments (Fig 2(a), thermal cycle denoted as A) are shown in Fig. 8 for samples 1, 2. 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. 8. The austenite grain sizes of Al-killed were larger than the size was observed in the Ti-killed steel. In the Ti-killed steel, particles were observed at the boundaries of smaller austenite grains. Fig. 9 shows the comparisons of austenite grain size of each sample at the end of the isothermal anneal and it can be seen that the austenite grain size in the Al-killed steel is 3–5 times as large as that in the Ti-killed steel. The finer grained structure observed in the Ti-killed samples are attributed to either of the following (i) the complex precipitate TiN–(Ti–Al–Mg–O) and TiN having a combined 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\(^6\) and this was used to investigate the plausible effect of grain-boundary pinning. The relation is based on Zener’s model (Eq. (2))\(^25\) where grain size is proportional to the radius of the pinning particle (r) and is inversely proportional to the particle volume fraction (f). The constant \(\beta\) depends on the geometry and force balance.

\[
R = \beta \left( \frac{r}{f} \right)^{\frac{1}{2}}
\]  

\(R\) is the grain size and \(f\) is the volume fraction of the inclusions. The factor \(\beta\) is a constant that depends on the geometry and force balance. A relation utilizing inclusion size and the spatial distribution between inclusions to predict grain size was proposed by Mizoguchi\(^6\) and this was used to investigate the plausible effect of grain-boundary pinning. The relation is based on Zener’s model (Eq. (2))\(^25\) where grain size is proportional to the radius of the pinning particle (r) and is inversely proportional to the particle volume fraction (f). The constant \(\beta\) depends on the geometry and force balance.

\[
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\]  

\(R\) is the grain size and \(f\) is the volume fraction of the inclusions. The factor \(\beta\) is a constant that depends on the geometry and force balance.
for his analysis. Here, the oxide particle has a stoichiometry, \(M_mO_n\), and therefore the radius of grain (\(R\)) is expressed by Eqs. (3a) and (3b), where \(f_o\) is volume fraction of oxide, \(d\) is diameter of particles (\(\text{cm}\)), \(O\) is oxygen atomic weight (16 g), \(M\) is cation atomic weight (g), \(\rho_o\) is oxide particle density (g/cm\(^3\)), \(\rho_s\) is steel density (g/cm\(^3\)) and \(T[O]\) is total oxygen content (ppm by weight fraction).

\[
R = (2/9)d f_o \quad \text{...............(3a)}
\]

\[
f_o = \left[ \frac{(nO + mM)(nO)}{(\rho_o / \rho_s)} \right] [T[O]]^{\frac{1}{(nO)}} \quad \text{............(3b)}
\]

In this study, nitride particle are observed, in addition to oxides in the Ti-killed samples. It is assumed in the above model that the ability to pin grain boundaries is independent of particle geometry, chemistry and crystallography, i.e. only size and spacing matters. Using this analysis, and the values for total oxygen from Table 3, the predicted grain size was evaluated for the cases of Al\(_2\)O\(_3\) in sample 1. It can be seen in Fig. 10, that the model significantly over-predicts the grain size when comparing to the experimental point representing the final grain size corresponding to the average inclusion size at the end of the isothermal anneal at 1300°C. In the case of sample 2 (Ti-killed) the precise inclusion stoichiometry is not known, and therefore predictions are made for Ti\(_3\)O\(_5\), Ti\(_2\)O\(_3\), TiO\(_2\), and TiN. For TiN, a similar expression as (3a) and (3b) is used but with total nitrogen in place of total oxygen and for the stoichiometry of TiN. Thermodynamically, Ti\(_3\)O\(_5\) would be expected to be stable oxide at the titanium content of this sample ([Ti]=0.087%).\(^{35}\) If both TiN and TiO\(_2\) are considered, this brings the relation closest to the experimental point for sample 2. In Fig. 10, the experimental point for sample 5 (no-addition) is also plotted. A few trends can be identified in this figure. (i) Firstly, if one ignores the particle chemistry, which in the current model essentially only influences that absolute particle density, then the linear grain size dependence upon particle size, i.e. 2/9 in Eq. (3a), is roughly followed for the three samples examined. (ii) Secondly, the predicted grain sizes are consistently lower than the measured one which is due to an error in the prediction of \(f_o\) in Eq. (3b). In the case of sample 2, this could be caused by the uncertainty in oxide chemistry (and thus stoichiometry) or the inability to detect smaller inclusions in the SEM. In the case of sample 1, were the inclusions are predominantly Al\(_2\)O\(_3\), the discrepancy is likely caused by that smaller inclusions were not detected in the SEM analysis. If this was true it would mean that the first trend, i.e. that the apparent 2/9 dependence among the three samples, would be a coincidence. Kanazawa et al.\(^{41}\) reported that TiN precipitates below 0.1 \(\mu\text{m}\) have a pinning effect on austenite grains, but such small inclusions were not observed in any appreciably
3.4. Austenite Decomposition

In-situ observations of Al-killed (sample 1) and Ti-killed (sample 2) during cooling from the austenite region at a rate of 5°C/s are shown in Figs. 11(a) and 11(b). Austenite decomposition, $\gamma \rightarrow \alpha$ (+ pearlite), was observed at 693°C (Al-killed), 733°C (Ti-killed) and 695°C (no addition). Figure 12 shows the comparison of the final decomposition structure. In no-addition and Al-killed samples, the decomposition proceeded by coarse Widmanstätten plate forming independently of the particles. On the other hand, in the Ti-killed steel, Widmanstätten ferrite precipitated at particles as well as at grain boundaries. The increased number of precipitated laths, result in a finer decomposed structure for the Ti-killed sample (Fig. 12(b)) compared to the Al-killed one (Fig. 12(d)). Figure 13 shows the similarity in microstructure between a typical etched surface and cross-section of the same sample, to illustrate that the observed structures are not results of surface phenomena.

