Interface Migration Behavior of the \( \delta \rightarrow \gamma \) Interface in Low Carbon High Manganese Steel Samples De-oxidized with Ti or Al

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The effect of inclusions, generated during de-oxidation and solidification, of low carbon (0.07 wt%) and high manganese (0.9 wt%) steels, on the rates of migrations of the boundaries between delta-ferrite/gamma-austenite interfaces, during austenite formation was investigated. The presence of two types of de-oxidation products were investigated, namely \( \text{Al}_2\text{O}_3 \) (1–3 \( \mu \)m) in Al-killed steel samples, and Ti-Al-(Mg)–O (0.3–1 \( \mu \)m) in Ti-killed steel samples. The samples were prepared in a vacuum-induction furnace and a Confocal Scanning Laser Microscope was used to image in real time the interface movement on the surface of the samples. 

Austenite was found to precipitate at the triple-points of the delta-ferrite grain boundaries during cooling from 1 500 to 1 460 and 1 450°C and the growth appeared to be diffusion controlled. The migration rates of delta/gamma interfacial boundaries were higher in the Al-killed steel samples than in the Ti-killed steel samples and this is attributed to the finer oxide particle population in the latter. When the samples were cooled to 1 440°C and below sword-like precipitation was observed in all samples that grew at a higher rate than what was observed at higher temperatures and the growth appeared to have linear time dependence, and thus the process appears to not be governed by long range diffusion. 

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

1. Introduction

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 Thermo Mechanical Controlling Process, TMCP, to be utilized to its fullest extent. As a result, inclusion control in the steelmaking and casting processes is becoming a pertinent tool for influencing the micro-structural evolution during solidification and in solid state micro-structure evolution. Many investigations concerning the inclusion precipitation control on the resulting effect on austenite grain growth and heterogeneous nucleation during the \( \gamma/\alpha \) transformation have been investigated.1–11)

It is however also important to control the initial microstructure evolution (during delta to gamma transformation and grain growth) in the steelmaking process to fully understand the effects of particles on the final micro-structure. While austenite decomposition has been extensively studied, to date, only a few investigations have been reported in these higher temperature transformations. The austenite precipitation behaviors on delta-ferrite has been studied by a few investigators12–14) and it has been shown that austenite precipitates at the triple-points of delta-ferrite grain boundaries, and subsequently spread along the boundaries15) or sub-boundaries.16) 

As for the effect of particles, on the micro-structural evolution during these transformations, Suito et al.15) reported that the ratio between the number of precipitated austenite grains and the number of original primary delta-ferrite grains, and subsequently spread along the boundaries12–14) or sub-boundaries.15)

In a recent publication,17) the difference between Al and Ti-killed steel was investigated in the view of inclusion, solidification microstructure, phase transformation and grain growth. It was shown that the solidification micro-structure and post solidification solid state evolution of the micro-
structure were positively influenced by replacing Al with Ti as the de-oxidant. The objective of this paper is to evaluate the effect of de-oxidation particles on the migration rates of delta-ferrite grain boundaries and the interface between delta-ferrite and austenite, in order to establish whether there is an effect of particles on microstructure on this process. The practical relevance is twofold. Firstly, the austenite structure influences the subsequent eutectoid-austenite decomposition structure and secondly, the transformation is important to control due to surface quality problems caused by the thermal mismatch between the delta-ferrite and austenite during continuous casting.

The approach is to utilize samples that have been de-oxidized by adding either Al or Ti in a vacuum induction furnace and carry out in-situ observation with a Confocal Scanning Laser Microscope (CSLM) in order to image the micro-structural evolution on the surface while the samples are maintained or cooled in the temperature region between 1440°C and 1460°C.

2. Materials and Methods

Melting of carbon steel (C/0.07%, Mn/0.9%) and de-oxidation was carried out in a vacuum-induction furnace, and the melt is subsequently cast in a water-cooled copper mold. The resulting inclusion morphologies, inclusion size, dispersion and chemistry were analyzed with SEM-EDS.

2.1. Material

A mother ingot (50 kg) was produced in a vacuum furnace using 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, Si/0.01, Mn/0.94, P/0.024, S/0.001 and T.O/0.0273 wt%. The ingot was sectioned and machined into small pieces (400 g, φ40×H=30 mm) for the use in de-oxidation tests. The Target compositions of Ti and Al were 0.05–0.10 wt%.

