Characterization of Inclusions Formed in Ti-containing Steel Weld Metals

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The influence of Ti addition on inclusion characteristics and their effects on the nucleation of acicular ferrite has been studied using as-deposited bainitic-type GMA weld metals prepared with oxygen content constant. TEM analysis was carried out to identify the inclusion phases and to investigate the local variation in chemical composition around the inclusions. It was found that the Ti-containing phase changes from (Mn,Ti)-spinel oxide to Ti2O3 at ~0.07 wt.% Ti while Mn-depleted zone (MDZ) starts to form at ~0.02 wt.% Ti. This indicates that MDZs are induced by the formation of Ti2O3 as well as a large amount of (Mn,Ti)-spinel oxide. Due to MDZ formation, acicular ferrite can nucleate to a great extent, even from the amorphous surface of the Mn-silicate phase in the 0.02% Ti weld.

KEY WORDS: weld metal; non-metallic inclusion; acicular ferrite; Mn-depleted zone.

1. Introduction

Numerous studies have shown that the addition of Ti is effective for refining the weld microstructure through the formation of acicular ferrite (AF), thereby increasing the toughness of low alloyed steel welds.1–7) Evans2–5) reported that the microstructure of weld deposits is AF predominantly when the Ti content is between tens of ppm to about 600 ppm, in contrast to Ti-free welds where ferrite with a second phase (FS) is dominant. To understand such beneficial effects of Ti, extensive studies have been performed on various factors with special attention paid to the changes in inclusion characteristics with Ti addition. However, there is no general agreement on the contributing factors that affect the formation of AF in Ti-containing welds.

Hori and others8) reported that even a minimal addition of Ti (as low as 0.005 wt.%) can change the weld microstructure from FS to AF. This was found associating with the change in inclusion phase from amorphous Mn-silicate to spinel-type, crystalline (Mn,Ti)(Al,Ti)2O4. Pointing out the fact that the spinel structure has a very low misfit value with ferrite, they claimed that one of the major roles of Ti addition, related with AF formation, is the modification of the inclusion phase into a spinel structure. Alternatively, several researchers8–11) have reported that the addition of Ti produces a Ti-rich phase on the inclusion surface; this phase was presumed to be TiO, which is also known to promote AF nucleation due to its low lattice misfit with ferrite.12) It was further suggested that the minimum content of Ti necessary to form a Ti-rich phase on the inclusion surface is about 39 ppm.11)

More recently, Blais and others13) studied the inclusion chemistry and elemental distributions in the inclusions formed over a wide range of Ti contents. They found that Mn2TiO4 is present on the surface of amorphous Mn-silicate in a weld containing 28 ppm Ti. Because this weld exhibited a maximum content of AF, they believed the presence of Mn2TiO4 to be very efficient for the formation of AF. However, at 410 ppm Ti, a mixture of two distinct Ti-rich phases was found. These phases possessed different concentration of Mn, one of them being thought to be TiO. The present authors14,15) also found such dual phase inclusions in the weld of 720 ppm Ti, but those phases were all identified as Ti2O3. In addition, these inclusions were characterized to be fully surrounded by a manganese-depleted zone (MDZ), which has been reported to be effective for AF nucleation in wrought steels.16,17) This result implies that, when the Ti content is high enough to form Ti2O3-type inclusions, the major role of Ti addition is to form an MDZ in the surrounding matrix. This, in turn, facilitates the nucleation of AF from the inclusions.

As described above, the literature agrees that Ti addition greater than several tens of ppm is very effective for increasing the AF content in the weld microstructure despite the fact that different types of Ti-containing phases form depending on the Ti content of the weld. This indicates that the phases responsible for AF nucleation are still controversial. Hence, the basic aim of the present work is to identify how the inclusion phases vary with Ti content and to determine which metallurgical factors are responsible for AF formation in Ti-containing welds. In order to isolate the
effect of Ti, the concentrations of other elements including oxygen are kept constant.

