Changing Behavior of Non-metallic Inclusions in Solid Iron Deoxidized by Al–Ti Addition during Heating at 1 473 K

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Changing behavior of non-metallic inclusions in composition and size distribution at high temperature was investigated by preparing three kinds of Fe–Al–Ti steels, heating at 1 473 K, and observing inclusions by SEM-EDS. In the case of the specimen in which thermodynamically stable inclusion at 1 873 K is Al2O3, mostly pure Al2O3 inclusions were observed in an as cast sample, while many dual phase inclusions were observed after heating. Iron content in inclusions increased and many Al–Ti–Fe–O inclusions in narrow composition range were observed. In the case of the specimen in which stable inclusion at 1 873 K is TiO, TiO inclusions were observed in an as cast sample. Inclusion compositions changed to Fe–Ti–O by heating and inclusion size became smaller to 2 to 3 μm. In the case of the specimen which composition is located at the boundary area of Al2O3, Al2TiO5, and TiO stable regions at 1 873 K, various inclusions from pure Al2O3 to TiO were observed in an as cast sample. By heating, three types of inclusions, namely, Al2O3, Al–Fe–O, and Al–Ti–Fe–O inclusions were observed and average inclusion size decreased. Although the stable phase of oxide equilibrated with Fe–Al–Ti–O system at 1 473 K are not clarified, inclusions equilibrated with molten metal are no longer stable in solid state steel and thus inclusion composition and size change by reacting with solid steel.

KEY WORDS: Al–Ti deoxidation; titanium oxide; oxide metallurgy; inclusion size and composition change.

1. Introduction

Titanium-alloyed steels have been widely used for various products such as automobile sheets, or heavy plates for ship construction, because titanium has a great advantage not only in its cost effectiveness but also in improvements of steel properties, e.g., formability, non-ageing property, prevention of austenite grain growth, and promotion of finer ferrite microstructure formation. Titanium forms various types of non-metallic inclusions; titanium oxide, nitride, carbide, sulfide and so on. Furthermore, titanium oxide exists in several forms such as TiO, TiO2 and TiO, depending on the steel compositions.

Since titanium also has a strong affinity with oxygen, it is normally added for alloying after deoxidation process. Aluminum is one of the common, strong and less expensive deoxidizer. Comparing to the cost of aluminum, titanium is relatively expensive and thus the combined process of deoxidation by aluminum and alloying by titanium is popular. Therefore, Al–Ti deoxidation process is one of the common processes for secondary refining. Thermodynamics for Al deoxidation or Ti deoxidation reaction have been studied well, while the complex deoxidation by Al and Ti addition has not been comprehensively understood. Ruby-Meyer et al.1) have estimated the Fe–Al–Ti–O equilibrium phase diagram by employing the multiphase equilibrium code CEQCSI based on the IRSID slag model2) at 1 793 K. The calculated stable phase diagram indicates the formation of Al2O3, Ti2O3, Al2TiO5 as well as TiO–Al2O3 liquid oxide. On the contrary, Jung et al.3) employed FACT databases and FactSage software, and calculated the phase diagram of oxides for the Fe–Al–Ti–O system at 1 873 K. They reported the existence of a Ti2O3 solid phase which did not exist in the reported diagram by Ruby-Meyer et al.1) while they did not find a liquid phase. Later, they revised the previous phase diagram in which Al2O3, Ti2O3, TiO2 and liquid oxide exist with equilibrating with metal.4) Kim et al. also reported the phase stability diagram of oxides equilibrating with Fe–Al–Ti–O melt at 1 873 K. The stable regions for Al2O3, Ti2O3 and TiO2 were shown, while those for other oxides and liquid oxides were not observed.5) As a conclusion, the chemical stability of Al–Ti–O oxides equilibrating with metal is still open for discussion.