2.2. De-oxidation and Casting

De-oxidation tests were carried out inside a vacuum furnace.17) 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 1600°C 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/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). A sample was also prepared were no de-oxidation was carried out as a reference.

2.3. Confocal Scanning Laser Microscope (CSLM)

The experiments for measuring the migration rate of delta-ferrite grain boundaries and the interface boundaries between delta-ferrite and austenite were carried out through surface visualization through 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,18–20 and the CSLM used in this study has been described in a previous paper.17) After polishing the surface, the steel sample to be investigated was placed in a Al2O3 crucible (Ozark ceramics 99.5%, φ5–4 mm×5 mm) which was inserted into the Pt-sample holder. A vacuum pump and gas delivery system were 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 $P_{O_2}$ of less than $5 \times 10^{-12}$ atm was maintained by following the Ar-gas through oxygen-getter furnaces that contained dry-erite, and heated Cu and Mg chips. During the experiment the purified Ar gas was allowed to flow through the heating chamber at a rate of 0.8 NL/min. The sample was 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. A temperature calibration was carried out, for the sample holder, by comparing the thermocouple response temperature to the observed melting points of pure nickel (Alfa Aesar, casting grain, 99.9%) and pure cobalt (Alfa Aesar, casting grain, 99.9%) and the observed ferrite to austenite transformation in pure iron (PURETRONIC, rod, 99.995%). Figure 1 shows the relation between the calculated temperatures and observed ones. Based on this procedure, a linear fit between the measured temperature, $T_{in}$ and the expected temperature, $T_e$, for three calibration points yielded a relation: $T_{in}=0.93 \times T_e+102$ with $R^2=0.982$.

The thermal profiles used for each sample are shown in Fig. 2 along with the thermodynamically calculated temperatures for the various phase transformations (these were estimated using Thermo-Calc®). The temperature was increased to 1500°C and maintained for 5 min. During this time-period the delta-ferrite grain growth appeared to have slowed down to an extent that the grain-structure seemed stable. Temperature was then lowered at a rate of 5°C/s, to one of the experimental temperatures, 1460, 1450 and...
1440°C. This study is based upon resolving continuously evolving surface relief structures and relates these to migrating interfaces during a phase transformation. In a Fe–C system such as the current one, decarburization is an unwanted process since changing the sample carbon content would influence both the thermodynamics and kinetics of the transformation. During the current experiments, decarburization would be expected to be most severe during the 5 min anneals at 1500°C depicted in Fig. 2. Under the current conditions, were purified Ar was used, the decarburization is expected to be controlled by the supply of oxygen impurity gas through gas-phase mass transport which after dissociating on the surface forms CO. In order to estimate the extent of decarburization, calculations were made in the following way. The oxygen gas flux to the surface was computed from the gas flow rate, oxygen partial pressure, by using the Ranz–Marshall equation for a plate. This was then used as a boundary condition for C flux out of the surface which, together with a semi-infinite condition in the bulk of the sample was used to solve Fick’s 2nd law to obtain the C-profile. It was found, that during 5 min, the amount of the carbon loss was negligible and thus decarburization is not expected to influence the results in the present study.

### 2.4. Characterization

The chemical composition of the cast samples were measured through infrared absorptiometric method after combustion in the current oxygen for the element of carbon and sulfur, inert gas carrier melting thermo-conductimetric method for total N, inert gas carrier melting infrared absorptiometric 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 pyo-potassium sulfate, and then, filtrated with hydrochloric acid as a specimen for ICP-OES.

Inclusions of the de-oxidized samples were evaluated. Sample was sectioned into ~2 mm thick slices, and cut into ~4×4 mm squares for observation of inclusion with SEM-EDX, and ~3 mm thick slices, and cut into ~2.5×2.5 mm squares for CSLM. 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, 1/4 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.

