Non-metallic inclusion and intragranular nucleation of ferrite in Ti-killed C–Mn steel

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Abstract

The influence of Ti addition on the development of acicular ferrite microstructure during the γ/α transformation in C–Mn steels has been studied. The optical microstructures of the heat-treated specimens with different Ti concentrations were characterized. Transmission electron microscopy analysis with thin foil specimens was carried out to investigate the phase composition of non-metallic inclusions and the local variation of chemical composition around the inclusions. It has been found that an acicular ferrite dominant microstructure could be produced when the Ti concentration is higher than about 50 ppm. The transition from the conventional bainitic microstructure to the interlocking acicular ferrite microstructure occurs in response to the change in the main-component of the non-metallic inclusions from Mn–Si oxide to Ti2O3. The Mn depleted zones around Ti2O3 particles were detected, which could explain how the intragranular nucleation is facilitated on Ti2O3 particles.

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Keywords: Steels; Nucleation; Transmission electron microscopy; Non-metallic inclusion

1. Introduction

In general, a microstructure consisting mainly of acicular ferrite provides optimum weld metal [1–4] and HAZ [5–8] mechanical properties, both from a strength and toughness point of view, by virtue of its fine effective grain size and high angle grain boundaries [9–11]. On the other hand, the formation of large proportions of relatively coarse grain boundary allotriomorphic ferrite and side plate ferrite (i.e. Widmanstätten ferrite or upper bainite) is considered detrimental to toughness as these structures provide preferential crack propagation routes at low temperatures. Acicular ferrite and upper bainite are considered to be formed by the same transformation mechanism [12]. Both microstructures develop at lower temperatures than allotriomorphic ferrite. In upper bainite, the ferrite initiates at the austenite grain boundaries, forming sheaves of parallel plates with the same crystallographic orientation, whereas acicular ferrite is nucleated intragranularly at non-metallic inclusions. The process of nucleation on the inclusions, together with the sympathetic
nucleation [13], leads to a chaotic arrangement of laths and a fine-grained interlocking microstructure characteristics of acicular ferrite. Most of the work on acicular ferrite has been carried out on welds [1–4,12,14–16]. The high density of inclusions present in steel weld deposits ensures a high density of nucleation sites, which favors the development of an acicular ferrite microstructure instead of a bainitic one. Recently, the application of this microstructure to wrought steels has been attempted by inoculating with selected non-metallic inclusions as nucleants of acicular ferrite [17–20]. Even though a limited number of steels containing effective oxide particles are available yet, the results obtained so far for Ti deoxidized steels are encouraging and clearly demonstrate the potential of using the concept of intragranular nucleation of ferrite at inclusions in wrought steels [21,22]. In such attempts, it must be well understood which phase in non-metallic inclusions of usually heterogeneous character is more effective for intragranular nucleation and how this non-metallic inclusion promotes intragranular nucleation. Although the mechanism by which inclusions nucleate acicular ferrite is yet unclear, there have been four suggestions: (1) simple heterogeneous nucleation on an inert particle [15,23]; (2) epitaxial nucleation on the inclusions which have a good coherency with ferrite [24,25]; (3) nucleation arising from the strain energy associated with the different thermal expansion coefficients of the inclusions and steel matrix [17,26,27]; and (4) nucleation assisted by solute depletion in the matrix near inclusions [28–35]. It depends on the chemistry and structure of non-metallic inclusions, that which mechanism would work to promote the intragranular nucleation on inclusions. For example, the effectiveness of TiO [36] for intragranular nucleation is suggested to be due to a small disregistry with appropriately oriented ferrite and that of TiO₂ [32] is suggested to be due to releasing oxygen to decarburize adjacent steel matrix, which is advantageous for ferrite nucleation. In case of Ti₃O₅ [28,30,31,33], the development of local Mn depleted zones (MDZs) around particles has been the most influential hypothesis, even though there has been no direct evidence.

It was not until recently that the compositions and phases present in inclusions could be thoroughly characterized because they are multiphase, too small for scanning electron microscopy (SEM) analysis and too thick for TEM analysis [12]. As a result, the oxidation state of titanium in them is often unknown and titanium has been variously reported as different oxides [37–41], even though it is well known that the effectiveness of particles for intragranular nucleation is markedly improved as titanium content increases [2,42,43]. Recently, there have been a few reports that had analyzed inclusions in steel matrix which were thinned transparently for TEM analysis [44–46]. However, it is still required to systematically investigate the phase change of non-metallic inclusions as Ti content increases.

