Effect of Ti Addition on Weld Microstructure and Inclusion Characteristics of Bainitic GMA Welds

Jun Seok SEO,1) Hee Jin KIM2)* and Changhee LEE3)


(Received on January 8, 2013; accepted on February 5, 2013)

The effects of titanium content on weld microstructure and inclusion characteristics have been studied using the two different bainitic welds fabricated to have similar oxygen content. Analytical transmission electron microscopy analysis with thin foil specimens was carried out to investigate inclusion characteristics focusing on the crystal structure and the chemical features of the constituent phases. Then, these results were related with the proportion of acicular ferrite measured under an optical microscope. For a weld containing 0.002 wt.% Ti, a Ti-rich oxide layer containing manganese is present on the surface of amorphous inclusions and appears to be responsible for acicular ferrite appreciably formed in the bainitic structure, ~50%. When the titanium content increases to 0.07 wt.% Ti2O3 inclusions were formed accompanying with manganese-depleted regions and eventually results in a significant increase in acicular ferrite content over 90%. Therefore, the manganese depletion developed along with the formation of Ti2O3 inclusions is concluded to be a possible mechanism for acicular ferrite nucleation in the high titanium welds.

KEY WORDS: acicular ferrite; nonmetallic inclusion; titanium addition; nucleation mechanism; manganese depletion.

1. Introduction

It is well known that nonmetallic inclusions play an important role in the evolution of microstructures of steel weld metals since they can act as the active nucleation sites for acicular ferrite plates.1–3) The presence of sufficient number of inclusions, however, does not guarantee that there will be a high proportion of acicular ferrite in the weld microstructure because the nucleation potency of inclusions can vary to a great extent depending on many other factors relating with geometric and chemical features of inclusions.4–8) As for the chemical features, titanium is particularly interesting since its addition has been numerously reported to promote the formation of acicular ferrite microstructure.4–6,8–15)

In 1970’s, Ito and Nakanishi9) reported that titanium addition over 0.03 wt.% could improve weld metal toughness significantly accompanied with the development of a fine acicular ferrite microstructure. Subsequently, X-ray diffraction analysis was carried out on the electrolytically extracted inclusions of Ti-B containing weld metal and showed that a large proportion of inclusions comprised with TiO, which in turn was believed to be a phase responsible for acicular ferrite nucleation.10) Since then, many other workers11–22) have observed the presence of titanium-rich phase on the inclusion surface when the welds contained titanium to some extent and this phase was reasonably considered to be TiO, TiN or Ti(C,N). Recently, researchers in Osaka University identified the titanium-rich surface layer found in the weld of 0.02 wt.% titanium as being titanium mono-oxide (TiO) conclusively by detailed electron diffraction analysis.23,24) In contrast, some researchers25) have reported that the addition of titanium promoted the crystallization of inclusions, changing from amorphous manganese silicate to crystalline galaxite (MnO·Al2O3), and resulted in weld microstructure predominant with acicular ferrite.

Those phases mentioned above (TiO, TiN, MnO·Al2O3) are the ones that exhibit a good lattice matching with bcc ferrite in a certain crystallographic orientation5,7,15) so this fact has been referred to explain why they have high potency for acicular ferrite nucleation and how titanium addition facilitates the formation of acicular ferrite. Furthermore, as those three phases were found to be the most effective nucleants for acicular ferrite in weld metals, ‘good lattice matching with bcc ferrite’ has been suggested to be the most likely mechanism for nucleation of acicular ferrite in weld metals.26,27)

In 1990’s, Evans and his colleagues13,14,28,29) performed a series of systematic studies on the effect of titanium content in C–Mn steel welds. They found that the addition of titanium in the order of ~20 ppm (~0.002 wt.%) could induce a dramatic increase in acicular ferrite content to over 60% and a further addition up to 0.05% did not affect acicular ferrite content significantly. Later, in the weld containing 28 ppm

* Corresponding author: E-mail: kimhj@kitech.re.kr
DOI: http://dx.doi.org/10.2355/isijinternational.53.880
titanium, a discrete island of titanium-rich phase identified as MnTi₂O₄ was found to have formed on the inclusion surface and was believed to be responsible for the high content of acicular ferrite formed in this weld.³⁰ However, the mechanism by which MnTi₂O₄ promoted acicular ferrite remained unclear because the misfit value between the lattice of MnTi₂O₄ and ferrite was 6.4%, relatively high compared with the values of TiO (3.0%), TiN (4.6%) and MnO-Al₂O₃ (1.8%).

