Effect of Al on the Evolution of Non-metallic Inclusions in the Mn–Si–Ti–Mg Deoxidized Steel During Solidification: Experiments and Thermodynamic Calculations

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The effect of Al on the evolution of non-metallic inclusions in the Mn–Si–Ti–Mg deoxidized steels during solidification were investigated based on the experiments and thermodynamic calculations. The inclusions belonged to the MgO–TiO2–Al2O3–MnS–TiN system. In particular, the major oxide inclusion was the Mg–Ti–Al–O spinel phase of which composition was continuously changed from the Mg–Ti–O to MgAl2O4 with the concentration Al in steels. The spinel compositions calculated from thermodynamic databases are in good agreement with experimental results. TiN was only observed on the surface of MnS. MgAl2O4 aggregates were also observed at high Al concentration. In general, the evolution of inclusions is well explained by thermodynamic calculations.

KEY WORDS: oxide metallurgy; evolution of inclusion; Mn–Si–Ti–Mg deoxidized steel; MgO–TiO2–Al2O3–MnS–TiN; thermodynamic calculation.

1. Introduction

Recently beneficial effect of inclusions on phase transformation behavior has been recognized and termed “oxide metallurgy”.1–3) Inclusions can act as intragranular nucleation sites for acicular ferrite, resulting in a reduced grain size and consequently improved physical properties of steel.

Several mechanisms of the intragranular nucleation have been purposed: (1) simple heterogeneous nucleation on an inert particle4–6); (2) epitaxial nucleation on the inclusions which have a good coherency with ferrite 7–10); (3) nucleation arising from the strain energy associated with the different thermal expansion coefficients of the inclusions and steel matrix11–12); and (4) nucleation assisted by solute depletion in the matrix near inclusions.6,13) Although the exact mechanism has not been elucidated yet, it is clear that the chemistry of inclusions plays an important role in the nucleation of acicular ferrite.

Inclusions formed in (Mn–Si–Ti)-deoxidized steels have attracted much attention because so-called “Mn-depleted zone” can be well developed14–16) around these inclusions after proper thermal treatments. The Mn-depleted zone can play a key role in the acicular ferrite formation.15) However, effects of other alloying elements such as Al and Mg on the inclusions chemistry and morphology in the Mn–Si–Ti deoxidized steels have not been investigated comprehensively.

Inclusions chemistry in (Fe–C–Mn–Si–Ti–Mg–Al–O–S–N) steels which are subjected to different thermal treatments has been investigated in the present authors group, and part of results for the (Mn–Si)- and (Mn–Si–Ti)-deoxidized steels were already published elsewhere.14,17–19) In the present study, effects of Al and Mg addition on the chemistry, morphology and size of inclusions formed in (Mn–Si–Ti)-deoxidized steels are presented. Since the chemistry of inclusions in the present study has been found quite complex, thermodynamic calculations have been employed in order to interpret the experimental results more accurately.

2. Experimental Procedure

Table 1 shows the chemical compositions of alloys investigated in the present study. The alloys were prepared using an induction melting furnace. The apparatus was well explained in the previous study.14) About 0.3 kg of electrolytic iron was first melted with 2.8×10–3 kg of FeS in an MgO crucible (40 mm in diameter and 125 mm in depth) at 1600°C. After stabilizing the melts for about 10 min at 1600°C, ferro-carbon (6 wt% C) was added to make 0.1 wt% C steel melt. After 30 s, proper amount of deoxidants was added in the order of Mn, Si, ferro-Ti (2 wt% Ti), ferro-Al (2 wt% Al) and Mg in order to obtain the target compositions. One minute after Mg addition, the melts were cooled to room temperature in the furnace by shutting down the electric power of the induction furnace. As reported earlier,14) the cooling rate was measured to be 32°C/min in average. During the entire procedure, the furnace was kept under an atmosphere of Ar gas, purified by passing
Mg(ClO₄)₂, and Mg chips at 450°C.

The samples were subsequently sectioned and the sections in the middle part of samples were used for various analyses in the present study. The content of oxygen and nitrogen were analyzed by NO spectrometry, and the content of carbon and sulfur were analyzed by CS spectrometry. The concentrations of other elements were analyzed by ICP-AES.