The aim of the present study is to investigate systematically the influence of Ti on the intragranular nucleation of ferrite in low carbon steels with very low sulfur content. The effects of the Ti content on the phases of non-metallic inclusions and the microstructures in low carbon steels have been investigated and the intragranular nucleation mechanism is discussed based on analytical TEM and thermodynamic calculation analyses.

2. Experimental procedure

Six low C–Mn steels with different Ti concentrations were prepared by a laboratory vacuum induction melting furnace as 2 kg ingots. The chemical compositions of the heat are presented in Table 1. The oxygen and nitrogen levels were about 50 and 10 ppm, respectively and the sulfur level was about 20 ppm. The ingots were hot-forged and machined to cylindrical specimens, 8 mm in diameter and 12 mm in height. These specimens were austenitized at 1523 K for 20 min and then continuously cooled to room temperature at a rate of 3 K/s using a thermomechanical simulator. After the heat treatments, all specimens were prepared by standard grinding and polishing methods followed by etching in 2% Nital solution for optical microscopy and SEM. Prior austenite grain size (PAGS) was measured by the mean linear intercept method. The number of inclusions larger than 1
Table 1
Chemical composition of the steels (wt%)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Ti</th>
<th>Al</th>
<th>S</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0</td>
<td>0.08</td>
<td>1.64</td>
<td>0.21</td>
<td>&lt;0.0003</td>
<td>&lt;0.0005</td>
<td>&lt;0.002</td>
<td>0.006</td>
<td>0.002</td>
</tr>
<tr>
<td>T20</td>
<td>0.08</td>
<td>1.56</td>
<td>0.19</td>
<td>0.0021</td>
<td>&lt;0.0005</td>
<td>0.002</td>
<td>0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>T45</td>
<td>0.08</td>
<td>1.57</td>
<td>0.20</td>
<td>0.0045</td>
<td>&lt;0.0005</td>
<td>0.002</td>
<td>0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>T60</td>
<td>0.08</td>
<td>1.57</td>
<td>0.18</td>
<td>0.0062</td>
<td>&lt;0.0005</td>
<td>0.002</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>T75</td>
<td>0.08</td>
<td>1.56</td>
<td>0.20</td>
<td>0.0074</td>
<td>&lt;0.0005</td>
<td>0.002</td>
<td>0.004</td>
<td>0.001</td>
</tr>
<tr>
<td>T110</td>
<td>0.08</td>
<td>1.65</td>
<td>0.22</td>
<td>0.011</td>
<td>&lt;0.0005</td>
<td>&lt;0.002</td>
<td>0.005</td>
<td>0.002</td>
</tr>
</tbody>
</table>

μm in diameter was counted in 1 mm² area under 1000× magnification.

The TEM and STEM analyses of inclusions were carried out using JEOL JEM-3000F and Philips CM-20 equipped with an energy-dispersive spectrometer (EDS) unit. Extracted carbon replicas from each steels were analyzed by EDS to know the overall chemistry of inclusions before observing the fine structure of the inclusions, which were thinned and transparent for TEM analysis. To achieve transparent foils with inclusions embedded in steel matrix, 3 mm disks were prepared by ion milling after perforating using a twin jet electropolisher. The electropolishing was performed using a 13% perchloric acid solution with methanol as a solvent at about 243 K. The subsequent ion beam thinning was performed at an angle of 4° in Gatan PIPS. The compositions of the constituent phases of inclusions have been analyzed by EDS and the crystal structures were determined by selected area electron diffraction patterns (SADPs). Furthermore, we have measured the local chemistry, especially the Mn concentration, near inclusions in steel T110 sample, which were water-quenched after reheating at the temperatures between 1623 and 1323 K for 20 min, using EDS. The measurement of Mn concentration was conducted in the intervals of 10 nm from the interface between TiO₃ particle and steel matrix, by EDS spot analysis. The average value of five measurements was adopted, as shown in Fig. 1 [35]. The beam size was 1.5 nm in an STEM mode and the acquisition time of X-ray in each spot analysis was 30 s.

