Formation and thermodynamic analyses of inclusions in Ti-containing steel weld metals with different Al contents

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ABSTRACT: The Ti-containing steel weld metals with Al contents of 0.01-0.085% were prepared. The effects of Al contents in weld metals on the inclusions evolution were in detail investigated by means of thermodynamic calculations coupled with electron probe micro-analyses. The results show that the inclusions in the 0.01% Al weld metal are mainly composed of ilmenite with more amounts of (Mn-Si-Al)-oxide and titanial-spinel. When Al content is increased up to 0.035%, a more amount of corundum and a small amount of pseudobrookite are formed. In 0.085% Al weld metal, the (Mn-Si-Al)-oxide phase disappears completely, and the inclusions contain a substantial amount of corundum, in addition to a minimal amount of pseudobrookite. Ti$_3$O$_5$, MnTi$_2$O$_4$, and MnTiO$_3$ are the primary constituents of pseudobrookite, titanial_spinel and ilmenite solid solutions, respectively. Titanial_spinel and ilmenite have higher amounts of Mn, but lower Ti levels compared with pseudobrookite.

KEYWORDS: Aluminium content; Electron probe micro-analyzer; Oxide inclusion; Phase diagram; Thermodynamic calculation; Weld metal


RESUMEN: Formación y análisis termodinámico de inclusiones en metales de soldadura de acero que contienen Ti con diferentes contenidos de Al. Se prepararon muestras de metales de soldadura de acero que contienen Ti con contenidos de Al de 0,01-0,085%. Los efectos del contenido de Al en los metales de soldadura sobre la evolución de las inclusiones se investigaron en detalle mediante cálculos termodinámicos junto con microanálisis de sonda de electrones. Los resultados muestran que las inclusiones en el 0,01% de metal de soldadura de Al están compuestas principalmente de ilmenita con más cantidades de (Mn-Si-Al) -óxido y titanial-spinel. Cuando el contenido de Al aumenta hasta un 0,035%, se forma una mayor cantidad de corindón y una pequeña cantidad de pseudobrookita. En el 0,085% de metal de soldadura de Al, el (Mn-Si-Al)- óxido desaparece por completo y las inclusiones contienen una cantidad sustancial de corindón, además de una cantidad mínima de pseudobrookita. Ti$_3$O$_5$, MnTi$_2$O$_4$, y MnTiO$_3$ son los componentes principales de las soluciones sólidas de pseudobrookita, titanial_spinel e ilmenita, respectivamente. Titanial-spinel e ilmenita tienen cantidades más altas de Mn, pero niveles más bajos de Ti en comparación con la pseudobrookita.

PALABRAS CLAVE: Cálculo termodinámico; Contenido de aluminio; Diagrama de fases; Inclusión de óxido; Metal de soldadura; Microanalizador de sonda de electrones

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1. INTRODUCTION

It is well known that some fine non-metallic inclusions in weld metals and/or steels can strongly contribute to the nucleation of acicular ferrite (AF) (Lin et al., 2018; Zhang et al., 2018a), which can noticeably improve the toughness. Among the non-metallic inclusions, such as oxides, titanium nitride, vanadium nitride and manganese sulfide, Ti-containing oxide inclusions have been often reported to have strong ability to induce AF formation. Yamada et al. (2009) and Takada et al. (2015) pointed out that the TiO contributes to the nucleation of AF and that the AF nucleated on TiO shows the Baker-Nutting (B-N) orientation relationship with the TiO. This orientation relationship achieves good lattice coherency and decreases the interfacial energy between the AF and TiO, resulting in a decrease in activation energy for AF nucleation. Several researchers (Shim et al., 2001; Kang and Lee, 2010; Seo et al., 2015) have reported that a Mn-depleted zone (MDZ) can be detected around TiO inclusions in steels and weld metals, so that the local depletion of Mn around the inclusions promotes AF nucleation by increasing the chemical driving force. Shim et al. (1999) also proved the above results in a steel-TiO diffusion bonding experiment.