Samples were polished and etched for 3 to 5 s in an etchant composed of potassium meta-bisulfite and distilled water of the ratio 1 to 10. Then the samples were examined by an optical microscopy and SEM. For high-definition images of inclusions, the SEM examinations were carried out by using a JEOL JSM-6330F with a field emission gun.

Minimum 30 inclusions were examined in each sample. The composition of inclusions was analyzed by the energy dispersive X-ray spectra (EDS) with the acceleration voltages of inclusions, the SEM examinations were carried out for at least 5 min in order to obtain enough intensity to resolve elemental peaks. Inca system was used to examine the results of EDS analysis. (Inca is the trademark of Oxford Instruments, UK.)

### 3. Thermodynamic Computations

The Gibbs energy minimization software of the FactSage® thermochemical computing system was used to perform the thermodynamic calculations in this work.

FACT databases20) were used for the non-metallic inclusion phases and SGTE solution database21) was employed to perform the thermodynamic calculations in this work.

Stoichiometric compounds: all relevant stoichiometric compounds.

Steel: The Fe–C–Mn–Si–Ti–Al–Mg–O–S–N system shows liquid, fcc and bcc phases. These three phases are all modeled using the Compound Energy Formalism.22) The deoxidation phenomena in liquid steel were modeled by a new Associate Model23) in order to accurately describe deoxidation phenomena in liquid steel.

### 4. Results and Discussions

Overall compositions of steels investigated in the present study are listed in Table 1. In order to investigate the effect of Al on the inclusions in the steel deoxidized by Mn–Si–Ti, the concentrations of all alloying elements except Al were closely controlled; 0.1–1.5Mn–0.1Si–0.014Ti–0.001Mg–0.0620–0.0035S–0.003N in mass percent. Mg was added intentionally in order to distribute smaller inclusions.

The inclusions observed in each steel sample were summarized in Table 2. Several different kinds of inclusions were observed in a same steel, and their relative abundance is also marked in the table. The morphology of abundant inclusions is shown in Figs. 1 and 2.

In order to clarify the context in the present study, the notation of (Mg–Ti–Al–O) spinel is used to represent the “Mg–Ti–Al–O spinel system”. Mg–Ti–(Al)–O, Mg–Ti–Al–O and Mg–Al–(Ti)–O mean (Mg–Ti–Al–O) spinel which contains low Al, similar Al and Ti, and high Al spinel, respectively. See Table 2 for more information.

#### 4.1. Morphology, Composition and Size of Inclusions

##### 4.1.1. Steel Containing 6 ppm Al

In the steel containing 6 ppm Al, the complex inclusions like MgO+(Mg–Ti–(Al)–O)+MnS (Fig. 1(a)) and MgO+MnS (Fig. 2(c)) were abundantly observed. The size of the MgO+(Mg–Ti–(Al)–O)+MnS inclusions was larger than that of the MgO+MnS inclusions. The EDS analysis showed that the mole fraction Mg/(Ti+Al) in the (Mg–Ti–(Al)–O) phase was varied between 0.44 and 0.63. The mole fraction Al/(Ti+Al) in the (Mg–Ti–(Al)–O) phase was varied from 0.05 to 0.2. Quite small amount of Mn appears to dissolve in the (Mg–Ti–(Al)–O) phase, but the exact amount could not be measured due to interference by surrounding MnS.