As described above, the literature today suggests that there is reasonable agreement on the beneficial effect of titanium addition for promoting acicular ferrite formation over a wide range of concentration from about 0.002 to 0.05 wt.%, but the exact nature of inclusions responsible for acicular ferrite nucleation is controversial. It is also worth to note that very little work has been done on the welds of high titanium concentration over 0.05 wt.%²⁸,³¹ and no detailed studies on inclusion characteristics for such a high titanium weld.³² In this context, the aim of the present study was the characterization of weld microstructures and inclusions formed in the two welds which are distinctively different in titanium concentration, i.e. 0.002 and 0.07 wt.%. Through the precise characterization of inclusion chemistry and constituent phases, it was expected that possible conclusions could be drawn as to which titanium-containing phases are favorable for the formation of acicular ferrite and which mechanism is applicable for those inclusions. In order to access the effect of titanium content itself, other elements including oxygen were intended to be constant in their concentrations and the aluminum content was kept to a minimum.

2. Experimental Procedures
2.1. Preparation of Experimental Welds

The welds investigated in this study were all obtained with bead-in-groove GMA welding. As described in the previous report,²² a two-step welding was performed to minimize the base metal dilution. The first weld was to deposit five buffering layers in the 10 mm deep V-groove machined on the steel plate. The second weld, referred to as an experimental weld, was subsequently deposited with a single run in the 5 mm deep groove made at the center of the buffered layers. As shown in Table 1, the welding wire selected for the present investigation was the one that is very low in titanium and aluminum contents, but relatively high in other alloying elements for satisfying the tensile properties required for AWS ER100S. All the welds were deposited with Ar+20%CO₂ shielding gas. The experimental welds were made with a rather high heat input (25 kJ/cm) to fill the groove completely by single pass welding.

In order to fabricate a high titanium weld, a small slot was machined at the bottom of the 5 mm deep groove as shown in Fig. 1 and then pure titanium fibers were inserted before depositing the experimental weld. Referring to the data of pre-experiments, three fibers of 0.3 mm in diameter were inserted to get a high-titanium weld containing about 0.07 wt% titanium. This weld was designated as '3Ti weld' while that made without titanium fiber was '0Ti weld'.

At the center of the experimental weld, the chemical analysis was carried out using an optical emission spectrometer (OES) except oxygen and nitrogen being determined by the vacuum fusion method.

2.2. Metallographic Examination and Inclusion Analysis

Metallographic examinations were carried out by optical microscope (OM), and the proportion of acicular ferrite was measured by a point-counting method from the micrographs taken at ×500 magnification from the specimens etched with 2% Nital solution. Nonmetallic inclusions were also observed by scanning electron microscope (SEM) and were analyzed to measure their size and density. In SEM analysis, backscattered electron images were taken at a magnification of ×10000 to account for the small particles of diameters down to 0.01 μm. To obtain reliable data, a minimum of 600 particles was counted in each weld.

Inclusion phases and chemistry were investigated by analytical transmission electron microscope (ATEM) in various modes. Thin foil specimens were prepared by twin-jet polishing followed by several steps of ion milling and examined in ATEM operating at 200 kV. Twin-jet polishing was performed in a solution of 5% perchloric acid+95% methanol and at 228 K. In order to facilitate the phase identification, the elemental mapping and line scanning were carried out using energy dispersive X-ray spectrometry (EDX) in STEM mode. In addition, electron energy loss spectroscopy (EELS) was employed to identify the presence of light elements such as carbon, nitrogen and oxygen.

2.3. Mechanical Tests

The Vickers hardness test was performed on both welds using a 98 N (10 kg) load. Five measurements were made on each specimen and the average values were recorded. Half size (10 × 5 mm) Charpy V-notch specimens were machined with a notch located at the center of the experimental weld metal. Impact tests were performed at various temperatures spaced over the range of 77 K to room temperature to construct full ductile-to-brittle transition curves and at least one specimen was tested at each of the testing temperatures.