![Fig. 2. Thermal profile used in the CSLM.](image)

![Fe/27 O/37 Al/31 Mn/3.0 (wt%)](image)

(a) Al oxide (sample 1)

![N/14.7 Ti/34.9 Fe/50.4 (wt%)](image)

(b) TiN (sample 2)

![N/8.3 O/28 Mg/1.9 Ti/40 Mn/1.5 Fe/15 Al/4.7 (wt%)](image)

(c) Inner : Ti-Al oxide Outer : TiN (sample 2)

![O/8.8 Mg/3.4 Al/6.1 Mn/1.0 Mg/3.3 Fe/77 (wt%)](image)

(d) Al-Mg oxide (sample 3)

![Table 1. Compositions of steel samples (wt%).](image)
3. Results and Discussions

3.1. Influence of Sample Chemistry on Non-metallic Inclusion Population

Chemical compositions of samples obtained through the de-oxidation tests are listed in Table 1. Samples 1, 2 and 3 are Al-killed, Ti-killed and no-addition samples respectively that are to be used for reasons of comparison.

Representative examples of inclusion of samples are shown in Fig. 3. In the Al killed steel Al_2O_3 (1–3 μm) was found predominantly in form of clusters. In the non-deoxidized sample, Al–Mg–O inclusions of sizes between 0.5–1 μm were found. The sources of Al and Mg in these inclusions, in sample 5, are not clear but most likely they result from unintentional interactions with the MgO crucible and the Al_2O_3 tube (oxygen sensor) during processing in the induction furnace. In the Ti de-oxidized samples, 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)). Table 2 shows the inclusion size distribution, inclusion densities and oxide densities for samples. The precipitations of the inclusions have been discussed in an earlier publication. In the Ti-killed steel, inclusions were found to be smaller than in the Al killed sample and inclusion density is higher than those in the Al-killed and no-addition samples. In Ti-killed steel, oxygen content was lower than the equilibrium oxygen content with the no-addition samples. In Ti-killed steel, oxygen content was calculated to be 0.0016% by using thermodynamic data from literature. Calculations showed that TiN could precipitate at the temperature ranges below 1460°C. In the Ti-killed steel, inclusions were predominantly de-oxidation inclusions that precipitated in the melt.

As for nitrides, nitrogen content in Ti-killed steel was 0.0019%, and the equilibrium nitrogen content with TiN was calculated to be 0.0016% by using thermodynamic data from literature. Calculations showed that TiN could precipitate at the temperature ranges below 1460°C. In order to observe the TiN precipitation and dissolution, in-situ observation was carried out with CSLM. In this experiment, Ti-killed sample was heated and cooled down repeatedly between room temperature and 1500°C. Both heating and cooling rates were 3°C/s. At the first cooling from 1500°C, TiN precipitation was observed at 1270°C, and during the next heating, TiN dissolved at 1300°C. From this observation, TiN was considered not to be present in the temperature range (1440–1500°C) of this work. In the Al-killed steel, the nitrogen content was 0.0014% which is much lower than the equilibrium nitrogen content (0.0158%).

3.2. Visualization of the δ to γ Phase Transformation

The observations of the phase transformation from delta-ferrite to austenite, at the late stage of isothermal conditions in each temperature described in Fig. 2 are shown in Figs. 4–6. In the Al-killed sample (Fig. 4), austenite precipitated at the triple-point of delta-ferrite grain boundaries, and spread along these boundaries. Columnar, precipitates were also observed at 1450°C (Fig. 4(b)). The finger-like precipitation from grain boundaries was observed as shown in Fig. 5(b) (Ti-killed sample). The migration rate of the interface appeared to increase with decreasing isothermal temperature, and the interface gradually became wavy (Figs. 4(b), 4(c)). At 1440°C, precipitates with a lath-type morphology were also observed (Fig. 4(c)). This type of morphology was found by earlier investigators who referred to it as “sword-like” and this definition will be used henceforth in this paper. The evolution of precipitates was similar for the Ti-killed and non-deoxidized samples and are shown in Fig. 5 and Fig. 6.