Single MgO inclusion (Fig. 2(b)) was quite rare. TiN (Fig. 2(e)) appeared in all steel samples, on the surface of MnS regardless of MnS forming either a single independent inclusion or part of a complex inclusion. This will be discussed later in more details. Large single MnS inclusions (Fig. 2(f)) were found very abundantly with elliptical shape. The shape of other inclusions was spherical in general.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>C</th>
<th>S</th>
<th>Mn</th>
<th>Si</th>
<th>Ti</th>
<th>Mg</th>
<th>Al</th>
<th>O</th>
<th>N</th>
</tr>
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<tbody>
<tr>
<td>MSTA1</td>
<td>0.1</td>
<td>0.0032</td>
<td>1.47</td>
<td>0.1</td>
<td>0.0154</td>
<td>0.0014</td>
<td>0.0006</td>
<td>0.0021</td>
<td>0.0027</td>
</tr>
<tr>
<td>MSTA2</td>
<td>0.09</td>
<td>0.0038</td>
<td>1.46</td>
<td>0.1</td>
<td>0.0123</td>
<td>0.0009</td>
<td>0.0012</td>
<td>0.0012</td>
<td>0.0039</td>
</tr>
<tr>
<td>MSTA3</td>
<td>0.11</td>
<td>0.0038</td>
<td>1.5</td>
<td>0.09</td>
<td>0.0145</td>
<td>0.0011</td>
<td>0.0040</td>
<td>0.0013</td>
<td>0.0016</td>
</tr>
<tr>
<td>MSTA4</td>
<td>0.1</td>
<td>0.0033</td>
<td>1.49</td>
<td>0.1</td>
<td>0.0124</td>
<td>0.0008</td>
<td>0.0007</td>
<td>0.0020</td>
<td>0.0028</td>
</tr>
<tr>
<td>MSTA5</td>
<td>0.11</td>
<td>0.0037</td>
<td>1.43</td>
<td>0.11</td>
<td>0.0123</td>
<td>0.0010</td>
<td>0.0147</td>
<td>0.0019</td>
<td>0.0030</td>
</tr>
</tbody>
</table>

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Table 2. Summary of inclusions observed in different steels in the present study.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>MSTG</th>
<th>MSTGA1</th>
<th>MSTGA2</th>
<th>MSTGA3</th>
<th>MSTGA4</th>
<th>MSTGA5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of Al, ppm</td>
<td>6</td>
<td>12</td>
<td>21</td>
<td>40</td>
<td>87</td>
<td>147</td>
</tr>
<tr>
<td>MgO</td>
<td>&lt;1 μm</td>
<td>8 (24)</td>
<td>8 (24)</td>
<td>8 (24)</td>
<td>8 (24)</td>
<td>8 (24)</td>
</tr>
<tr>
<td>MgAl₂O₄</td>
<td>&lt;1 μm</td>
<td>8 (24)</td>
<td>8 (24)</td>
<td>8 (24)</td>
<td>8 (24)</td>
<td>8 (24)</td>
</tr>
<tr>
<td>MnS</td>
<td>&gt;1 μm</td>
<td>8 (24)</td>
<td>8 (24)</td>
<td>8 (24)</td>
<td>8 (24)</td>
<td>8 (24)</td>
</tr>
<tr>
<td>MgO+MnS</td>
<td>1–2 μm</td>
<td>8 (30)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
</tr>
<tr>
<td>MgAl₂O₄+MnS</td>
<td>1–2 μm</td>
<td>8 (30)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
</tr>
<tr>
<td>Mg₃(Al,Ti)O₄+MnS</td>
<td>1–2 μm</td>
<td>8 (30)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
</tr>
<tr>
<td>MgO+MgAl₂O₄+MnS</td>
<td>2–3 μm</td>
<td>8 (30)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
</tr>
<tr>
<td>MgO+Mg₃(Al,Ti)O₄+MnS</td>
<td>2–3 μm</td>
<td>8 (30)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
</tr>
<tr>
<td>MgO+Mg₃(Al,Ti)O₄+MnS</td>
<td>2–3 μm</td>
<td>8 (30)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
</tr>
<tr>
<td>TiN+MnS</td>
<td>&gt;5 μm</td>
<td>8 (30)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
</tr>
<tr>
<td>MgAl₂O₄, not trapped by MnS</td>
<td>&gt;5 μm</td>
<td>8 (30)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
<td>8 (34)</td>
</tr>
</tbody>
</table>

- : abundant, ▲ : less abundant and □ : rare.

A + B: a complex inclusion containing A and B together.

In the present study, the Mg₃TiAlO₄ spinel phase is classified into four groups for convenience as follows:

a. Mg₃TiAlO₄ : 0.05 < Al(Ti+Al) < 0.20
b. Mg₃TiAlO₄ : 0.20 < Al(Ti+Al) < 0.82
c. Mg₃Al(Ti+Al)O₄ : 0.82 < Al(Ti+Al) < 0.95
d. Mg₃Al₂O₄ : Al(Ti+Al) > 0.95

Values in parenthesis represent the number frequency in percentage of each inclusion type in a sample.