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Al</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Metal</td>
<td>0.04</td>
<td>0.25</td>
<td>1.56</td>
<td>0.008</td>
<td>0.004</td>
<td>0.30</td>
<td>0.23</td>
<td>0.06</td>
<td>0.04</td>
<td>0.018</td>
</tr>
<tr>
<td>Welding wire</td>
<td>0.06</td>
<td>0.32</td>
<td>1.53</td>
<td>0.006</td>
<td>0.007</td>
<td>0.26</td>
<td>1.93</td>
<td>0.34</td>
<td>0.01</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Fig. 1. Preparation of the weld specimens for high titanium (3Ti) weld.
3. Results

3.1. Chemical Composition

The chemical compositions of both welds are given in Table 2. The weld made without fiber addition (0Ti weld) recorded a titanium concentration of 0.002 wt.% that is somewhat lower than that of welding wire (0.005 wt.%). By adding three titanium fibers (3Ti weld), the titanium concentration increased to 0.072 wt.% but with a minimal variation in other oxidizing elements such as silicon, manganese and aluminum. Of importance is the oxygen content that is almost identical in both welds: 347 ppm in 0Ti and 366 ppm in 3Ti weld. This result is in disagreement with the findings of the previous results reported for the SMAW welds\(^{13,14,28,29}\) in which the oxygen content decreased from ~500 to ~250 ppm when the titanium concentration increased from 0.006 to 0.04 wt.%. This discrepancy may result from the difference in welding processes and in the method of adding titanium; SMAW welds being made by adding titanium powders into the electrode coatings and the present GMAW welds by inserting titanium fibers in the groove. However, the constant oxygen content recorded in the present welds allowed us to investigate the titanium effect at the same level of oxygen content, which was not possible in the previous studies performed with SMAW welds.

3.2. Weld Microstructure and Mechanical Properties

Optical and SEM micrographs taken from both welds are shown in Fig. 2. Due to the high concentrations in Ni, Cr and Mo (Table 2), the formation of primary ferrite (PF(G)) along austenite grain boundaries was suppressed completely. Instead, what appeared in 0Ti weld is a mixed microstructure of acicular ferrite and bainite and that in 3Ti weld is predominantly acicular ferrite. This fact was demonstrated that the acicular ferrite content of 0Ti was 50% and that of 3Ti reached 92%. Nonetheless, little change in weld hardness was observed: the hardness of 0Ti and 3Ti weld being recorded as 269 and 266 Hv\(_{10}\), respectively.

Such a change in weld microstructure is well reflected in the result of impact toughness test, as shown in Fig. 3. From the fact that the DBTT of 3Ti weld is much lower than that of 0Ti weld, the grain refinement effect with the increased proportion of acicular ferrite can be realized. It is also noted in this result that the upper shelf energy of 3Ti weld is much higher than that of 0Ti weld, implying that acicular ferrite have a profound influence on the fracture behavior of ductile mode as well.

3.3. Inclusion Size and Density

Table 3 shows quantitative results of the geometric features of inclusions that were examined under SEM. The inclusion size was represented as the average diameter of inclusion particles imaged in BSE mode. As mentioned earlier, the present SEM analysis was performed at a magnification of \(\times10000\) and thus the inclusions with a diameter down to 0.01 \(\mu m\) could be counted for the inclusion density measurement. From this table, it can be realized that both factors are nearly constant and are little affected by titanium content. This fact certainly resulted from the similar oxygen content of the welds studied, as shown in Table 2. Hence, the microstructural difference shown in Fig. 2 cannot be explained relating with the geometric factors of inclusions and thus the balance of this article focuses on the chemistry and constituent phases of inclusions of both welds.