The thermodynamic stabilities of various non-metallic inclusions and the driving force for ferrite nucleation were calculated using the calculation-of-phase-diagram (CALPHAD) method [47] and the actual calculations were carried out by ThermoCalc [48].

3. Results and discussion

3.1. Optical microstructure

The optical microstructures of the steels which were reheated at 1523 K for 20 min and cooled at a rate of 3 K/s, are presented in Fig. 2. They consist mainly of bainitic ferrite, which in this article implies both acicular ferrite and side plate ferrite, even though there is a small amount of allotriomorph ferrite along prior austenite grain boundaries. In steel T0 in which Ti was not added, side plate ferrite microstructure is obtained as shown in Fig. 2(a). However, with Ti content increasing, the sheaf morphology of bainitic ferrite laths change...
to more chaotic one as shown in Fig. 2(a) and (c). In the steels of above 60 ppm Ti, a typical acicular ferrite microstructure is produced (Fig. 2(d)–(f)).

Whether the interwoven microstructure of acicular ferrite or the sheaf morphology of side plate ferrite is formed, would be determined by the competition of the ferrite nucleation sites between prior austenite grain boundaries and non-metallic inclusions within prior austenite grains, if we assume that the growth mechanisms of acicular ferrite and side plate ferrite are the same. Table 2 compares steels T0 and T110 in PAGS and the density of non-metallic inclusions. Ti addition produced a little smaller PAGS and the number of

Table 2
Comparison of PAGS and the density of inclusions in steels T0 and T110

<table>
<thead>
<tr>
<th></th>
<th>PAGS (µm)</th>
<th>Density of inclusions (mm⁻²)</th>
<th>Intragranular nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0</td>
<td>400</td>
<td>126</td>
<td>No</td>
</tr>
<tr>
<td>T110</td>
<td>330</td>
<td>102</td>
<td>Yes</td>
</tr>
</tbody>
</table>
non-metallic inclusions larger than 1 µm in steel T0 was slightly higher than that in steel T110, even though the number of non-metallic inclusions below 1 µm in steel T0 might be lower than that of steel T110. However, as shown in Fig. 3, the non-metallic inclusion in steel T0, which was analyzed to be Mn- and Si-rich phase could not nucleate ferrite grain, while on a Ti-rich inclusion in steel T110 ferrite laths were nucleated and grown. The final microstructures of the steels T0 and T110 were dominantly side plate ferrite and acicular ferrite, respectively. Therefore, the microstructural transition by Ti addition as shown in Fig. 2 must be due to some characteristics of non-metallic inclusions, which could promote intragranular nucleation.

### 3.2. Non-metallic inclusions

In order to understand the reason why the microstructure varies with Ti content, we investigated the phase transition of the particles with Ti content. Fig. 4 shows the calculated equilibrium mole fractions of inclusion phases dependent on Ti content at 1750 K, at which the steels are under solidification. The inclusion phases considered in the present calculation were MnO, SiO₂, MnSiO₃, Mn₂SiO₄, Mn₃TiO₄, MnTiO₃, MnTi₂O₄, Ti₃O₃, TiO and TiO₂. The other compositions used for the calculations are fixed as 0.08 wt% C, 1.7 wt% Mn, 0.2 wt% Si, 0.004 wt% O, 0.001 wt% N. With increasing Ti content, the equilibrium phase of inclusions change from MnSiO₃ through Mn₂TiO₄.
and MnTiO$_3$ to Ti$_2$O$_3$. There was neither TiO nor TiO$_2$ in the range of the Ti content used in the present calculations.

Fig. 5 shows the results of TEM analysis of a typical particle in the steel T0. From the EDS analysis, it was found that most of the particles in steel T0 are heterogeneously composed of Mn–Si–O and Mn–S phase. The atomic ratio between Mn and Si is about 1:1 without absorption correction, which is in agreement with the result of the equilibrium phase calculation. The SADP of the Mn–Si–O phase is represented in Fig. 5(c), indicating that it is amorphous MnSiO$_3$. The SADPs of the Mn–S phase, as one of them is shown in Fig. 5(e), shows that it is cubic MnS.