2. Experimental Procedures

2.1. Weld Preparation

Five low C–Mn–Ni welds with different Ti concentrations were fabricated by bead-in-groove welding. To minimize the base metal dilution, the welds were prepared using a two-step welding technique, which has been described previously. First, five-pass buttering was performed using the gas metal arc welding (GMAW) process to fill the 10-mm-deep groove using ER 100S-grade wire and an Ar+20%CO₂ shielding gas. After buttering, a 5-mm-deep V-groove was machined at the center of the buttering weld metal. Prior to the second welding, pure Ti fibers (0.3 mm in diameter) were inserted into the groove to change the titanium concentration of the second weld. Using the same wire and shielding gas, single-pass bead-in-groove welding was performed with a rather high heat input (25 kJ/cm) to fill the groove and to melt the inserted Ti fibers. This resultant weld is referred to as the ‘experimental weld’. The weld thermal history was recorded by inserting the R-type thermocouple directly in the molten weld pool and the cooling time for 800–500°C, Δtₘₕₙₗ, was measured to be 10 sec. The number of fibers inserted varied between zero and four so that a total of five experimental welds (labeled as 0Ti, 1Ti, 2Ti, 3Ti, and 4Ti) were made. The number in each weld corresponds to the number of fibers inserted into the groove before depositing the experimental weld. The chemical uniformity within the experimental welds was checked for 4Ti weld by EPMA analysis and no difference in Ti concentration was found.

The chemical analysis of the experimental welds was conducted using an optical emission spectrometer (OES). Oxygen and nitrogen analyses were carried out by vacuum fusion method using LECO equipment. The chemical compositions of the five experimental welds are listed in Table 1. As shown in this table, the weld chemistry is very consistent with the exception of Ti, which varies from 0.002 wt.% for 0Ti to 0.091 wt.% for 4Ti weld. Such a wide range in Ti content, however, has little affected the oxygen concentration, which remains within the narrow range of 330–366 ppm. Due to this, the oxygen effect, which is also well-known to affect the AF content of ferritic welds, could be neglected in this study.

2.2. Metallographic Examination and Inclusion Analysis

Optical microscope (OM) examinations were carried out on experimental welds etched with a 2% Nital solution. From the optical micrographs taken at ×500 magnification, the proportion of AF was measured using a point-counting method. Using un-etched OM specimens, inclusion analysis was also performed using a field-emission scanning electron microscope (FE-SEM) to measure the size and number density of inclusions.

Extraction of inclusions was also performed using an electrolysis technique. The extracted particles were examined in a FE-SEM equipped with an energy dispersive X-ray spectrometer (EDX) at acceleration voltage of 20 kV to figure out the inclusion shape and the overall chemistry of the inclusions. EDX spectra were acquired at the center of the inclusions. Acquisition time and processing parameters were kept constant. Inclusion phases were further investigated with an analytical transmission electron microscope (ATEM) equipped with an EDX unit to identify the inclusion phases by selected area diffraction (SAD) analysis and to analyze their compositions. Thin foil specimens were prepared by twin-jet polishing followed by several steps of ion milling.

3. Results

3.1. Microstructural Analysis

Figure 1 shows the OM microstructures of the 1Ti and 3Ti welds. All welds display a mixed microstructure of AF and bainite, their proportions being varied with Ti content. AF content increased from about 50% for 0Ti and 1Ti to a maximum of 92% for 3Ti and then decreased to 62% for 4Ti. The results of the metallographic studies investigating the weld microstructure and those of the inclusion analysis are summarized in Table 2. This table shows no appreciable differences in inclusion size (0.48–0.42 μm) or number density (15.5–17.1×10³/μm²). This is not surprising given the fact that the oxygen contents of the welds are almost identical.

3.2. Inclusion Morphology and Composition

Typical morphologies of inclusions extracted from 0Ti, 1Ti, and 2Ti welds are shown in Fig. 2, from which the spherical nature of the inclusions was confirmed. Of note in these figures is the difference in surface roughness: very smooth for 0Ti and 1Ti welds but rather rough for the 2Ti weld. Inclusions from 3Ti and 4Ti welds also showed rough surfaces as much as 2Ti weld. For the extracted inclusions, the overall chemistry was quantitatively analyzed using an EDX in FE-SEM.