### Table 2. Chemical composition of the weld metals, mass pct except oxygen and nitrogen (ppm).

<table>
<thead>
<tr>
<th>ID</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Al</th>
<th>Ni</th>
<th>S</th>
<th>Ti</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0Ti</td>
<td>0.07</td>
<td>0.20</td>
<td>1.31</td>
<td>0.005</td>
<td>1.80</td>
<td>0.006</td>
<td>0.002</td>
<td>347</td>
<td>126</td>
</tr>
<tr>
<td>3Ti</td>
<td>0.06</td>
<td>0.22</td>
<td>1.28</td>
<td>0.006</td>
<td>1.80</td>
<td>0.006</td>
<td>0.072</td>
<td>366</td>
<td>118</td>
</tr>
</tbody>
</table>

Others: 0.24Cr–0.34Mo–0.20Cu

### Table 3. Calculated results of inclusion size and density.

<table>
<thead>
<tr>
<th>ID</th>
<th>Inclusion size, (\mu m)</th>
<th>Inclusion density, (10^3/\text{mm}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0Ti</td>
<td>0.461</td>
<td>14.7</td>
</tr>
<tr>
<td>3Ti</td>
<td>0.403</td>
<td>15.1</td>
</tr>
</tbody>
</table>
of a number of discrete phases. **Figure 4** shows an example of three constituent phases found in an inclusion of 0Ti weld. The bulk phase rich in manganese and silicon is partly enveloped by thin layers of titanium-rich layer and also by sulfur-rich layer. As the bulk phase has a uniform distribution of manganese, silicon and aluminum, it can be regarded as a single phase of manganese silicate (MnO·SiO2). In addition, this phase was confirmed to be purely amorphous through the SAD analysis. This type of amorphous inclusions has been reported by many researchers not only in the welds nearly free in titanium22,25,33) but also in the titanium-containing welds21,34). Of great importance in this inclusion is the formation of titanium-rich layer on the inclusion surface. Not all inclusions exhibited the titanium-rich layer, but only four out of ten inclusions examined were partly coated with titanium-rich layer. Considering the previous findings that both amorphous and sulfide phase are not effective for acicular ferrite,6,22,25,30,35,36) such a titanium-rich layer seems to play a favorable role for the formation of acicular ferrite in this weld. Thus, further examination on the chemical nature of this layer was performed. Firstly, EDX line scanning was performed across the titanium-rich layer and the profiles for titanium and manganese are shown in **Fig. 5**. These results show that the titanium-rich layer is about 30 nm in thickness and is very rich in manganese as well. Secondly, ELLS analysis was performed at the titanium-rich layer and two other locations nearby, and their results are shown in **Fig. 6**. The spectrum taken from surface layer (point B) shows that, among the light elements, oxygen is the only element present in this layer. Other elements such as carbon and nitrogen are totally absent, indicating no nitride or carbide formed. Based on the qualitative results described above, the titanium-rich layer shown in Fig. 4 was concluded to be a certain type of manganese-titanium oxide, i.e. (Ti,Mn)-oxide. As the (Ti,Mn)-oxide possesses a variety of crystal structures (e.g., MnTiO2, Mn2TiO4 and MnTi2O5), it would have been valuable to obtain the exact nature of the
(Ti,Mn) oxide. However, it could not be achieved because the number of diffracted spots from this layer was not enough for clear identification.

Blas et al. have observed, in the SMA welds containing 0.0028 wt.% titanium, a similar phase formed on the inclusion surface and they regarded this phase as MnTi2O4 following the chemistry obtained by semi-quantitative analysis. They also could predict its formation by thermo-chemical calculation but the conclusive evidence for MnTi2O4 has not been given.

EDX elemental maps taken from a typical inclusion of 3Ti weld are shown in Fig. 7. These maps illustrate that the inclusion comprises two distinct phases, i.e. titanium-rich phase and aluminum-rich phase. The titanium-rich phase can be divided further into two due to the difference in manganese content. EDX point analysis showed that the manganese concentrations in region C was about 5 at.% while that in region D is about 2 at.%. Figure 8 shows the results of SAD analysis performed on each phase, demonstrating that the aluminum-rich phase is γ-Al2O3 having FCC structure and titanium-rich phases are Ti2O3 regardless of manganese content.