However, in the case of chemical compositions of commercial steels and/or ordinary weld metals, the complex Ti-containing oxide inclusions, such as MnTiO4 and MnTiO3, rather than simple ones mentioned above are usually formed (Kang et al., 2016; Wang et al., 2018). Therefore, it is much more meaningful to investigate the potency of complex Ti-containing oxide inclusions to nucleate the intragranular AF. Some researchers have done related investigations. Nako et al. (2014) and Kang et al. (2016) found that MnTiO4 on the surfaces of the inclusions is responsible for the formation of AF. In their studies, it was revealed that AF can have not only the B-N orientation relationship with MnTiO4 but also the Kurdjumov-Sachs (K-S) orientation relationship with the austenite matrix. Kang et al. (2016) reported that in the presence of large amounts of MnTiO4 and MnTiO3 constituents of inclusions, the Mn in the matrix around the inclusions is consumed, and as a result, the MDZ is developed.

Therefore, the formation of Ti-containing inclusions mentioned above is essential for AF nucleation regardless of Mn depletion or crystallographic lattice match mechanisms, and accurate control of the formation of such inclusions is very important. The chemical compositions of steels and/or weld metals have strong effect on the formation, types and structures of inclusions. Kang et al. (2014) studied the evolution of Ti-containing inclusions, and pointed that with an increase in the Ti content, the Ti-rich oxide is changed from MnTiO4 to rich spinel to the mixture of TiO2 and MnTiO3, and the TiO2 content is increased. Moreover, some researchers also investigated the influences of Zr (Zou et al., 2018), Mg (Zhang et al., 2016) elements, etc., on the inclusions formation. As a strong deoxidizer, Al is usually used to deoxidize the liquid Fe solubility above the liquidus temperature of the liquid steel. Therefore, the steels and/or weld metals for structural applications inevitably contain a certain amount of Al element. Al should be expected to influence the oxide formation process in weld metals. However, so far few studies have been done to investigate the effect of Al element on the evolution of the inclusions in Ti-containing weld metals.

On the other hand, the formation of inclusions is rather complex because the inclusions found in ordinary weld metals and/or commercial steels usually consist of a mixture of several complex crystalline solid solutions and/or amorphous phases instead of simple stoichiometric compounds such as Mn3TiO4, MnTi2O6, MnTiO3 and Ti2O3 (Kang et al., 2016; Wang et al., 2018). Therefore, it is a little difficult to accurately analyse the types, contents and of chemical compositions of constituent phases in inclusions only by means of experimental ways. By the commercial thermochemical computing package FactSage™, thermodynamic calculation approach can be used to effectively predict the formation of multi-phase inclusions based on the Gibbs free energy minimization principle. The FactSage commercial thermochemical computing package is very helpful in understanding the inclusions evolution, and has been widely applied to evaluate various complex non-metallic inclusion systems (Zhang et al., 2018b; Li et al., 2018).

The present study analysed how Al element affects the inclusions evolution including the types, contents and of chemical compositions of constituent phases of inclusions in Ti-containing steel weld metals using FactSage commercial thermochemical computing package combined with electron probe micro-analyzer.

2. MATERIALS AND METHODS

2.1. Weld metals preparation

Figure 1 indicates the process of weld metals preparation. Build-up welding using pure Fe powder was first performed in a 15 mm deep trapezoid slot in C-Mn steel plates with thickness of 20 mm, and then a V-groove with depth of 7 mm is again machined at the build-up welds. After that, a single pass submerged-arc welding (SAW) process is performed using a C-Mn steel welding wire with a diameter of 4 mm under a voltage of 35 V and current of 450 A. Three weld metals with different Al contents, but almost the same Ti and Mn concentrations were obtained by adding different amounts of pure Al powder and a certain amounts of Ti-Fe.
powder (33% Ti) and Mn-Fe powder (81% Mn) to the groove prior to SAW. The chemical compositions of the welding wire and weld metals are listed in Table 1 and Table 2, respectively. In light of the Al content, weld metals were labeled as WL (0.01% Al), WM (0.035% Al) and WH (0.085% Al).