3.3. Interface Migration Rate

Examples of the interface position change with time during the isothermal holds are shown in Fig. 7 for the cases were growth occurred at fronts that had a finger-like morphology at 1440°C. The migration rates of the interface boundaries in Al-killed sample were higher than those in the Ti-killed and no-addition samples. It can be seen that all the fronts have decaying rates indicative of parabolic growth. If the growth is controlled by diffusion then the time dependency of the size of the growing phase (ξ) can be written as described in Eqs. (1) and (2) if semi-infinite conditions are assumed. The concentration profiles and the boundary conditions that lead to Eqs. (1) and (2) are schematically shown in Fig. 8.25

\[ \xi = K \sqrt{4D_\delta t} \] ..........................(1)

\[ K = \frac{1}{\sqrt{\pi}} \left( \frac{C^{\alpha\beta} - C^{\alpha\beta}}{C^{\beta\alpha} - C^{\alpha\beta}} \right) \exp(-K^2) \frac{1}{1 - \text{erf}(K)} \] ..........................(2)

where, \( \xi \) is the position of interfacial boundary, \( K \) is migration rate, \( D_\delta \) is the diffusion coefficient of carbon in delta ferrite and \( t \) is time in seconds. \( C^{\alpha\beta} \) is the carbon concentration in the ferrite phase far from the migrating interface, and \( C^{\beta\alpha} \) and \( C^{\alpha\beta} \) are the carbon concentrations at the migrating boundary were local equilibrium is assumed to exist. Figure 8 shows the concentration profile resulting in 

| Sample No.  | Density /μm | S. No. | S. No. | S. No. | S. No. | S. No. |
|-------------|-------------|-------|-------|-------|-------|-------|
| Al-killed   | 24          | 0.1–0.3| 8     | 12    | 4     | 1.58   |
| Ti-killed   | 60          | 0.3–0.5| 4     | 32    | 12    | 0.68   |
| No-addition | 24          | 0.5–1.0| 8     | 16    | 4     | 0.63   |

Table 2. Inclusion populations of steel samples.
from quenching a sample with a uniform concentration ($C_{\infty}$) initially at equilibrium in the α field of the phase diagram at temperature $T_2$ to a lower temperature, $T_1$. The β phase is presumed to nucleate, and grow as a platelet of β through diffusion of carbon. $K$ expressed by Eq. (1) was estimated from the experimental data in Fig. 7 and the diffusion coefficient of carbon in delta ferrite, $D_{\delta}$. The diffusion coefficients from reference 22–26.

| Ref. number | $D_{\delta}$(cm/²) |
|-------------|-------------------|
|             | 1460 °C           | 1450 °C         |
| 260         | 4.62E-04          | 4.40E-04        |
| 270         | 5.80E-05          | 5.60E-05        |
| 280         | 1.24E-04          | 1.19E-04        |
| 290         | 1.54E-05          | 1.49E-05        |
| 300         | 1.13E-03          | 9.24E-04        |

Fig. 4. Phase transformation and interface migration behaviors in Al-killed sample ((a) 1460°C, (b) 1450°C, (c) 1440°C).

Fig. 5. Phase transformation and interface migration behaviors in Ti-killed sample ((a) 1460°C, (b) 1450°C, (c) 1440°C).

Fig. 6. Phase transformation and interface migration behaviors in no-addition sample ((a) 1460°C, (b) 1450°C, (c) 1440°C).

Fig. 7. Position changes of $\delta\gamma$ interfacial boundaries during isothermal holding at 1440°C.

Fig. 8. Concentration profile for a semi-infinite system in the $\delta$ and $\gamma$ fields of the phase diagram.
sion coefficient of carbon in delta ferrite, \( D_\delta \) \((10^{-4} \text{ m}^2/\text{s})\), was obtained from literature based on extrapolation of data for carbon diffusion in alpha-ferrite\(^{26-30})\) and values at 1460 and 1450°C are shown in Table 3.

The minimum and maximum values of \( K_{\text{obs}} \) which correspond to the maximum and minimum values of \( D_\delta \) are listed in Table 3 are shown in Table 4. The calculations include only the finger like precipitates which all exhibited parabolic rates. The data of sword like precipitation observed at 1440°C were not included in these calculations since they did not exhibit a rate that decayed with time. The mean \( R^2 \)-values for linear correlations between \( \xi \) and \( \rho^{0.5} \) were found to be a 0.85 \pm 0.05 for the data. Data can be obtained for each condition and is listed in Table 4. It can be seen that the \( K_{\text{obs}} \) values in Al-killed sample were higher than those in Ti-killed sample.