Fig. 1. Morphology of typical inclusions observed in the Fe–C–Mn–Si–Ti–Al–Mg–O–S–N steel. (a) MSTG, (b) MSTGA1, (c) MSTGA2, (d) MSTGA3, (e) MSTGA4 and (f) MSTGA5. The Mg₃TiAlO₄, Mg₃AlTiO₄ and MgAl₂O₄ belong to the Mg₃TiAlO₄ spinel phase.

Fig. 2. Morphology of inclusions observed in the Fe–C–Mn–Si–Ti–Al–Mg–O–S–N steel. (a) MgO in MSTG, (b) (Mg₃TiAlO₄)+MnS in MSTG, (c) MgO+MnS in MSTGA1, (d) MgAl₂O₄ in MSTGA5, (e) MnS+TiN in MSTGA3 and (f) MnS in MSTGA2.
4.1.2. Steel Containing 12 ppm Al

Single MgO inclusions were not observed anymore in the steel containing 12 ppm Al. Single MnS (Fig. 2(f)) and complex MgO+MnS (Fig. 2(c)) inclusions were abundant. The most significant difference of inclusions in this steel is the appearance of the (Mg–Ti–Al–O) phase instead of the (Mg–Ti–(Al)–O) phase. According to EDS analysis, the mole fraction Al/(Al+Ti) in the (Mg–Ti–Al–O) phase was varied from 0.22 to 0.82. Because the (Mg–Ti–Al–O) phase was found together with MgO and MnS, it was difficult to determine the concentration of Mg in this phase accurately. However, the mole fraction Mg/(Ti+Al) could be estimated to be about from 0.55 to 0.65 from a systematic analysis of inclusions. Similar to the MgO+(Mg–Ti–(Al)–O)+MnS inclusion (Fig. 1(a)), the size of the MgO+(Mg–Ti–Al–O)+MnS inclusions (Fig. 1(b)) was about 2 to 3 μm. The (Mg–Ti–Al–O)+MnS inclusion was not observed.

4.1.3. Steel Containing 21 ppm Al

The (Mg–Al–(Ti)–O) phase appeared instead of the (Mg–Ti–Al–O) phase. The mole fraction Al/(Ti+Al) was over 0.8 and the Mg/(Ti+Al) was varied from 0.36 to 0.43. The (Mg–Al–(Ti)–O) phase was precipitated together with MgO and with MnS. The amount of MgAl2O4+MnS inclusions (Fig. 1(e)) was much small compared to the MgO+(Mg–Al–(Ti)–O)+MnS inclusions (Fig. 1(c)). Due to the interference of MgO, the exact ratio of Mg to Al in the (Mg–Al–(Ti)–O) phase was difficult to determine in the MgO+(Mg–Al–(Ti)–O)+MnS inclusions. However, 1:2 ratios were clearly measured in the MgAl2O4+MnS inclusions.

4.1.4. Steel Containing 40 ppm Al

Inclusions in this steel were quite similar to those of the steel containing 21 ppm Al. The composition of the (Mg–Ti–Al–O) phase was almost MgAl2O4 with less than 0.05 of Ti/(Al+Ti). The noticeable difference is that large elliptical-shaped MnS inclusions with size more than 5 μm were formed with entrapping an MgAl2O4 aggregates (Fig. 3). This type of inclusions was observed only in the steels containing Al more than 40 ppm. This will be discussed later in more details. The volume of MgO in the MgO+MgAl2O4+MnS inclusions (Fig. 1(d)) was only about 10 vol% of the complex inclusion compared with similar inclusions observed in the steels containing Al less than 40 ppm.

4.1.5. Steel Containing 87 and 148 ppm Al

Single MgAl2O4 inclusions (Fig. 2(d)) began to appear, and MgO+MgAl2O4+MnS inclusions (Fig. 1(d)) were diminished. MnS (Fig. 2(d)), and MgAl2O4+MnS (Figs. 1(e) and 1(f)) inclusions were abundant. However, no separate Al2O3 inclusions were observed yet.