Figs. 6–9 show the change in the phase composition of typical particles as Ti content increases. The more Ti content increases more amount of amorphous MnSiO$_3$ phase is substituted by Mn–Ti complex oxides. The atomic ratios of Mn to Ti without absorption correction were about 45:55 in steel T20 and about 25:75 in steel T45. The steels, which contain more than 60 ppm Ti, show a fluctuation in Mn content in the range of less than 10 at.% Mn. The result of the EDS analysis means that the increase in Ti content produces more Ti-rich Mn–Ti complex oxide. Figs. 6 and 8 are the BF images of typical particles in the steels T20 and T45 and the SADPs of Mn–Ti complex oxides obtained from the three different zone axes, respectively. The SADP obtained from (001) zone axis (Fig. 6(e)) reveals that the Mn–Ti oxide in steel T20 has a near cubic symmetry. On the other hand, we could not obtained such near cubic symmetrical SADP in the Mn–Ti oxide of steel T45. By comparing EDS and SADP results with the crystallographic data from the JCPDS cards of possible Mn–Ti complex oxides shown in Table 3, it could be concluded that the Mn–Ti oxide in steel T20 is Mn$_2$TiO$_4$ and that the Mn–Ti oxide in steel T45 is MnTiO$_3$, which also agrees qualitatively with the calculation result (Fig. 4). All SADPs could be indexed as Mn$_2$TiO$_4$ in steels T20 and MnTiO$_3$ in steel T45. In steel T20, however, Mn$_2$TiO$_4$ is not the only phase in Mn–Ti oxide, but there is also MnTiO$_3$ as shown in Fig. 7.

Fig. 9 represents typical particles in the steels containing more than 60 ppm Ti, in which we could not find MnSiO$_3$ nor Mn–Ti complex oxide of cubic or tetragonal structure. That is, neither MnSiO$_3$ nor Mn$_2$TiO$_4$ was found, which also agrees with the calculation result. Fig. 9(d)–(f) shows the SADP of the Mn–Ti oxide in steel T60, which indicate a similar structure to those of
MnTiO$_3$. But the Mn content of the oxides in the steel containing more than 60 ppm Ti is in the range of 3–10 at.% Mn, which is much less compared with that of MnTiO$_3$ in steel T45. Therefore, by comparing the EDS data and SADPs with JCPDS data, it was concluded that the oxides in the steels containing more than 60 ppm Ti are Ti$_2$O$_3$, which has more Mn content. The Mn content in the Ti$_2$O$_3$ particles seems to be a clue to understand intragranular ferrite nucleation on the particles, which will be described in detail in Section 3.3.

In addition, Al oxides or Al–Ti complex oxides are frequently observed in Ti$_2$O$_3$ non-metallic inclusions as shown in Fig. 9, where the Al oxide was Al$_2$O$_3$. These Al oxides are mostly in the interior of the Ti$_2$O$_3$ non-metallic inclusions, which indicates that Ti$_2$O$_3$ nucleates heterogeneously on an Al oxide particle. In relation to the sequence of oxide phase formation, MnSiO$_3$ seems to have liquid phase when Fe matrix is already solidified, which can be inferred from the fact that the interphase boundary between the MnSiO$_3$ particle and the Fe matrix is composed of many facets as shown in Figs. 6–8 unlike that of Ti$_2$O$_3$ particle.

In summary, as Ti content increases, the amorphous MnSiO$_3$ which is the main phase of non-metallic inclusions in steel T0 is substituted by Mn–Ti complex oxides. The phase of Mn–Ti complex oxide is Mn$_2$TiO$_4$ or MnTiO$_3$ in steel T20 and MnTiO$_3$ in steel T45. In the steel containing more than 60 ppm Ti, Ti$_2$O$_3$ is formed with a small amount of Al oxide and MnS. This result is in good agreement with the phase equilibrium calculation, even though the calculated equilibrium phases are identified experimentally to be formed in the lower Ti range. The change in oxide phase with Ti content is directly related to that of the optical microstructure. That is, side plate ferrite is formed in steel T0 with MnSiO$_3$ particles, while acicular fer-
rite is obtained in the steel with Ti$_2$O$_3$ particles. In steels T20 and T45 that have particles composed of MnSiO$_3$ and Mn–Ti complex oxide phases, there is a transition from a side plate ferrite microstructure to acicular ferrite one. Therefore, it is concluded that Mn–Ti oxide particles, especially Ti$_2$O$_3$, have more potency than MnSiO$_3$ for intragranular nucleation.