\( K_{\text{calc}} \) values were also computed with Eq. (2) with \( C_{\text{ab}} \) and \( C_{\text{ba}} \) as schematically shown in Fig. 8. \( K_{\text{calc}} \) was obtained from the phase diagram data calculated by ThermoCalc and \( C_{\text{eq}} \) was assumed to be the starting (bulk) carbon composition. Unfortunately, the interface concentrations, \( C_{\text{ab}} \) and \( C_{\text{ba}} \) may be influenced by other solutes, which in the present samples are Mn, Al, and Ti and the distribution of these elements could not be readily predicted. Our experimental visualization is dependant upon surface observations sensitive to decarburization (as discussed in Sec. 2.3) and therefore long time annealing to homogenize the alloy in the delta-ferrite regime could not be carried out.

Apart from equilibrium, two different conditions were considered in the analysis. Firstly, if the substitutional elements were indeed homogenized then the assumption of paraequilibrium where only carbon may have been equilibrated in the system while the other species are considered relatively immobile can be made. In this case, calculated carbon concentration on the gamma side of the interface decreased whereas that on the delta side increased (\( K_{\text{hom}} \)). Secondly, if segregation occurred during solidification, local concentrations of the components would be modified and Mn owing to its large content (0.9 wt\%) could be distributed in the sample non-homogeneously. If, as a result, Mn was completely depleted in the region of our observation, this would result in different calculated values (\( K_{\text{zero Mn}} \)). In Table 5, computed \( K \) values corresponding to the aforementioned non-equilibrium conditions and equilibrium are listed. The smallest theoretical value (\( K_{\text{zero Mn}} \)) would be 0.176 if assumed manganese was completely depleted locally, whereas the smallest equilibrium one (\( K_{\text{calc}} \)) equals 0.51 for Ti-killed at 1460°C. By comparing Tables 4 and 5, it can be seen that the observed values (\( K_{\text{obs}} \)) are at least 1/2.9 of the calculated ones and the difference cannot be explained by the presence and influence of Mn on local equilibrium nor the variation in the available diffusion coefficient data. Schmidt et al.\(^{31})\) measured the interfacial migration rate during the austenite formation in IF steels, and suggested the effect of the inclusion particles on the migration rate. In the previous work,\(^{17})\) de-oxidation particles have a strong effect on the austenite grain growth in isothermal treatments at 1200–1300°C. Hence, the difference between the observed and the calculated \( K \) values could be caused by the pinning effect of de-oxidation particles but the mechanism of this phenomenon is not clear.

In order to ensure that surface and bulk micro-structures

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**Table 4.** Comparison between the observed and calculated \( K \) values.

|          | Al-killed | Ti-killed | No addition | Reference |
|----------|-----------|-----------|-------------|-----------|
| \( K_{\text{obs}} \) |           |           |             |           |
| 1400°C   | 0.0071    | 0.0062    | 0.0053      | 30        |
|          | 0.0038    | 0.0037    | 0.0039      |           |
| 1450°C   | 0.0071    | 0.0059    | 0.0046      | 30        |
|          | 0.0049    | 0.0039    | 0.0043      |           |
|          | 0.0046    |           |             |           |
|          | 0.0042    |           |             |           |
|          | 0.0033    |           |             |           |

**Table 5.** Range of calculated \( K \) values.

|          | \( K_{\text{calc}} \) | \( K_{\text{hom}} \) | \( K_{\text{zero Mn}} \) |
|----------|------------------------|----------------------|-------------------------|
| Ti-killed| 0.760                  | 0.760                | 0.400                   |
| Al-killed| 0.510                  | 0.760                | 0.176                   |
| No addition | 0.760                  | 0.760                | 0.431                   |

Note that \( K_{\text{calc}} \) is calculated at equilibrium, \( K_{\text{hom}} \) under paraequilibrium and \( K_{\text{zero Mn}} \) with complete Mn depletion.

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Fig. 9. Microstructure of (a) surface compared with (b) cross-section in Ti-killed sample after CLSM (2%-nital etching).
were similar (to ensure that present observations were not attributed to surface effects such) surface and cross-sectional images of the same sample (Ti-killed) are compared in Fig. 9, and it can be seen that they are quite similar.