In the literature, Ti2O3 is generally agreed as effective nucleant as it can develop the manganese depleted zone (MDZ) near the inclusion surface. In order to confirm whether MDZ is present in the present inclusions, EDX line scanning across the Ti2O3/Fe-matrix was performed and the results are shown in Fig. 9. This result clearly demonstrates the presence of MDZ in the adjacent matrix of inclusion. Note that no silicon depletion occurs, consistent with the zero concentration of silicon in inclusion. Figure 10 is another example showing the typical MDZ profile across the whole inclusion, which was verified on five separate inclusions. Therefore, it could be concluded that the higher...
content of acicular ferrite in 3Ti weld is attributable to the development of MDZ around the Ti$_2$O$_3$ inclusions.

4. Discussion

There are various factors that control the nucleation behavior of acicular ferrite in ferritic welds such as (1) chemical composition or hardenability of weld metal, (b) cooling rate, (c) austenite grain size, (d) inclusion characteristics. Once a suitable condition has been established for the first three factors, then the only factor remained are the inclusion characteristics. Regarding acicular ferrite nucleation, two different aspects of inclusion characteristics have been widely investigated; (1) geometric factors$^{3,39–43}$ such as inclusion size, number density and volume fraction and (2) chemical factors$^{4,6,44}$ such as inclusion chemistry and constituent phases. The present study employs the welds that are similar in oxygen content to minimize the effect of geometric factors but greatly different in titanium concentration to maximize the chemical factors, as shown in Table 2. This fact allows us to evaluate the resultant difference in weld microstructure shown in Fig. 2 in terms of the corresponding change in chemical factors with titanium addition.

Based on the results of this and previous studies,$^{14,29}$ it could be said that the promotion of acicular ferrite can be accomplished in a wide range of titanium concentration from 0.001 to 0.07 wt.% However, the exact nature of inclusions that appears to be responsible for acicular ferrite nucleation is certainly different depending on the titanium concentration, as has been emphasized by Blais et al.$^{30}$

In 0Ti weld containing 0.002 wt.% titanium, an appreciable amount of acicular ferrite was observed to be formed and appeared to be attributable to (Ti,Mn) oxide layer developed on the inclusion surface as illustrated in Figs. 2 and 4. Although TiO is most commonly encountered in the inclusions of titanium-containing welds, (Ti,Mn) oxides have been often reported to be formed as well.$^{15,30,45–47}$ For example, at extremely low titanium concentration (~28 ppm) similar to that of 0Ti weld, Mn$_2$TiO$_3$ phase was reported to be found on the inclusion surface and was believed to make inclusions very effective for acicular ferrite nucleation.$^{30,47}$ It therefore seems that the presence of (Ti,Mn) oxide on the inclusion surface is quite effective in promoting the nucleation ability of inclusions. As for nucleation mechanism, lattice matching is a popular explanation when TiO is formed on the inclusion surface. However, rhombohedral Mn$_2$TiO$_4$ and other (Ti,Mn) oxides should not be expected to offer good lattice matching with ferrite so the lattice matching mechanism would not be appropriate for the (Ti,Mn) oxides. Accordingly, Blais et al.$^{30}$ have discussed several other possibilities including the lower surface energy associating with the formation of Mn$_2$TiO$_4$ particles on inclusion surface. Indeed, calculation made by Suzuki et al.$^{42}$ showed that interfacial energy between Ti$_2$O$_3$ and bcc-iron was much lower than that between Al$_2$O$_3$ and bcc-iron, and this fact was used to explain the acicular ferrite nucleation from MDZ-free Ti$_2$O$_3$ particles. They further demonstrated that MnTiO$_3$ particles also have an ability to form acicular ferrite, suggesting the nucleation potential of inclusions increases to some extent when the inclusions have titanium-containing phases. This fact and the present result strongly suggest that (Ti,Mn) oxide possesses low interfacial energy with bcc-iron intrinsically and thus can improve the nucleation ability of inclusions when they are coated with (Ti,Mn) oxide. However, the true mechanism by which (Ti,Mn) oxides facilitate the nucleation of acicular ferrite is still under consideration and obviously requires further investigations with a much wider range of stoichiometry.