More than three inclusions in the size of 0.3–0.5 μm were

| ID   | C  | Si | Mn | Al | Ni | S  | Ti  | O   | N   |
|------|----|----|----|----|----|----|-----|-----|-----|
| 0Ti  | 0.07 | 0.20 | 1.31 | 0.005 | 1.80 | 0.006 | 0.002 | 347  | 126 |
| 1Ti  | 0.06 | 0.20 | 1.31 | 0.006 | 1.82 | 0.006 | 0.023 | 351  | 115 |
| 2Ti  | 0.06 | 0.21 | 1.29 | 0.006 | 1.83 | 0.006 | 0.049 | 330  | 113 |
| 3Ti  | 0.06 | 0.22 | 1.28 | 0.006 | 1.80 | 0.006 | 0.072 | 366  | 118 |
| 4Ti  | 0.06 | 0.23 | 1.28 | 0.006 | 1.82 | 0.006 | 0.091 | 353  | 114 |

Others: 0.24Cr–0.34Mo–0.20Cu
analyzed for each weld and then averaged to get a representative composition of inclusions. The calculated results are plotted in Fig. 3. In this figure, oxygen and sulfur were deliberately omitted because the oxygen peak has a severe convolution with the Ti L and Mn L peaks, and the sulfur content is very low (normally less than 1%). The contents of the remaining elements were then normalized to 100% and reported in units of atomic percentage (at.%).

In the 0Ti weld (0.002 wt.% Ti), Mn and Si are the main elements and are present in nearly equal atomic percentages. This suggests that the Mn-silicate is a major phase of the inclusions and is in the form of MnSiO₃. As the Ti content increases, its content in the inclusions also increases at the expense of Mn and Si. It is noteworthy that the Si content decreases more rapidly than Mn and eventually becomes zero when the Ti content increases to greater than 500 ppm (as in the 3Ti and 4Ti welds). In contrast, Al is rather insensitive to the addition of Ti, which may be because the Al oxidizes prior to the titanium reaction.

### 3.3. Inclusion Phases and MDZ Formation

As reported previously by several investigators, many different phases have been reported to be found even within a single inclusion, and their characteristics varied significantly with the Ti concentration of the weld. Among the large number of inclusions characterized by ATEM, the typical examples are described below.

#### 3.3.1. 0Ti Weld (0.002 wt.% Ti)

The STEM micrographs shown in Fig. 4 present two typical inclusions, similar in size (~0.5 μm) but different in nucleation ability. One acts as a nucleation site for AF (nucleant) and the other is non-nucleant. EDX mapping images for the nucleant are shown in Fig. 5. As shown in this figure, this inclusion contains as many as three different phases: a (Mn, Si)-rich oxide, Mn-S, and a Ti-rich oxide. The bulk phase is a (Mn, Si)-rich oxide, which is covered with thin layers of the other two phases. The atomic ratio between Mn and Si in the (Mn, Si)-rich oxide was about 1:1, which is in agreement with the results of the extracted inclusions (Fig. 3), and thus this phase is regarded as MnSiO₃. SAD analysis performed for many inclusions showed that MnSiO₃ is mostly amorphous and the Mn-S phase is cubic.
MnS. In contrast, Ti-rich layer was not present on the surface of the non-nucleant inclusion shown in Fig. 4(b) while other features were similar. Numerous TEM examinations indicated that the non-nucleant inclusions are mostly absent from the Ti-rich layer, suggesting that the Ti-rich layer plays an important role in AF nucleation in this weld.

Figure 6 shows the composition profiles of Mn, Ni, and Ti across the Ti-rich layer formed on the inclusion shown in Fig. 5. Like Ni, no appreciable change in Mn concentration takes place in the adjacent matrix. This indicates that no MDZ forms in the surrounding matrix. Due to the absence of the MDZ, it can be concluded that the Ti-rich layer itself makes the inclusion effective for AF nucleation in this weld.