3.4. Effect of Particles on the Migration Rate

Zener pinning force can be expressed by Eq. (3),

\[ Z_p = \frac{3 \cdot \sigma \cdot V \cdot f_v}{d} \]  

where \( \sigma \) are the interfacial energy (4.5 \times 10^{-13} \text{J/m}^2), \( d \) is a mean particle diameter (10^{-3} \text{m}) and \( f_v \) calculated by Eq. (4) is a volume fraction of oxide particles. In the Ti-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. (4), \( n \) and \( m \) are the numbers of cation, \( M \), and oxygen respectively in a oxide, \( M_mO_n \), \( \rho \), \( \rho_o \) are the density of oxide and iron respectively, \( T[O] \) is analyzed total oxygen content.

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

The parameters used for calculations and the resulting \( Z_p \) for each sample are shown in Table 6. Figure 10 shows the relation between \( Z_p \) and \( K_{obs} \) at 1440–1460°C and it can be seen that \( K_{obs} \) decreases with increasing \( Z_p \). In this figure, \( K_{obs} \) values were the average value calculated with the maximum \( D_k \) value29 in Table 3. \( K_{obs} \) values at 1440°C are not included the data of sword-like transformation. The percentage of observed migration events for sword-like transformation was 10–30% of the total precipitation events. They were observed to occur earlier than the other precipitations. As a result, these sword-like precipitation was observed, during cooling, in all the samples at the temperature range 1440–1450°C during cooling from 1500 to 1440°C. In contrast, the non-sword like precipitation occurred after the isothermal temperature (1440°C) was reached in these experiments.

3.5. Effect of Isothermal Transformation Temperature

Figure 11 shows the phase diagram of Fe–C system of the sample in this work. At 1500°C the sample would be in the single phase region of delta-ferrite. In the range 1440–1460°C the sample would be in the two-phase region of delta-ferrite and austenite and below 1440°C the sample would be in the single-phase austenite region. When finger like precipitation occurred, the interface migration rate was significantly higher at 1440°C than at the two higher temperatures. Maruyama et al.33,34 reported that delta-ferrite phase by itself restrains the austenite grain growth. Hence, at 1460 and 1450°C, the migration rate could be restrained by a combination of particles and delta-ferrite phase, whereas it is restrained primarily by particles at 1440°C. That suggests that the effect of particles [\( Z_p \)] is larger at 1440°C than at 1450 and 1460°C as a result of the afore-

| Sample | \( [O] \) (ppm) | \( \rho \) | \( \rho_o \) | \( \sigma \) | \( d \) (mm) | \( Z_p \) (J/mol) |
|--------|--------|--------|--------|--------|--------|--------|
| Al-killed | 7 | 3.97 | 7.8 | 0.0000076 | 0.0017 | 0.000042 |
| Ti-killed | 7 | 4.47 | 7.8 | 0.0000112 | 0.0006 | 0.000176 |
| No addition | 8 | 3.97 | 7.8 | 0.0000088 | 0.0010 | 0.000083 |

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Fig. 10. Relation between \( Z_p \) and \( K_{obs} \) at 1440–1460°C.

Fig. 11. Phase diagram of Fe–C system.

Fig. 12. Sword-like shape precipitation in Al-killed sample.

mentioned effect of ferrite, i.e. the influence of particles is less at the two higher temperatures.

As mentioned previously, sword-like precipitation was observed in all the samples at 1440–1450°C during cooling from 1500 to 1440°C. A higher resolution image of the sword-like precipitation is shown in Fig. 12. As mentioned earlier the occurrence of such “sword-like” was reported by
Liu et al.\textsuperscript{141} in low carbon steel samples during cooling at rapid cooling rate of 30 K/s but was not observed at a slow cooling rate of 0.33 K/s. In this work, a cooling rate of 5 K/s was applied for all cases. Interface migration, defined as precipitate sizes change with time, of sword-like precipitation compared with the other non-sword like precipitates are shown in Fig. 13. It can be noted that the sword-like precipitates grow significantly more rapidly that the others and furthermore, the growth is linear with time.