3.3. Intragranular nucleation mechanism

By investigating the inclusions in the steels of different Ti concentration, it is known that Ti$_2$O$_3$ is more potent for ferrite nucleation than MnSiO$_3$, which means that there must be other mechanisms in addition to a simple heterogeneous nucleation mechanism. In order to explain the nucleation of intragranular ferrite on certain particles, they have suggested several plausible mechanisms for the particles of their own. In the case of Ti$_2$O$_3$, it has been proposed that the local depletion of austenite stabilizing element such as Mn around the inclusions promote ferrite nucleation by increasing the chemical driving force. In regard to the origin of the local solute depletion around Ti$_2$O$_3$ particle, however, there have been two different viewpoints. One is that MDZ is produced by MnS precipitation on Ti$_2$O$_3$ during cooling process [28,33]. That is, as temperature decreases, MnS precipitates by the difference in sulfur solubility to result the Mn depletion around MnS precipitates. Using TEM/EDS, Shigesato et al. [34,35] showed the depleted zone near MnS, even though the MnS was not the precipitated one on Ti$_2$O$_3$. In principle, however, this mechanism cannot explain the differences in nucleation potency among many kinds of inclusion, particularly between Ti$_2$O$_3$ and MnSiO$_3$. Moreover, sulfur content in the steels used in the present work is about 20 ppm, which is much lower than those of the literatures suggesting the effect of MnS precipitation. For example, there have been reports that acicular ferrite was well developed and the impact toughness was excellent when sulfur content was about 50 ppm [30,49]. Also, in the results of Shigesato’s TEM/EDS analysis [34], the width and the depth of the MDZ were dependent on sulfur content. In case of 24 ppm S, they could not find a depleted zone. In addition, it must be pointed out that the MDZ by MnS precipitation is diminished, when holding the steel specimen at temperatures in the range where the diffusivity of Mn in steel is high enough but further MnS precipitation by following cooling is negligible [29,35]. Therefore, an additional mechanism is needed to explain the high potency of Ti$_2$O$_3$.

The other possible mechanism of the MDZ formation and intragranular nucleation is that a Ti$_2$O$_3$ particle itself, which is reported to have many cation vacancies [33], absorbs Mn atoms from an Fe matrix [31,32]. It seems to be reasonable because Mn$^{3+}$-ion has a similar radius to Ti$^{3+}$-ion [50] and MnTiO$_3$ has a very similar structure to Ti$_2$O$_3$ as shown in Table 3. This mechanism could explain

![Fig. 7. Non-metallic inclusions in steel T20: (a) BF image of inclusion; and (b,c) SADPs of MnTiO$_3$.](image)
that acicular ferrite was well developed in the steels of Ti$_2$O$_3$ particles compared to the steels with Mn–Si oxide particles. In previous works [31], the authors checked this possible mechanism by conducting bonding experiment between Ti$_2$O$_3$ and Fe matrix, which was analyzed by electron probe microanalysis (EPMA). It was found that Ti$_2$O$_3$ actually absorbs Mn atoms from Fe matrix during austenitization heat-treatment and that the width of the MDZ near Ti$_2$O$_3$ is dependent upon autenitization temperature. However, there had been no direct evidence of the MDZ around individual Ti$_2$O$_3$ particle in wrought steels. Thus, we have analyzed the local chemistry near Ti$_2$O$_3$ particle in steel T110 using TEM/EDS.