Considering the effective role of the Ti-rich layer for AF nucleation,9–12 we attempted to identify the crystallographic nature of this layer using SAD and dark field (DF) analysis in TEM mode. We attempted this in a previous study but were unsuccessful.14 Figure 7 shows the results of SAD analysis performed for the Ti-rich layer, revealed as in a Ti-mapping image (Fig. 7(b)). The SAD pattern shown in Fig. 7(c) was indexed as a face-centered cubic (FCC) structure, and the planar distance of the (220) plane, \( d_{(220)} \), was calculated to be 0.300 nm. The DF image shown in Fig. 7(d) illuminates the Ti-rich layer very clearly. Among the Ti-containing FCC compounds, the \( d_{(220)} \) distance obtained is quite consistent with those of \( \text{MnTi}_2\text{O}_4 \) (0.304 nm) and \( \text{Mn}_2\text{TiO}_4 \) (0.306 nm). Either of these distances is well within the accuracy limit of SAD analysis. Therefore, the Ti-rich phase could be one of these two phases or a mixture of both in a solid solution. However, a third phase, commonly referred to as galaxite (\( \text{MnAl}_2\text{O}_4 \)), also has a cubic spinel
structure with a $d_{220}$ of 0.293 nm. Thus, a possible presence of galaxite phase in the form of Mn(Al,Ti)$_2$O$_4$ cannot be excluded since a part of this layer appears to contain a substantial amount of Al, as shown in the Ti and Al mapping images in Fig. 5.

3.3.2. 1Ti Weld (0.023 wt.% Ti)

Figure 8 shows the EDX maps for a nucleant inclusion found in the 1Ti weld. In contrast to the 0Ti weld, the Ti-rich phase turns out to be in the form of large particles that are fully enveloped with a Mn-silicate phase. As a consequence, the Ti-rich phase has negligible contact with the iron matrix. Overlapping with the Mn image, the Ti-rich phase is found to consist of two distinct phases with different Mn contents. For example, the Ti-rich particle marked as A in the STEM image contains less Mn compared to the particle marked as B. The composition of each phase analyzed by EDX is listed in Table 3, along with that of Mn-silicate phase marked as C in the STEM image, showing that the Ti:Mn atomic % ratio of particle A is about 3:1 while that of B is 1:1. In addition, the Mn content in the Mn-silicate phase (point C) is very low, resulting in an Si:Mn atomic % ratio of 7:2. This is very different from that observed in the 0Ti weld (nearly 1:1). Another phase observed in this inclusion was MnS; this usually forms on the surface of Mn-silicate, as shown in the S and Mn maps.
Figure 9 shows another inclusion containing several Ti-rich particles; one of these was used for SAD analysis. The SAD pattern of particle B (high-Mn Ti-oxide) was indexed as an FCC structure; thus, this phase can be indexed as either MnTi$_2$O$_4$ or Mn$_2$TiO$_4$, both of them being identical in crystal structure and lattice parameter as shown in Table 4. The other phase marked as C is amorphous Mn-silicate, as shown in Fig. 9(c). Considering the large range of the Ti:Mn atomic % ratio (from 3:1 to 1:1), we concluded that the Ti-rich particles are a solid solution mixture of MnTi$_2$O$_4$ and Mn$_2$TiO$_4$, and that their relative proportion varies with the Mn content in the Ti-rich particles. Hereinafter, the mixture of MnTi$_2$O$_4$ and Mn$_2$TiO$_4$ will be referred to as (Mn,Ti)-spinel oxide.