The stability of non-metallic inclusions containing titanium in solid steel would be more complex due to the formation of nitride, carbide and so on, which are normally not found at high temperatures. The behavior of non-metallic inclusions in solid state steel is quite important to understand the relationship between microstructure of steel and mechanical properties, and thus to maximally bring out such properties for best performance. Especially, titanium oxide or titanium nitride has positive effects on the prevention of the growth of coarse γ-Fe grains, and on the promotion of the development of fine α-Fe microstructure. If composition, number density, morphology or size distribution of titanium-bearing inclusions could be controlled properly.

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and optimized, various properties of steel would be improved. Nevertheless, even the stability of oxides containing aluminum and/or titanium in solid steel at heat treatment temperatures has not been studied.

In the present study, the evolution and modification of oxide inclusions in three kinds of Fe–Al–Ti steels were investigated and the change in inclusion compositions and morphologies with heating time was discussed.

2. Experimental

2.1. Materials

Three kinds of Fe–Al–Ti–O specimens (hereafter, named as A, B, and C) were prepared. About 200 g of electrolytic iron was put in an MgO crucible (OD 38 mm, ID 26 mm, height 123 mm) and the crucible was put in a quartz tube (OD 50 mm, ID 46 mm, length 360 mm). After the atmosphere of the reaction tube was replaced to high purity Ar gas (99.9%, flow rate: about 400 cm³/min), the sample was melted in an induction furnace (200 kHz, approximately 3 kW) at 1 873 K for 1 h, and then Al followed by Ti were added at an interval of 2 min to specimens A and C, or only Ti were added to specimen B. The melt was further kept for 10 min and then the crucible was taken out from the reaction tube and quenched by immersing a crucible into water. About 1 g of steel pieces were cut off and dissolved into acid. The compositions were analyzed by ICP-OES for soluble Al and Ti, and by combustion analyzer for total oxygen.

2.2. Heating

A piece of sample (25 mm diameter, thickness 10 mm) was machined from each sample and hanged in the reaction tube of an electric furnace by steel wire. Then, samples were heated at 1 473 K for 1 to 3 hours and the atmosphere was replaced by high purity Ar gas (99.9%, flow rate: about 350 cm³/min). After prescribed heating time, the samples were quickly taken out of the reaction tube and quenched by immersing into water.

2.3. SEM-EDS Analysis

As cast and heated samples were embedded in the polyester resin, and polished by SiC papers and diamond suspensions up to 0.25 μm to characterize the inclusions through observations by a scanning electron microscope (SEM, JEOL JSM-6060LV) and composition analyses by energy-dispersive spectrometry (EDS, JEOL EX-54175JMU) attached to the SEM. About 30 to 50 inclusions were observed and analyzed in each specimen, and the compositions of Al, Fe, Mg and Ti were determined.

3. Results and Discussion

Compositions of prepared specimens are summarized in Table 1 and shown on the stability diagram of oxide phases equilibrated with Fe–Al–Ti melt at 1 873 K in Fig. 1. Compositions of specimens A, B and C are located in the Al₂O₃ stable region, the Ti₃O₅ stable region, and at the boundary between Al₂O₃, Al₂TiO₅ and Ti₃O₅ stable regions, respectively. Mg content in all inclusions of all specimens was lower than 1 mass%, and therefore the observed inclusions were treated as the Al–Ti–Fe–O system. Although it was confirmed that observed inclusions were oxide by EDS, quantitative analysis of oxygen content in inclusions was difficult by EDS. Therefore, the compositions of inclusions are shown hereafter on the pseudo ternary diagram of the Al–Fe–Ti system, which is equivalent to the Al2O3–FeO–TiO2 oxide system.

Inclusion size was defined by the largest length of the cross section of inclusions in the present study. Typical inclusion morphology was spherical in the case of Al₂O₃-type inclusions. However, some inclusions had quite irregular shapes such as long-bar-like shape, or bar-like shape with several arms. The shape of inclusions will be explained in detail in the following sections.

3.1. Specimen A (Al: 0.0341 mass%, Ti: 0.0444 mass%)

Typical SEM images of inclusions in as cast, and heated samples are shown in Fig. 2. The shape of inclusions in an as cast sample was mainly spherical and it did not change clearly by heating at 1 473 K.