By comparing the effect of isothermal anneal temperature (Figs. 8, 9), it is expected that the decomposition structure would be influenced by the starting austenite grain size. This is confirmed by observing that the decomposition structure in Fig. 12(a) is finer than that in Fig. 12(b). Widmanstätten ferrite precipitation was classified as precipitates at grain boundary and particles by counting the number of these in each sample. Widmanstätten ferrite precipitations at particles are shown in Fig. 12(c), which are surrounded by the circles. The number of Widmanstätten ferrite was counted in the specific area (2.5 mm×2.5 mm). The ratio of Widmanstätten ferrite precipitation at particles, $R_p$, was calculated as Eq. (4) with the number of Widmanstätten ferrite at particles, $N_p$, and at grain boundaries, $N_g$.

$$R_p(\%) = \frac{N_p}{N_g + N_p} \times 100$$

The area fraction covered by Widmanstätten ferrite, $R_A$, was calculated by measuring the percent ferrite area in a specific area. Figure 14 shows the relation between austenite grain size at the end of isothermal treatment and $R_p$ and $R_A$ respectively. $R_p$ of Ti-killed steel are much higher and have strong dependence on the austenite grain size than that of no addition and Al-killed steels. In general the ferrite formed at particles appeared finer than those that originated at grain boundaries. As a result, $R_A$ of Ti-killed steel are much lower than that of no addition and Al-killed steels. The changes of $N_p$ and $N_g$ as function of temperature during cooling are shown in Fig. 15. $R_A$ of Ti-killed steel is lower than Al-killed steel, but the sizes of ferrite form are smaller and the number of ferrite is much higher than Al-killed steel. In Ti-killed steel, $N_p$ and $N_g$ increased nearly at the same temperature, in Al-killed steel, only $N_g$ increased. From Fig. 14, it is evident that the starting austenite size influences the decomposed micro-structure. In Fig. 9, the grain sizes at the end of isothermal treatment of Al-killed steel (1200°C) and Ti-killed steel (1300°C) are nearly same. If $R_p$ and $R_A$ of the decomposed structures from these samples are compared it is found that $R_p$ of Al-killed steel is 1/13 of the Ti-killed steel, while the $R_A$ of Al-killed is nine times larger than that of the Ti-killed steel. Therefore, the effectiveness of Ti de-oxidation in controlling the
micro-structure lies not only in controlling the austenite grain growth, but also in providing precipitation sites other than austenite grain-boundaries for ferrite formation.

The temperatures of austenite decomposition obtained by CSLM were compared with the result of DSC analysis, and the results are shown in Table 5. In both cases, that temperature was defined as starting temperature of austenite decomposition. Austenite decomposition is affected by austenite grain size and inclusions which are not homogeneously completely. Therefore, observed temperature with CSLM was compared with the result of DSC analysis, and the results are shown in Table 5. In both cases, that temperature was defined as starting temperature of austenite decomposition. Therefore, observed temperature with CSLM was compared with the result of DSC analysis, and the results are shown in Table 5.

4. Conclusions

Low carbon (0.07%) high Mn (0.9%) steel was deoxidized by aluminum and titanium in 400 g-scale vacuum furnace, and the relation between the inclusions and microstructure was investigated.

(1) In terms of inclusion morphology Al₂O₃ and Al–Mg–O (1–3 μm) were observed in Al-killed steel and Ti–Al–Mg–O (0.3–0.5 μm) and TiN (0.5–1 μm) precipitated around that oxide were typically observed in Ti-killed steel. Inclusion size of Ti-killed steel was smaller and inclusion density was higher than that of Al-killed steel.

(2) Solidification structure was finer with increasing the inclusion (particle) density. As a result, solidification microstructure of Ti-killed steel was finer than that of the Al-killed steel. In Ti-killed steel, inclusion density increased and inclusion size decreased with increasing the cooling rate, whereas in Al-killed steel, cooling rate did not have a similar effect. From these results, a fraction of the inclusions particles observed in the Ti-killed steel are considered to be the result of secondary de-oxidation.

(3) Austenite grain growth was investigated through CSLM observations in the temperature range 1200–1300°C. The grain size after isothermal treatment of Al-killed steel was much higher than in the Al-killed steel, and cooling rate did not have a similar effect. From these results, a fraction of the inclusions particles observed in the Ti-killed steel are considered to be the result of secondary de-oxidation.

(4) Relation between inclusion density and grain size was compared with the previous model based on the pinning effect of particles on the grain growth process. Observed grain sizes were smaller than the calculated ones.

(5) Austenite decomposition was observed with CSLM. In Al-killed steel, coarse Widmanstätten ferrite precipitated at grain boundaries and in Ti-killed steel, TiN precipitated in advance, and fine Widmanstätten ferrite precipitated at both grain boundaries and particles. The ratio of Widmanstätten ferrite precipitation at particles in the Ti-killed steel was much higher than in the Al-killed steel, and increased with the austenite grain size.

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