In order to confirm the presence of the MDZ, EDX line scan analysis was performed for the inclusion analyzed in Fig. 8 in the direction shown in the inserted STEM image of Fig. 10. Comparing the Mn concentration profile with that of Ni, it is quite evident that Mn depletion has occurred in the matrix adjacent to the Mn-silicate phase; no change in the Ni concentration occurs in this region. The width of the MDZ is estimated to be about 70 μm. A total of six inclusions, including one non-nucleant, were examined. All of these were found to be accompanied by an MDZ in the adjacent matrix of the Mn-silicate phase. Therefore, it can be concluded that MDZ formation is responsible for AF formation in this weld because the amorphous interface cannot nucleate AF by itself. 8)

### Table 3. Results of EDX point analysis (at.%) performed at the locations shown in the STEM image of Fig. 8.

| Location | Ti | Mn | Si | Al |
|----------|----|----|----|----|
| A        | 65 | 24 | 3  | 6  |
| B        | 45 | 45 | 3  | 7  |
| C        | 3  | 24 | 60 | 13 |

3.3.3. 2Ti Weld (0.049 wt.% Ti)

Figure 11 shows the EDX mapping images obtained for a typical inclusion found in the 2Ti weld. Basically, the inclusion phases formed in this weld are the same as those in 1Ti except for an increased proportion of the Ti-rich oxide at the expense of Mn-silicate. As a result, a portion of the Ti-rich phase is able to directly contact the iron matrix. This was not possible for the inclusions of 1Ti weld. SAD analyses performed on the high-Mn (region A) and the low-Mn (region B) Ti-oxides, were all indexed as FCC spinel structure, suggesting that they are (Mn,Ti)-spinel oxide for the same reason explained above.

MDZ formation was also confirmed as shown in Fig. 12. In Fig. 12(a), two lines are drawn for scanning: Line 1 was formed across the surface of the Ti-rich phase, and Line 2 crosses the Mn-silicate phase. As shown in the results of Figs. 12(b) and 12(c), MDZ formation takes place regardless of the inclusion phase with a width of about 150 μm, which is much wider than that of 1Ti weld. This difference appears to be caused by the increased amount of (Mn,Ti)-spinel oxide and may explain why the 2Ti weld has a higher content of AF than the 1Ti weld (Table 2).

### Table 4. Crystal structure and lattice parameters of Ti-containing oxides observed in the weld inclusions.

| Oxides     | JCPDS no. | Space group     | Lattice parameter (nm) | Weld metals |
|------------|-----------|-----------------|------------------------|-------------|
| MnTi$_2$O$_4$ | 73-0580   | Cubic (Fd$ar{3}$m) | a = b = c = 0.8600    | 0Ti, 1Ti, 2Ti |
| Mn$_2$TiO$_4$ | 74-2290   | Cubic (Fd$ar{3}$m) | a = b = c = 0.8679    | 0Ti, 1Ti, 2Ti |
| MnTiO$_3$   | 29-0902   | Rhombohedral (R$ar{3}$) | a = b = 0.5139, c = 1.4290 | 3Ti, 4Ti |
| Ti$_2$O$_3$ | 43-1013   | Rhombohedral (R$ar{3}$c) | a = b = 0.5158, c = 1.3611 | 3Ti, 4Ti |

**Figure 9.** Results of SAD analysis performed on an inclusion found in the 1Ti (0.0023 wt.%) weld: (a) BF image and (b and c) SAD patterns taken from regions B and C, respectively.
3.3.4. 3Ti Weld (0.072 wt.% Ti)

The inclusion characteristics of this weld have been reported previously,\textsuperscript{14,15} thus this study simply reaffirms the previous results. The inclusions of this weld were composed mainly of two Ti-oxides having different Mn contents and Al-oxide along with a minimal amount of Mn-silicate. Through SAD analysis, the Ti-oxides were all re-identified as Ti$_2$O$_3$ regardless of Mn content, and the Al-oxide was determined to be Al$_2$O$_3$.

Reconfirmation of MDZ formation was made along the line shown in the inserted STEM image of Fig. 13. In addition to Mn and Ni, an Al profile is added to visualize the Al-rich layer formed on the inclusion surface. This result reaffirms the MDZ formation in this weld associating with Ti$_2$O$_3$. The MDZ width is measured to be over 150 $\mu$m.