Compositions of inclusions in the Al–Fe–Ti ternary system as shown in Fig. 3. Most of inclusions observed in an as cast sample had the composition of almost pure Al₂O₃ and Ti content in inclusions were less than 4 mol%. Although Fe content was observed up to 25 mol%, Fe content of smaller inclusions tend to increase due to the X-ray signal from Fe matrix. Therefore, the inclusion composition was concluded as almost pure Al₂O₃ containing small content of TiO₂.

The inclusion compositions changed from Al₂O₃ to Al–Fe–O, or Al–Ti–Fe–O system by heating at 1 473 K, which were not seen in an as cast sample. After 60 min, three types of inclusions were observed, namely Al₂O₃, Al–Fe–O, and Al–Ti–Fe–O inclusions. Most Al–Fe–O inclusions contained from 30 to 40 mol% Fe as the Al–Fe binary system.
The composition of Al–Ti–Fe–O inclusions as the Al–Fe–Ti ternary system was in the range between 35 and 75 mol%Fe, and 5 and 20 mol%Ti.

After heating for 180 min at 1473 K, Al₂O₃ inclusion was no longer observed and Al–Fe–O or Al–Fe–Ti–O inclusions were observed. Composition of Al–Fe–O inclusions dispersed widely and the Fe content as the Al–Fe binary system was between 30 and 75 mol%. The Al–Ti–Fe–O inclusions contained from 10 to 20 mol%Al, from 60 to 80 mol%Fe, and from 10 to 20 mol%Ti as the Al–Fe–Ti ternary system. Number of inclusions with large Fe content increased with increasing heating time. From these results, Al₂O₃ inclusions changed to Al–Fe–Ti–O inclusions by heating at 1473 K.

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Figure 4 shows the size distribution of inclusions. Inclusion size clearly became smaller with heating samples at 1473 K. In an as cast sample, inclusion size dispersed widely from less than 1 to over 10 μm, which is due to the formation of bar-like irregular shape inclusions. The shape of inclusions with large Ti content tends to be quite irregular.

3.2. Specimen B (Ti: 0.028 mass%)

Figure 5 shows the typical inclusion shapes in Specimen B. Inclusions in an as cast sample had very irregular shape, while mainly spherical shape inclusions were observed in samples after heating at 1473 K. The size of inclusions became smaller by heating as explained in detail below.

Figure 6 shows the compositions of inclusions observed in Specimen B. In an as cast sample, TiO₂ inclusions with small Fe content were mainly detected. On the contrary, Ti–Fe–O inclusions were observed in samples heated at 1473 K. In the sample heated at 1473 K for 60 min, Fe content as the Fe–Ti binary system varied from 50 to 100 mol% and the average composition was 75 mol%Fe-25 mol%Ti. Composition of inclusions in a sample heated for 180 min clearly showed the change of inclusions composition from TiO₂ in an as cast sample to 75 mol%Fe-25 mol%Ti as the Fe–Ti binary system.

Figure 7 shows the size distribution of inclusions. Inclusion size clearly became smaller with heating samples at 1473 K. In an as cast sample, inclusion size dispersed widely from less than 1 to over 10 μm, which is due to the formation of bar-like irregular shape inclusions. The shape of inclusions with large Ti content tends to be quite irregular.
The reason of these shape characteristics has not been clarified and the several reasons could be considered, such as the softness of Ti-containing oxide at steelmaking temperature, easier coagulation of formed inclusions and so on. On the other hand, many smaller inclusions were observed after heating and about half of observed inclusions in heated sample for 180 min were in the size range between 2 and 3 μm.

From compositional and size change of inclusions during heating at 1473 K, it is considered that the dissolution of TiO\textsubscript{x} inclusions into the metallic phase and the nucleation of smaller Fe–Ti–O inclusions occurred simultaneously, because TiO\textsubscript{x} is no longer stable in Fe-0.028 mass% Ti but Fe–Ti–O oxide is.