2.2. Inclusion analyses and thermochemical computing on the formation of inclusion

The specimens were cut from the weld metals, and examination planes perpendicular to the welding direction were prepared by mechanical polishing. The morphology and chemical compositions of the inclusions were analysed by a JEOL JXA-8530F electron probe micro-analyzer (EPMA).

The commercial thermochemical computing package FactSage™ (version 7.2) was employed to calculate the thermodynamic stability of various inclusion phases using the FToxid, FTmisc and FSstel databases containing model parameters, the thermodynamic properties and structures of thermodynamic models of the inclusion phases as functions of temperature and composition. According to the chemical compositions of weld metals and selected databases, the major constituent phases of inclusion considered in the present thermochemical calculations are as followed:

- Pseudobrookite: Ti$_3$O$_5$-FeTi$_2$O$_5$-MnTi$_2$O$_5$ solid solution
- Titanial_Spinel: (Mn, Fe)(Ti, Al)$_2$O$_4$ solid solution
- Ilmenite: Ti$_2$O$_3$-FeTiO$_3$-MnTiO$_3$ solid solution
- Corundum: Al$_2$O$_3$ + (Ti$_2$O$_3$ in dilute amount)

Stoichiometric compounds: all relevant stoichiometric compounds

Slag phase: Al$_2$O$_3$-SiO$_2$-MnO-TiO$_2$-Ti$_2$O$_3$-FeO multi-component liquid oxides solution formed by oxidation reactions of several elements in weld metals

The equilibrium cooling mode was applied to predict the formation of inclusions between 1000-1600 °C. Moreover, various reactions during further cooling in the solid state, were not considered, for simplicity.

Phase Diagram module was used to generate a ternary isothermal phase diagram at 1000 °C for the system containing Al$_2$O$_3$-MnO-SiO$_2$ components in order to study the effect of Al on the formation of complex inclusions.

3. RESULTS AND DISCUSSION

Figures 2-4 present the EPMA analysis results of inclusions in the weld metals containing different levels of Al. According to the chemical composition characteristics displayed in EPMA maps of the inclusions, the inclusion in WL is mainly composed of the (Mn-Si-Al)-oxide and (Mn-Ti)-oxide accompanied by a certain amount of Al-containing oxide phase and small amount of discrete MnS patches distributed at the periphery of the inclusion. Compared with the inclusion in WL, the amounts of (Mn-Ti)-oxide and Al-containing oxide of the inclusion in WM are increased, and (Mn-Si-Al)-oxide nearly disappears. In WH, as shown from EPMA maps, the Mn and Si element contents in the inclusion are lower than those of the matrix located near the inclusion. Due to the absence of Mn and Si, the inclusion predominantly consists of Al-oxide in addition to minimal amount of Ti-oxide, and does not contain (Mn-Si-Al)-oxide.

Figure 5 presents the thermodynamic analyses about inclusions evolution. It can be clearly observed from the constituent phases of the inclusions at 1000 °C (liquid oxides have been completely decomposed at this temperature) that, in WL, the inclusion contains a large amount of ilmenite solid solution in addition to more amounts of Mn$_2$Al$_6$Si$_2$O$_18$ and titanial_spinel. In WM, a large amount of corundum and a small amount of pseudobrookite are formed. Moreover,
titanial spinel solid solution and Mn$_2$Al$_6$Si$_5$O$_{18}$ compound disappear. In WH, the inclusion is mainly composed of corundum with minimal amount of pseudobrookite.