![Fig. 11. EDX elemental mapping images of a typical inclusion found in the 2Ti (0.0049 wt.%) weld.](image1)

![Fig. 12. Results of EDX line scanning in two different directions: (a) STEM image of an inclusion in 2Ti (0.0049 wt.%) weld and (b and c) concentration profiles of Mn and Ni following lines 1 and 2, respectively.](image2)

![Fig. 13. Results of EDX line scanning for a 3Ti (0.0072 wt.%) weld inclusion along the direction shown in the inserted STEM image.](image3)
3.3.5. 4Ti Weld (0.091 wt.% Ti)

As shown in Fig. 14, the inclusion phases formed in the 4Ti weld are basically the same as those of the 3Ti weld: Al-oxide and Ti-oxide. The Mn-silicate phase was barely seen in the inclusions of this weld. As shown in SAD patterns, the Al-oxide is indexed as $\gamma$-$Al_2O_3$ and the Ti-oxide is designated as $Ti_2O_3$. In addition to these phases, TiN phase was often observed on the $Ti_2O_3$ inclusions and appeared to promote AF nucleation. TiN is a phase having good lattice matching with ferrite and has been believed to be effective for AF nucleation.\textsuperscript{19,20)}

Figure 15 shows the Mn and Ni concentration profiles near the Ti-oxide, demonstrating the presence of an MDZ in this inclusion. Of note in this result is that the Mn content in the Ti-oxides is much lower and the MDZ width is narrower than those of the 3Ti weld.

4. Discussions

The weld metals studied in this investigation have nearly identical chemical composition with the exception of Ti content. However, they exhibit clear differences in AF content, indicating that the inclusion characteristics varied with Ti content are related to the formation of AF microstructure. Table 4 summarizes the Ti-containing phases observed in the present welds along with their crystal structure and lattice parameters. The most popular inclusion characteristics (or mechanisms) that have been suggested as being responsible for AF nucleation are the low lattice misfit of the inclusion phase with the ferrite and the MDZ formation in the vicinity of the inclusions.

Characterization of the inclusions found in the 0Ti weld (0.002 wt.% Ti) shows that Mn$Ti_2O_4$ layer is often present on the surface of the Mn-silicate bulk without forming an MDZ but is rarely found on the non-nucleant inclusions. Based on these results, it was concluded that the presence of this Mn$Ti_2O_4$ layer is a major factor that causes inclusions to nucleate AF. Unfortunately, this study was unable to elucidate the mechanism by which this phase promotes AF nucleation. However, as MDZ mechanism was ruled out for this weld, good lattice matching can be considered as a possible mechanism; the lattice misfit between Mn$Ti_2O_4$ and ferrite has been reported to be 6.4\%,\textsuperscript{19} which is close to those of TiO (3.1\%) and TiN (3.0\%).\textsuperscript{21)} Clearer evidence has been reported by Okazawa and others,\textsuperscript{22)} demonstrating that the phase identified as Mn$Ti_2O_4$ has a Baker-Nutting orientation relationship with the bainite matrix. Such an experimental result strongly supports the idea that the low lattice misfit is a major mechanism when the inclusions are covered with a Mn$Ti_2O_4$ layer, like in the 0Ti weld.

Accordingly, if Mn$Ti_2O_4$ is fully wrapped with amorphous Mn-silicate and thus no longer contacts the steel matrix like the inclusions of the 1Ti weld, these inclusions could not nucleate AF because the amorphous phase is known to be non-nucleant for AF.\textsuperscript{81) Nonetheless, the 1Ti weld contains as much AF as the 0Ti weld (Table 2). Therefore, in order to explain the relatively high content of AF recorded in the 1Ti weld, an MDZ mechanism need to be considered.