4.2. Thermodynamic Calculations and Interpretation of Inclusion Formation

Thermodynamic calculation for evolution of inclusions in each specific steel chemistry listed in Table 1 was carried out, and the results are presented in Fig. 4. In general, the calculated results are in agreement with the experiment except MgO. No liquid inclusion phase was predicted in the calculations. According to the calculations, the inclusion phases are mainly composed of the (Mg–Ti–Al–O) spinel and MnS. In addition very small amount of ilmenite can precipitate.

4.2.1. MgO–TiO2–TiO2–Al2O3 System

The inclusions precipitated in the present steels belong to the MgO–TiO2–TiO2–Al2O3 system. S and N are nearly insoluble in solid oxides of MgO–TiO2–TiO2–Al2O3 system. In the case of the steels investigated in the present study, the solubility of Mn into the oxide is calculated to be very small, which is also confirmed by the present experimental results. Thus MgO–TiO2–TiO2–Al2O3 oxide phases, MnS and TiN can be considered separately in the present study.

Pelton et al. measured the phase equilibria in the ternary Mg–Ti–O system by the quench method combined with a microscopic and X-ray diffraction analysis. They found that the composition of the Mg2TiO4–MgTiO2 spinel is significantly changed by the oxygen partial pressure; the composition of the spinel is closer to MnTiO4 (Ti4O7) under oxidizing atmosphere, and to MgTiO2 (Ti3O7) under reducing atmosphere.

Figure 5 shows the schematic phase diagram of the MgO–TiO2–TiO2–Al2O3 system. Three large solid solutions exist in this system; spinel, ilmenite and pseudobrookite. MgO and Al2O3 stay almost a stoichiometric compound below 1 600°C. According to the phase diagram information, Al is almost insoluble in ilmenite, and a pseudobrookite is composed of the MgTiO2–MgTiO2–TiO2–Al2O3 system. A spinel phase composed of the Mg2TiO4–MgTiO2–MgAl2O4 seems to be completely soluble each other. A miscibility gap between Mg2TiO4 and MgAl2O4 was reported in air, and its consolute temperature is about 1 370°C. However, no phase diagram or thermodynamic information for this system has been reported under reducing atmosphere like a metal saturation. In the development of database, the similar miscibility gap was considered for the Mg2TiO4–MgAl2O4 binary system.

In the calculations, the formation of a miscibility gap in the (Mg–Ti–Al–O) spinel phase was intentionally suppressed because it is believed that a miscibility gap does not easily form during the relatively rapid solidification like the present experimental study. The miscibility gap might be developed later during the annealing process at a high temperature.

4.2.2. (Mg–Ti–Al–O) Spinel Phase

Figure 6 shows the compositional trajectories of the (Mg–Ti–Al–O) spinel calculated from the thermodynamic
databases at different Al contents. The trajectories show very interesting behaviors. The composition of the spinel changes very rapidly and significantly during the solidification from liquid to bcc phase at about 1520°C. When the steel is in liquid state, the spinel phase is composed of more MgAl2O4 and less MgTi2O4 than the one precipitated just after solidification at about 1500°C. This is due to the large difference of activity coefficient of Ti (s) in liquid and solid bcc phase. The activity coefficient of Ti in bcc is almost 4 times bigger than in liquid steel. Thus, following reaction is believed to occur during the solidification.

\[
\text{MgAl}_2\text{O}_4 \text{ (spinel)} + 2\text{Ti (bcc)} \\
\rightarrow \text{MgTi}_2\text{O}_4 \text{ (spinel)} + 2\text{Al (bcc)}
\]
Therefore, the MgTi$_2$O$_4$ in the spinel can be increased rapidly during the solidification.

However, when TiN begins to precipitate at about 1460°C, the amount of Ti (that is, the activity of Ti) in solid steel decreases and the MgTi$_2$O$_4$ is changed back to the MgAl$_2$O$_4$:

$$2\text{Al (fcc)} + \text{MgTi}_2\text{O}_4 \text{ (spinel)} \rightarrow \text{MgAl}_2\text{O}_4 \text{ (spinel)} + 2\text{Ti (fcc)}$$

When the concentration of Al increases, the MgAl$_2$O$_4$ content in the spinel phase steeply increases. This is why such a peculiar compositional trajectories of spinel phase can be calculated in (Fig. 6).