To investigate whether Ti$_2$O$_3$ particle actually absorbs Mn at austenitizing temperature or not, steel T110 specimens were reheated and held at 1323, 1523 and 1623 K for 20 min, followed by water quenching. The samples were water-quenched to observe the Mn profile at the reheating temperature, where the MDZ by MnS precipitation would be diminished because of the high diffusivity of Mn. Thin foils were prepared by the method described earlier and the Mn concentrations in Ti$_2$O$_3$ and Fe matrix near Ti$_2$O$_3$ have been analyzed by TEM/EDS in at least five inclusions at each reheating temperature. The average Mn contents of several Ti$_2$O$_3$ particles for each specimen were 3.5, 3.9 and 4.2 at.% in the specimens heat-treated at 1323, 1523 and 1623 K, respectively. There was slight increase in Mn content in Ti$_2$O$_3$ inclusions, which agrees well with the previous result [31]. Fig. 10 shows the Mn concentration near Ti$_2$O$_3$ inclusion in steel T110 reheated at 1523 K for 20 min followed by water quenching. It must be noted that MnS precipitates were frequently observed on Ti$_2$O$_3$ inclusion and that EDS was therefore, intentionally measured near the surface of Ti$_2$O$_3$ inclusions far from MnS. As shown in Fig. 10(c), there was decrease in Mn concentration and increase in Ti near the surface of Ti$_2$O$_3$.
inclusion. The increase in Ti concentration is due to beam broadening in EDS analysis, which was also confirmed in Mn profile near MnSiO$_3$ inclusion. The broadening parameter, $b$, containing 90% of the scattered electrons, can be expressed as

$$b = 7.21 \times 10^2 \frac{Z}{E_0} \left(\frac{\rho}{A}\right)^{1/2} t^{3/2}$$

where $Z$ is the atomic number, $A$ the atomic weight, $\rho$ the density, $E_0$ the beam energy, and $t$ is the foil thickness [51]. In our analysis using 300 kV FEG TEM, $b$ is less than about 9 nm assuming that foil thickness is less than 100 nm. In Fig. 10(c), the increase of Ti concentration in the distance of 10 nm was less than 1 wt%, while the concentrations of Mn and Ti measured at the surface of Ti$_2$O$_3$ inclusion were about 2.5 and 40 wt%, respectively. Therefore, it is concluded that there was Mn depletion near Ti$_2$O$_3$ inclusion. Fig. 11 shows the Mn concentrations near Ti$_2$O$_3$ inclusions in steels reheated at 1323, 1523 and 1623 K for 20

Table 3
Crystal structure and lattice parameters of possible Mn–Ti oxides

<table>
<thead>
<tr>
<th>JCPDS no.</th>
<th>Space group</th>
<th>Lattice parameter</th>
<th>$V_{pc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_2$TiO$_4$</td>
<td>20-0728</td>
<td>Tetragonal</td>
<td>$a = b = 8.726, c = 8.567$</td>
</tr>
<tr>
<td>MnTiO$_3$</td>
<td>29-0902</td>
<td>Rhombohedral (R3)</td>
<td>$a = b = 5.1396, c = 14.29$</td>
</tr>
<tr>
<td>MnTi$_2$O$_4$</td>
<td>41-0064</td>
<td>Cubic (Fd3m)</td>
<td>$a = b = c = 8.627$</td>
</tr>
<tr>
<td>Ti$_2$O$_3$</td>
<td>10-0063</td>
<td>Rhombohedral (R3c)</td>
<td>$a = b = 5.139, c = 13.659$</td>
</tr>
</tbody>
</table>
Fig. 10. STEM images of: (a) a Ti$_2$O$_3$ inclusion in steel T110; (b) a MnSiO$_3$ inclusion in steel T0; and (c) Mn concentration profiles from the inclusion/matrix interfaces measured in steels reheated at 1523 K for 20 min and water-quenched (error bar in each distance indicates the range of the five measurement results).

min followed by water quenching. When reheated at 1623 K, the range of sudden decrease in Mn content was about 50 nm wide and the average Mn concentration at 10 nm distant from the Ti$_2$O$_3$ inclusions was 0.6 wt%. When reheated at 1523 K for 20 min, the Mn depletion near Ti$_2$O$_3$ particle seems to be a little reduced. When reheated at 1323 K for 20 min, the Mn depletion near Ti$_2$O$_3$ inclusion was further reduced. The Mn depletion as shown in Fig. 11 was always detected in specimens reheated at 1523 and 1623 K, while that was indistinct at 1323 K in consideration of error range.

That is, as reheating temperature decreased, the width and the depth of MDZ decreased, which is in agreement with the previous result from the bonding experiment [31]. If the MDZs in Fig. 11 were the ones which had been produced by MnS precipitation in the casting process and remained through the reheating process, however, the increase in reheating temperature would reduce the extent of the MDZ, as reported by Shigesato et al. [35]. Therefore, regarding the Ti$_2$O$_3$-particle-dispersed steels reheated in the temperature where the MDZ by the precipitation of MnS is diminished, the main working mechanism of MDZ formation is likely to be the direct Mn absorption of Ti$_2$O$_3$ particles.