The MDZ is a local depletion of Mn around the inclu-
sions, which can increase the chemical driving force for AF nucleation. As for the origin of the MDZ, two different viewpoints have been discussed in the literature. One is that the MDZ can develop when MnS particles precipitate on the surfaces of inclusions during cooling due to the decreased solubility of S in the iron matrix. In order to produce an MDZ through this process, newly precipitated MnS particles must be formed on the surfaces of the inclusions. However, as shown in Fig. 2, 0Ti inclusions had mirror-like clean surfaces and no precipitated particles were observed on the inclusion surfaces. Thus, the MnS layer shown in Fig. 5 is believed to be extracted from the Mn-silicate due to the decreased solubility of MnS in the slag phase upon cooling.23)

The other possible mechanism for MDZ formation is the absorption of Mn atoms by Ti2O3, which is reported to have many cation vacancies.24) Due to its association with Ti2O3 inclusions, numerous experimental evidences for MDZ formation have been reported in Ti-killed steels.16,17,25) Accordingly, this mechanism can explain why the MDZ forms in the 3Ti and 4Ti welds; these welds contain Ti2O3-dominant inclusions. However, this mechanism is still not relevant to the MDZs found in the 1Ti and 2Ti welds because the Ti-oxide formed in these welds is (Mn,Ti)-spinel oxide, not Ti2O3. Therefore, we propose a new mechanism to explain how the MDZ can be formed in association with the formation of spinel (Mn,Ti)-spinel oxide.

In 1Ti weld, as shown in Fig. 8, (Mn,Ti)-spinel oxide particles are completely enveloped with an Mn-silicate phase, which indicates that these particles start to form within a slag inclusion that contains Mn, Ti, and Si as the major metallic elements. Upon cooling, these particles would grow by getting Ti and Mn from the slag; therefore, the Mn content of the remaining slag decreases continuously during cooling. As a result, the final composition of the Mn-silicate slag would be very low in Mn but very high in Si. As can be seen in Table 3, the atomic ratio between Mn and Si in the Mn-silicate phase of the 1Ti weld is about 1:3. If a stable phase of Mn-silicate is assumed to be some form of MnSiO3 whose atomic ratio of Mn:Si is 1:1,26 then the remaining slag needs to take Mn from the neighboring phases (e.g., from the steel matrix). In other words, some Mn transfers from the steel matrix to the slag phase through a slag-metal reaction that occurs at the interface. Once this happens, Mn depletion takes place in the surrounding region of Mn-silicate phase. In order to support this hypothesis, we are currently conducting thermodynamic calculations.

5. Conclusions

The present study was performed to understand how the inclusion characteristics vary with the Ti content in welds. Special attention was made to identify the Ti-containing phases and to confirm the MDZ formation. The main conclusions are as follows:

(1) At a low Ti concentration of 0.002 wt.%, thin layer of MnTi2O4 is found on the surfaces of the MnSiO3 inclusions and this phase is believed to promote AF nucleation. As for the possible mechanism for AF nucleation, the low lattice misfit was proposed following the results of previous investigators.

(2) At an intermediate level of Ti, between 0.02~0.5 wt.%, (Mn,Ti)-spinel oxide becomes a dominant phase. However, this is wrapped by a Mn-silicate phase such that the spinel phase is either barely exposed at 0.02 wt.% Ti or partially exposed to the inclusion surface at 0.05 wt.% Ti. Regardless of the morphological differences, all of the inclusions are found to be surrounded with an MDZ. This implies that AF can be nucleated to a great extent, even from the surface of an amorphous Mn-silicate phase, in the 1Ti (0.023 wt.% Ti) weld. Based on these observations, an MDZ mechanism was introduced to explain the AF formation in the intermediate-Ti welds.

(3) At a high Ti concentration over 0.07 wt.%, Ti2O3-dominant inclusions are formed with an MDZ. The MDZ width varies to some extent as the Ti content of the welds changes. Thus, MDZ formation can explain the high content of AF recorded in the high-Ti welds, as well as the change in AF content with varying Ti content. The exact mechanism for Mn diffusion into Ti2O3 inclusions has not been determined; however, based upon the results of other researchers, it is considered to be caused by the intrinsic feature of Ti2O3 possessing a large amount of cation vacancies.

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