Since the solidification is relatively rapid (32°C/min) in the present experiments, it is believed that the inclusions formed in liquid steel should be mostly maintained without significant transformation during the solidification. Compositions of the (Mg–Ti–Al–O) spinel determined from the present experiments are plotted in Fig. 7 together with the thermodynamic equilibrium predictions. As can be seen in the figure, the experimental results show a reasonably good agreement with the calculated trajectories at 1600°C to 1500°C. The extent of disagreement shown in the figure is attributed to the non-equilibrium continuous cooling in the present experiments. Nevertheless, the experimental data points lie near the equilibrium predictions in the compositional triangle.

4.2.3. MgO

According to the thermodynamic calculations, MgO can hardly form. However, a lot of MgO were observed in the present experimental study. This discrepancy is believed due to non-equilibrium heterogeneous reaction to form MgO. In the present study Mg was added after the addition of all other alloying elements. Since the deoxidizing power of Mg is much stronger than other elements such as Al and Ti, locally enriched Mg can easily react with not only dissolved oxygen but even with Al$_2$O$_3$ and Ti$_2$O$_3$ (or Ti$_3$O$_5$) oxides which have possibly formed already.

With increase of Al in steels, it was found that the amount of MgO in the inclusions is diminishing and finally disappears at 147 ppm Al. When enough Al is dissolved in the steel, since the amount of dissolved oxygen becomes smaller and the activity of Al is large enough, even local enrichment of Mg might be insufficient to form MgO.

Thermodynamic calculations were performed for liquid steels (Fe–0.1C–1.5Mn–0.1Si–0.014Ti–0.0035S–0.0025N in mass%) to find out the solubility of oxygen at 1600°C. The equilibrium solubility of oxygen in the liquid steel is calculated to be 28 and 27 ppm at 1600°C with 6 and 12 ppm Al, respectively. Pseudobrookite which is mainly composed of Ti$_3$O$_5$ can precipitate at Al content below 12 ppm. When Al content exceeds 21 ppm, Al$_2$O$_3$ can precipitate at 1600°C. The solubility of oxygen at 21, 40, 87 and 147 ppm Al contents is calculated to be 20, 13, 8 and 7 ppm, respectively. On the other hand, the solubility of oxygen in the liquid steel with no Al is calculated to be 6 ppm at 10 ppm Mg and 1600°C. Compared with the experimental data in Table 1, the calculations show that no stable solid oxides such as Al$_2$O$_3$ and Ti$_3$O$_5$ would form at Al content below 21 ppm prior to Mg addition into liquid steel at 1600°C. When Al is over 40 ppm, Al$_2$O$_3$ would form prior to Mg addition. Thus, MgO could easily form at low Al content by local enrichment of Mg. The tendency would be reduced with increasing the Al content.

4.2.4. Formation of MgO+(Mg–Ti–Al–O)+MnS Complex Inclusions

In the steels containing Al less than 40 ppm, the (Mg–Ti–Al–O) phase precipitated to form a complex MgO+(Mg–Ti–Al–O)+MnS type of inclusions rather than an (Mg–Ti–Al–O)+MnS type. This type of inclusions are possible to form by two different mechanisms depending on Al concentration in the steel. In the steels containing 6 and 12 ppm Al, the morphology of many complex inclusions shows that MgO is covered by the (Mg–Ti–Al–O) spinel and MnS (Fig. 1(a) and (b)). This means that MgO might be originally formed and the dissolved Ti and Al subsequently reacted with the MgO to form the (Mg–Ti–Al–O) spinel on the surface of the MgO. Even if there were Ti or Al oxides prior to Mg addition, these oxides should be reduced by Mg first to form MgO. Then, MnS precipitates...
around this oxide inclusion during solidification due to the large solubility difference of sulfur between liquid and solid steel. In the case of steel containing 21 and 40 ppm Al, MgO is attached to the (Mg–Ti–Al–O) spinel with MnS. This means that Ti2O3 or Al2O3, inclusions existed originally in liquid steel. When Mg was added in the steel, Mg reacted with the Ti or Al oxides and partially transformed these oxides to the (Mg–Ti–Al–O) spinel phase and the remaining Mg was precipitated on the surface as MgO. Then, MnS would precipitate on this oxide inclusion (Figs. 1(c) and 1(d)). Change of the formation mechanism of MgO in the present condition should be similar to what has been described in the previous Sec. 4.2.3.