### 3.3. Specimen C (Al: 0.0162 mass%, Ti: 0.29 mass%)

Typical inclusions in Specimen C are shown in Fig. 8. The shape of inclusions in an as cast sample were similar to those of Specimen B, namely very irregular shape. Although the shape of inclusions did not clearly change by heating at 1473 K, many inclusions had two phases in an inclusion as Fig. 8(c) shows the typical SEM image of inclusions in Specimen C after 180 min heating at 1473 K.

Figure 9 shows the compositions of inclusions in Specimen C. Though Al\textsubscript{2}O\textsubscript{3} inclusions were mostly observed, various types of inclusions such as TiO\textsubscript{x} with small FeO\textsubscript{x} content, or FeO\textsubscript{x} with small Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{x} contents, were also detected. This is because the metal composition is at the boundary between Al\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}TiO\textsubscript{4} and Ti\textsubscript{3}O\textsubscript{5} stable regions at 1873 K as shown in Fig. 1. Therefore, the inclusions have not been equilibrated comprehensively with metal before solidification.

As described above, the compositions of inclusions changed to two compositions, one is Al–Fe–O inclusions containing approximately 40 mol% Fe as the Al–Fe binary system and also with small Ti content, the other is Al–Ti–
Fe–O inclusions which average composition is 20 mol% Al-20 mol% Ti-60 mol% Fe as the Al–Ti–Fe ternary system. Though some Al2O3 inclusions were also observed, the fraction of Al2O3 inclusions decreased by heating. The changing behavior of inclusion compositions with heating was similar to that observed in the case of Specimen A. However, many observed inclusions in Specimen C after heating had two phases as shown in the figure, which was different from the case of Specimen A.

Figure 10 shows the size distribution of inclusions. The effect of heating on the change of inclusion size distribution was not clearly observed, which is similar to Specimen A.

3.4. Mechanisms of Size and Compositional Change of Inclusions
Effect of heating at 1473 K on the size distribution and composition of inclusion was studied for three different specimens. Regarding the effect on the size distribution, the fraction of smaller inclusions increased in the case of Specimen B, while the size distribution did not change obviously in Specimens A and C. Therefore, the nucleation and dissolution of inclusions expressed as Eqs. (1) and (2) occurred simultaneously and thus the fraction of finer inclusions increased by heating in Specimen B,

\[ \text{TiO}_x (s) \rightarrow \text{Ti} + x \text{O} \] ................. (1)

\[ \text{Fe} + \text{Ti} + (x + 1) \text{O} \rightarrow \text{FeO–TiO}_x (s) \] ........... (2)

On the other hand, the dissolution of inclusions did not occur and therefore the size distribution did not change obviously in the case of Specimens A and C. Although the reason of this difference is not clear at this moment, one
The oxygen source would be the dissolved oxygen in Fe matrix or the partial dissolution of Al₂O₃, depending on the steel composition. Further physicochemical properties must be clarified for understanding the behavior of inclusions more in detail, such as the chemical stability diagram for the Fe–Al–Ti–O system in solid steel, or the activities of Al, Ti and O.

4. Conclusions

Behavior of non-metallic inclusions in Al–Ti deoxidized steels at 1473 K was studied with three different steels. In the case of Fe-0.0341 mass%Al-0.0444 mass%Ti and Fe-0.0162 mass%Al-0.29 mass%Ti, different inclusions were observed in as cast specimens, while Al–Fe–O and Al–Ti–Fe–O inclusions were observed in both samples after heating and those compositions between two specimens were the same. The size distribution of inclusion did not clearly change by heating. In the case of Fe-0.028 mass%Ti, Ti–O inclusions with small content of Fe were observed in as cast sample and composition of inclusions changed to Ti–O after heating, and the fraction of fine and coarse inclusions increased and decreased, respectively. Though the stable phase of oxide equilibrated with Fe–Al–Ti steel at 1473 K was studied with three different steels. In

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