The results suggest that the sword-like precipitation could be controlled by interface processes rather than long-range diffusion. This could be the result of a massive transformation where the interface migration rate is as a result of that partition-less transformation becomes possible below a critical temperature defined as $T_{cr}$\textsuperscript{35,36}. The $T_{cr}$ line was calculated by Thermo-Cale and shown in Fig. 14 for a case where a single phase austenite is cooled. $T_{cr}$ lies between 1466 and 1478°C corresponding to the carbon contents in Table 1. Borgenstam and Hillert\textsuperscript{37} measured the critical limit for massive $\gamma \rightarrow \alpha$ transformation in the Fe–Ni system by means of diffusion couples. The measured limit for massive transformation was 45–75 degrees lower than $T_{cr}$. In this work, sword-like precipitation occurred at 1440°C which is 26–38 degrees lower than $T_{cr}$.

Boundary migration rate $R$, controlled by interface processes rather than long-range diffusion can be expressed through Eq. (5)\textsuperscript{38}

$$R = \left( \frac{\delta}{kT} \right) v \cdot \exp \left( -\frac{\Delta G^*}{kT} \right) \Delta G_m^{\delta \rightarrow \gamma}$$

where $\delta$ is the boundary thickness, $k$ is the Boltzman constant, $v$ is the atomic jump frequency, $\Delta G^* (=\Delta H^* - T\Delta S^*)$ is the activation energy per atom for migration and $\Delta G_m^{\delta \rightarrow \gamma}$ is the Gibbs energy difference between the $\delta$ and $\gamma$ phases per atom. By assuming $\delta = 5 \AA$, $\Delta H^* = 2.76 \times 10^{-17}$ J/atom for grain boundary diffusion, and the energy difference $= 4.18 \times 10^{-21}$ J/atom, Speich et al.\textsuperscript{39} estimated $v \cdot \exp(-\Delta S^*/k)$ to be $1.65 \times 10^{-17}$ s$^{-1}$ from experimental data on $\alpha \rightarrow \gamma$ transformation at 950°C. By adopting the same treatment with the present migration rate, the activation enthalpy $\Delta H^*$ is evaluated to be $5.41 \times 10^{-19}$ J/atom for the Ti-killed steels and $5.02 \times 10^{-19}$ J/atom for the Al-killed steels. These values are approximately two times larger than that for grain boundary diffusion. The high activation enthalpy in the present study may be due to high impurity content, causing the stronger pinning effect. It should be mentioned that due to the rapid nature of the transformation, conditions were not strictly isothermal due to that the transformation began somewhat before the targeted isothermal temperature was reached. This amounted to a variation of temperature and the temperature at these times was averaged when carrying out the calculations described above.

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 effect of particles on the migration rate of $\delta$ grain boundaries and $\delta\gamma$ interface boundaries was investigated.

(1) In terms of inclusion morphology Al$_2$O$_3$ (1–3 μm) cluster were typically observed in Al-killed steel, and TiN and Ti–Al–Mg–O (0.3–0.8 μm) in Ti-killed steel and the later inclusion were typically in the core of the former. Al–Mg–O below 1 μm were found in the no-addition sample.

(2) Austenite precipitated at the triple point of $\delta$-ferrite grain boundaries and expanded along the grain boundaries as finger-like or wavy shape. In other cases, austenite precipitated with a columnar shape or sword-like shape in the $\delta$-ferrite grains.

(3) Migration of $\delta\gamma$ interfacial boundaries at 1450 and 1460°C appeared to be parabolic and thus long-range diffusion controlled but the observed rates were at least 1/3 lower than those predicted by a semi-infinite diffusion model.

(4) Migration rates of $\delta\gamma$ interfacial boundaries at 1440, 1450 and 1460°C decreased with increasing the Zener pinning force due to 2nd phase particle population which resulted in that migration rates in Ti-killed steel were lower than those of the Al-killed and no-addition steel samples.

(5) Migration rates of $\delta\gamma$ interfacial boundaries at 1440°C were higher than those at 1450 and 1460°C. This is attributed to the amount of remaining $\delta$ phase, which restrains the austenite grain growth.

(6) Sword-like austenite precipitations were confirmed during cooling from 1500 to 1440°C. During sword-like precipitation, migration rate of $\delta\gamma$ interfacial boundaries were much faster than the others. 1440°C is 26–38 degrees lower than $T_{cr}$ and that was considered to be interface reac-

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**Fig. 13.** Position changes of $\delta\gamma$ interfacial boundaries during cooling from 1500°C.

**Fig. 14.** Phase diagram of Fe–C system including $T_{cr}$.
tion controlled-massive transformation.

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