4.2.5. Formation of TiN
As can be seen in Fig. 3 for the thermodynamic calculations, TiN forms almost at the same temperature and same amount in all steels, regardless of steel chemistry. According to the calculations, about 10 wt% of FeN and 10 wt% of TiC are also dissolved in TiN phase to form (Ti,Fe)(N,C) at the temperature between 1450° and 1200°C.

In the present study, TiN phase was observed always on the surface of MnS (Fig. 2(e)). No TiN was observed on the surface of oxides in the present study. On the contrary, Eijk30) reported the TiN could precipitate on the surface of (Mn–Ti–O) oxide phase by diffusion of N. However, he also observed TiN precipitated on the surface of MnS more frequently.

Based on experimental results in the present study and partially on the results of Eijk, it is concluded that TiN precipitates preferentially on the surface of MnS sulfide rather than MgO and spinel, probably due to the lower interfacial energy; both MnS and TiN have the same crystal structure, Pm3n, and the lattice parameters are different by 19%; MnS (5.22 Å)31) and TiN (4.24 Å).32) In this case, not only MgO aggregates were observed, as expected from the known zero interaction between MgO.33,34) MgAl2O4 can form aggregates on the front side of solidification and subsequently be encapsulated by MnS. Actually MgAl2O4 aggregates which were not encapsulated by MnS were observed in the steels containing Al more than 87 ppm (Fig 1(f)). In comparison, no MgO aggregates were observed, as expected from the known zero interaction between MgO.35,36) MnS Entrapping MgAl2O4 Aggregates
Several MgAl2O4 aggregates were found entrapped by MnS in the steel containing Al more than 40 ppm. As can be seen in Fig. 3, the small MgAl2O4 granules are entrapped in a large MnS. It is not certain how this kind of MnS is possible to form in the present state. However, since this kind of MnS is observed in the steel which contains large amount of MgAl2O4, the following mechanism may be postulated. If MgAl2O4 has negative interaction each other like Al2O3,33,34) MgAl2O4 can form aggregates on the front side of solidification and subsequently be encapsulated by MnS. Actually MgAl2O4 aggregates which were not encapsulated by MnS were observed in the steels containing Al more than 87 ppm (Fig 1(f)). In comparison, no MgO aggregates were observed, as expected from the known zero interaction between MgO.35,36)

5. Conclusions
The effect of Al on the morphology, composition and size of the inclusions formed in the Fe–C–Mn–Si–Ti–Mg–Al–O–S–N steel during the solidification were investigated in the present study. In order to interpret the complex mechanism of inclusions formation, the FACT and SGTE thermodynamic databases were employed for the simulation of the evolution of inclusion during the solidification. The simulated results are in good agreement with experimental results. The results can be summarized as follows:

The inclusions in the present study belong to the MgO–Ti2O3–TiO2–Al2O3+MnS+TiN system. One of major inclusion phases was the (Mg–Ti–Al–O) spinel, which is composed of Mg3TiO4–Mg3Ti2O5–MgAl2O4. With the increase of Al in steels, the composition of spinel phase was changed continuously from Mg–Ti–O to MgAl2O4. At 21 ppm Al, the Mg–Ti–Al–O spinel was already very closed to MgAl2O4.

Non-equilibrium MgO which was formed by the deoxidation in liquid steel seems to be readily used for the formation of complex inclusions MgO+(Mg–Ti–Al–O)+MnS. The precipitation of TiN was only observed on the surface of MnS. In high concentration of Al in steels, MgAl2O4 aggregates entrapped in large MnS were also observed. From the observation of MgAl2O4 aggregates, we could postulate that there is attractive force between MgAl2O4.

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