On the other hand, the increase in titanium concentration from 0.002 to 0.072 wt.% gives rise to a substantial increase in the proportion of acicular ferrite as a result of the formation of inclusions comprising predominantly with Ti$_2$O$_3$ surrounded by MDZ. In the literature, the experimental evidence of manganese-depletion in the vicinity of Ti$_2$O$_3$ has been well reported in steel plates$^{37,38,48}$ but, to the best of the authors’ knowledge, no reports showing MDZ have been made for the weld deposits. This is probably because the weld metals previously studied were low in titanium concentration so that inclusions could not contain a large amount of Ti$_2$O$_3$ phase. The diffusion distance (\(\sqrt{D}t\)) of manganese in austenite held at 1200°C for 1 sec is calculated to be ~100 nm and thus the MDZ having a width shown in Fig. 10 can be developed during the cooling stage of weld thermal cycle. Once MDZ is formed in the vicinity of inclusions, it increases the chemical driving force for the austenite-to-ferrite transformation around the inclusions and thus promotes nucleation of intragranular ferrite at the Ti$_2$O$_3$ inclusions, which in turn gives rise to the weld microstructure predominant with acicular ferrite, as can be seen in Fig. 2.

In regard to the origin of MDZ formation around Ti$_2$O$_3$ particles, there are two different viewpoints. One is that, as Ti$_2$O$_3$ has a significant amount of cation vacancies,$^{49}$ it can absorb manganese atoms from the surrounding iron matrix by itself.$^{37,38}$ The other possibility is the enhancement of manganese absorption to Ti$_2$O$_3$ inclusion through the phase transformation from Ti$_2$O$_3$ on cooling.$^{50}$ Thermodynamic calculation suggested that equilibrium manganese content in titanium oxide increased by the phase change from the Ti$_2$O$_3$ (stable phase at high temperature), to Ti$_2$O$_3$ (stable phase at low temperature) so that MDZ could be developed easily when such a phase change took place on cooling.
5. Conclusions

For the two bainitic GMA welds made with different titanium concentration of 0.002 and 0.072 wt.% but with similar oxygen content, the following conclusions can be drawn for the relation between the weld microstructure and the chemical nature of inclusions;

(1) As-deposit microstructure of bainitic GMAW welds consists of bainite and acicular ferrite, their proportions being varied with titanium content in weld metal. A trace of titanium of the order of 0.002 wt.% produces ~50% acicular ferrite in the weld while an addition of titanium to 0.07 wt.% promotes the formation of acicular ferrite reaching to 92%. This change in weld microstructure was well reflected by the low DBTT and high upper-shelf energy in 0.07 wt.% Ti weld.

(2) The chemical feature of inclusions is closely linked with the titanium concentration of weld metals. At 0.002 wt.% titanium, crystalline (Ti,Mn)-oxide layer forms on the surface of amorphous manganese silicate inclusions. Not all but about 40% of inclusions have (Ti, Mn) oxide layer. It appears that this (Ti,Mn) oxide phase is responsible for the formation of acicular ferrite in this weld, near 50%. As for the nucleation mechanism, the concept of ‘intrinsic low interfacial energy with ferrite’ can be considered.

(3) At titanium concentration of 0.07 wt.% (3Ti weld), weld inclusions are composed predominantly with Ti2O3 phase surrounded by MDZ. Therefore, the valid mechanism governing the formation of acicular ferrite in this weld can be regarded as the MDZ formation associating with Ti2O3 particles acting as a sink for manganese.

(4) Based on the above findings and the other’s results, it is further concluded that all Ti-containing inclusions can be regarded as nucleant species when the Ti-containing phases are sufficiently exposed on the inclusion surfaces. The possible mechanism for ferrite nucleation would be regarded as nucleant species when the Ti-containing phase is present on the inclusion surface, i.e. the mechanism of MDZ formation being responsible in case of Ti2O3-dominant inclusions formed in 0.07%Ti weld and the concept of low interfacial energy being able to be considered for the inclusions coated with (Ti,Mn)-oxide layer as in 0.002%Ti weld.

REFERENCES

36) G. M. Evans: *Metal Constr.*, 18 (1986), No. 10, 139.