The constituent contents and chemical compositions of solid solution in the inclusions were obtained based on the thermodynamic calculation results, and shown in Fig. 6. MnTi$_2$O$_4$, MnTiO$_3$, MnAlO$_2$.
Ti$_3$O$_5$ and Al$_2$O$_3$ are the primary constituents in respective solid solutions (i.e., titanial_spinel, ilmenite, pseudobrookite and corundum). It is worth noting that although titanial_spinel, ilmenite and pseudobrookite are all Ti-rich solid solutions, titanial_spinel and ilmenite have higher amounts of Mn, but lower Ti levels compared with pseudobrookite.
Based on thermodynamic calculations shown in Figs. 5, 6, it is clear that (Mn-Si-Al)-oxide appeared in EPMA analyses should be $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ compound, while Ti-containing phases are undoubtedly titanial_spinel, ilmenite and pseudobrookite solid solutions. Additionally, Al-containing oxide phase in EPMA maps should be corundum and titanial_spinel. Comparisons between Figs. 2-4 and Figs. 5, 6
show that thermodynamic analyses on constituents and chemical compositions characteristics of inclusions well agree with experimental results of EPMA maps.

As mentioned above, Al element has a strong effect on the formation and evolution of inclusions in weld metals. It is well known that during welding, a series of complex metallurgical physics chemical reactions are expected to take place in weld pool. Elements of Al, Ti, Si, Mn, etc., can combine with soluble oxygen in weld pool, which results in the formation of a variety of liquid oxides such as Al$_2$O$_3$, TiO$_x$, and MnO (i.e., molten slag) above liquidus temperature of slag, and the decrease in the amount of the dissolved oxygen in the weld pool. There are the competition relationships between Al, Ti, Si and Mn during oxidation process. Compared with Si and Mn elements, Al and Ti have much stronger affinities with oxygen under the same contents due to their lower oxygen potentials of forming oxides (Mitsutaka and Kimihisa, 2010). Moreover, the content of metal elements also has a noticeable effect on the oxidation process of metals. In order to clarify the effect of Al element content on the oxidation products, equilibrium calculation on compositions of liquid oxides at 1600 °C was carried out with Fe-0.05C-3.1Mn-0.23Si-0.014S-0.019Ti-0.039O$_x$Al$_x$ (0<$_x$<0.09) alloy system (in mass%) similar to the chemical compositions of weld metals, and shown in Fig. 7. Under low Al content (for example,
0.01% Al), despite high affinity with oxygen of Al, the amount of Al₂O₃ in oxidation product is lower compared with that of MnO due to high content of Mn element. With an increase in Al content, the amount of Al₂O₃ is strongly raised accompanied by the drops of other constituents such as MnO, SiO₂ and TiO₂. However, when content of Al is increased to the range of about 0.02-0.045%, the content of Al₂O₃ in liquid oxide is slightly lowered, while those of TiO₂ and TiO₃ are increased. The combining ability with oxygen for metals dissolved in Fe solution (i.e., oxygen potential of forming corresponding oxides) is determined as followed (Mitsutaka and Kimihisa, 2010):

\[ \pi_{(M,O)} = \Delta G_m^O + \frac{2}{y} RT \ln a_{(M,O)} - \frac{2v}{y} RT \ln a_M \]  

(1)

where \(a_{(M,O)}\) and \(a_M\) denote the activities of \(M\)₂\(O\) in the liquid oxide solution and the metal element dissolved in liquid Fe solution, respectively.

The liquid oxide and liquid Fe solutions can be regarded as ideal solutions. Thus, the concentrations (mole ratio) of \(M\)₂\(O\) in the liquid oxide solution and the metal element dissolved in liquid Fe solution are respectively their activities (Mitsutaka and Kimihisa, 2010).