The variation of the driving force for ferrite nucleation with Mn content is represented in Fig. 12, which is calculated by Thermo-Calc for the steel of 0.08 wt% C and 0.2 wt% Si. If the Mn content decreases from 1.6–0.6 wt%, $A_e$ increases from 1003 to 1035 K and the driving force increases from 320–380 J/mol at 973 K, which results in about 30% reduction in the activation energy for ferrite nucleation. Fig. 13 compares spherical particles with austenite grain boundaries as simple heterogeneous nucleation sites by calculating the activation energy for ferrite nucleation when the driving force is 320 J/mol, as the work of Ricks et al. [52]. It was assumed that the austenite grain boundary energy ($\sigma_{gg}$) and the interface energy between ferrite and austenite ($\sigma_{ff}$) be the same (0.75 J/m$^2$) and that the interface energy between inclusion and austenite ($\sigma_{ia}$) and the interface energy between inclusion and ferrite ($\sigma_{if}$) be also the same. The effect of the increased driving force by MDZ is also represented along with the
Fig. 11. Mn depletion zone around the Ti$_2$O$_3$ inclusion; STEM images of the inclusions and Mn concentration profiles from the Ti$_2$O$_3$/matrix interfaces measured in steel T110 reheated at: (a) 1623, (b) 1523, and (c) 1323 K for 20 min and water-quenched (error bar in each distance indicates the range of the five measurement results); (d) Mn profiles in (a–c) are compared.
Fig. 12. Calculated driving force at 973 K, according to Mn contents in the steel of 0.08 wt% C and 0.2 wt% Si.

Fig. 13. Activation energy of heterogeneous nucleation as a function of inclusion radius.

original graph. From Fig. 13, it is shown that MDZ could make Ti$_2$O$_3$ particles much more effective for ferrite nucleation than other inert particles and comparable to austenite grain boundaries. Assuming that $\sigma_{\text{g}} = 0.85$ J/m$^2$ and $\sigma_{\text{g}}/\sigma_{\text{f}} = 0.72$ [53], however, the activation energy of austenite grain boundary will be more reduced than the value shown in Fig. 13. Therefore, even though we could not calculate each activation energy precisely because of the lack in the data of the interface energies of Ti$_2$O$_3$, it seems that the austenite grain boundaries are still more advantageous as nucleation sites, as long as $\sigma_{\text{g}} = \sigma_{\text{f}}$. If $\sigma_{\text{g}} > \sigma_{\text{f}}$ or other precipitates having lower $\sigma_{\text{f}}$ such as TiN are added on Ti$_2$O$_3$ particle surface [33,54], the particles could become more effective nucleation sites than the austenite grain boundaries. Meanwhile, it should be noted that the consideration above is based on the high temperature transformation products such as polygonal ferrite, which is transformed definitely by the diffusive mechanism. However, acicular ferrite is transformed in the temperature range where side plate ferrite can be transformed from austenite. In regard to the nucleation and growth mechanism of bainitic ferrite, there are controversies between the diffusive and the displacive mechanisms [55]. Even though the consideration of the nucleation of bainite based on the displacive mechanism [56,57] is beyond the scope of the present study, the increase in chemical driving force by MDZ formation might make Ti$_2$O$_3$ particles more effective than austenite grain boundaries.

4. Conclusion

By adding Ti, the microstructure in C–Mn steels was changed from side plate ferrite to acicular ferrite, which is due to the change in the main phase of the non-metallic inclusions. That is, as Ti content increases, the amorphous MnSiO$_3$ was substituted by Mn$_2$TiO$_4$ and MnTiO$_3$ and finally by Ti$_2$O$_3$. It was observed that there was MDZ near Ti$_2$O$_3$ particles, which was more significant when reheating temperature increased, even though sulfur content is very low. The MDZ is formed by the Mn absorption by Ti$_2$O$_3$ itself and makes Ti$_2$O$_3$ particles much more effective for intragranular ferrite nucleation than inert particles.

References

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