When the Al content is increased up to a certain range (for example, 0.02-0.045%), the liquid oxide solution can contain higher amount of Al₂O₃, which increases the activity of Al₂O₃, but lowers the activities of other constituents including TiO₂ (i.e., Ti₂O₃ and TiO) in liquid oxide solution. Therefore, according to Eq. (1), the oxygen potentials of forming TiO₂ oxides should be lowered, which can promote the formation of TiO₂. Meanwhile, the amount of Al₂O₃ can be lowered due to the competition relationship between Al and Ti. When the content of Al is further increased (for example, more than 0.045%), according to Eq. (1), the oxygen potential of forming Al₂O₃ can be lowered. Thus, a large amount of Al₂O₃ can form to strongly consume soluble oxygen in liquid Fe solution. The decrease of soluble oxygen in liquid Fe solutions is expected to suppress the oxidation reactions of other metal elements including Ti (Hsieh et al., 1996), which leads to a remarkable decrease in the amounts of TiO₂, MnO, SiO₂ and so on, so that the amounts of MnO and SiO₂ are very low in the case of very high Al content, for example 0.085%.

During cooling after welding, different kinds and amounts of constituent phases in inclusions are expected to precipitate in light of the chemical compositions characteristics of liquid oxides. In order to further demonstrate this effect, slag compositions in equilibrium at 1600 °C were calculated with Fe-3.1Mn-0.23Si-0.039O-xAl (0.01<x<0.09) alloy system (in mass%), and superimposed to a ternary isothermal diagram of Al₂O₃-MnO-SiO₂ system at 1000 °C to reveal the inclusion trajectory with Al content, as shown in Fig. 8. Al-spinel (mainly MnAl₂O₄) and olivine (mainly Mn₂SiO₄) do not appear in the case of present compositions in weld metals, as shown in Fig. 5. Thus, with the increase of Al₂O₃ amount (correspondingly, the contents of MnO and SiO₂ are lowered), the evolution of Al-containing oxide phases is followed as: Mn₃Al₂Si₅O₁₂ → corundum + Mn₃Al₂Si₅O₁₂ + Mn₃Al₂Si₅O₁₂ → corundum.
In the case of 0.01% Al, the liquid oxide contains a large amount of MnO constituent and a certain amounts of TiO₂, which favours the formations of titanial_spinel and ilmenite rather than pseudobrookite. Similarly, the formation of (Mn-Si-Al)-oxide is also promoted due to high amount of MnO and a certain amount of SiO₂, as shown in Fig. 2. When Al level is increased up to 0.035%, as analysed above, the amounts of TiO₂, SiO₂, and Al₂O₃ constituents in molten slag are increased, but those of MnO and SiO₂ are correspondingly decreased, which results in formations of pseudobrookite and corundum at the expense of amount of (Mn-Si-Al)-oxide in the inclusions, as shown in Fig. 3. In the case of 0.085% Al, the liquid oxide is mainly composed of Al₂O₃ with small amounts of TiO₂. Meanwhile, the amounts of SiO₂ and MnO in the liquid oxide are very low, and in particular, the SiO₂ content is almost zero, resulting in the absence of (Mn-Si-Al)-oxide in the inclusions. Similarly, a very low content of MnO accompanied by small amounts of TiO₂ contributes to the formation of a small amount of pseudobrookite. Thus, the inclusions have a very high amount of corundum and a very low content of pseudobrookite, as shown in Fig. 4.

4. CONCLUSIONS

• The kinds and amounts of the constituent phases of the inclusions are remarkably changed with the Ti content in the weld metals. The inclusions in the 0.01% Al weld metal are mainly composed of ilmenite with more amounts of (Mn-Si-Al)-oxide and titania_spinel. When Al content is increased up to 0.035%, a more amount of corundum and a small amount of pseudobrookite are formed. In 0.085% Al weld metal, the (Mn-Si-Al)-oxide phase disappears completely, and the inclusions contain a substantial amount of corundum, in addition to a minimal amount of pseudobrookite.

• TiO₂, MnTiO₃ and MnTiO₄ are the primary constituents of pseudobrookite, titania_spinel and ilmenite solid solutions, respectively. Titanial_spinel and ilmenite have higher amounts of Mn, but lower Ti levels compared with pseudobrookite.

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REFERENCES


