Corrosion resistance of alumina-magnesia castable to slag in steel ladle lining

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The corrosion resistance of alumina-magnesia castable to a basic slag was evaluated to find the highly-resistive castable composition for steel processing. Stable solid phases were CA6, alumina and spinel after firing of the castable of Al₂O₃–MgO–CaO–SiO₂ system. The slag corrosion was simulated thermodynamically for CA6, alumina, spinel and castables. The solubility of each oxide component is expected in the order of MgAl₂O₄ > CA6 > Al₂O₃ at 1600°C because of the formation of CA2 on CA6 and the formation of CA2 and CA6 on alumina, suggesting the protection of castable from slag. However, CA2 and CA6 disappear at 1800°C and the solubility changes in the order of CA6 and the formation of CA2 and CA6 on alumina, suggesting the protection of castable from slag. However, CA2 and CA6 disappear at large amount of slag and a high temperature. The solubility of castable decreases with increasing MgO/CaO ratio owing to spinel formation. The practical immersion test demonstrated the high corrosion resistance of high MgO/CaO castable against slag, exhibiting the importance of spinel formation.

1. Introduction

Alumina-magnesia castables have been used as refractory for lining steel ladles.¹² The castables are composed of alumina aggregates and fine-grain matrix consisting of alumina, magnesia, fumed silica and alumina cement. Corundum (α-Al₂O₃), spinel (MgAl₂O₄), CA6 (Ca₆Al₁₂O₁₉) and glass phase are generated by heat in contact with molten steel.³ Slag is a molten liquid of metal oxides floating on molten steel, and corrodes the castables. The mechanism of slag corrosion is classified as follows: wetting of molten slag to refractory, dissolution of refractory component into slag, penetration of molten slag into refractory, and formation of reaction products. The deterioration by slag penetration and chemical reaction leads to spalling of the surface layer of refractory. The authors have studied on the reaction behaviors of alumina-magnesia and alumina-spinel castables with molten slag.⁴ They reported that alumina-rich spinel forms in the alumina-magnesia castable and that the excessive alumina is released to molten slag and increases the viscosity of slag, leading to low wettability and retarded slag-penetration. Next, the authors focused on the reaction and dissolution behaviors of refractories in molten slag. The slag corrosion depends on the chemical compositions of refractory and slag. However, the slag composition is changed depending on the demanded steel. The importance is to find an appropriate composition of refractory available to various slag compositions. Thermodynamic simulation is useful to anticipate the stable solid and liquid phases in the final stage of slag-refractory reaction.⁵–⁸ F. Melcher et al.⁷ thermodynamically analyzed the stability of alumina-magnesia and alumina-spinel castables in steel slags, reporting that castables with a large amount of spinel are supposed to have a better slag resistance, whereas the formation of CA6 and CA2 (Ca₆Al₁₂O₁₉) layers at a low temperature has a positive effect on the corrosion resistance. Generally speaking, however, when the content of spinel is large, the castable has an excellent corrosion resistance.⁹

In the present study, the corrosion resistance of alumina-magnesia castable was thermodynamically simulated with emphasis on MgO/CaO ratio. The assumed slag was a highly basic and corrosive one for acidproof steel refining. The simulated results were compared to the practical data by an immersion test of the castables with the slag.

2. Experiments

2.1 Preparation of alumina-magnesia castables

Four kinds of alumina-magnesia castables (Cast 1–4) were prepared at the formulation in Table 1. The raw materials were of industrial grade in Krosaki Harima Co. The castables were composed of coarse alumina aggregates less than 8 mm, intermediate alumina aggregates less than 1 mm, and matrix consisting of fine grains of 75 μm or less of alumina, magnesia, alumina cement and fumed silica. The fractions of coarse aggregates, intermediate aggregates and matrix were 50, 19 and

<table>
<thead>
<tr>
<th>Chemical composition/mass %</th>
<th>Cast 1</th>
<th>Cast 2</th>
<th>Cast 3</th>
<th>Cast 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse aggregate (1–8 mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Intermediate aggregate (1 mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>18.9</td>
<td>18.9</td>
<td>19.0</td>
<td>18.9</td>
</tr>
<tr>
<td>Matrix (75 μm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>24.2</td>
<td>23.4</td>
<td>22.5</td>
<td>21.7</td>
</tr>
<tr>
<td>MgO</td>
<td>4.8</td>
<td>6.0</td>
<td>7.1</td>
<td>8.3</td>
</tr>
<tr>
<td>CaO</td>
<td>1.4</td>
<td>1.0</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
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</tbody>
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31 mass %, respectively. The MgO/CaO ratio of the matrix was changed in the range of 3.4–20.8 in mass. The alumina cement was composed of calcium aluminate (CA, CA2, etc.). The content of calcia in the matrix was changed with the content of alumina cement. The alumina content in the matrix was adjusted at the stoichiometry to form spinel and CA6. An appropriate amount of conditioning agent (dispersing agent, retardant, etc.) was added to adjust the fluidity and hardening time of castable.

The powders were mixed with 6.1 mass % water for 3 min, and casted into a polystyrene mold of 40 mm × 40 mm × 160 mm. The casted sample was removed from the mold after curing for 2 days at 20°C in a temperature-controlled room and dried for over 24 h at 110°C in a drying chamber. The casting was conducted for 3 h at 1500°C in an ambient atmosphere with an electric furnace. The apparent porosities of the castables were measured by water immersion method.

The fired castables were cut with a diamond wheel and polished with a diamond slurry. The microstructure was observed with an electron probe microanalyzer (EPMA, JEOL Ltd., JXA-8200), and the elemental distribution was locally analyzed by energy dispersive X-ray spectroscopy (EDS) to determine the crystalline species of grains. The crystalline phases were identified by X-ray diffractometry (XRD, Rigaku Co. Ltd., RU-200B) using Cu Kα radiation.

### 2.2 Corrosion test

The model slag of Al₂O₃-CaO-MgO-SiO₂-FeO-MnO system was supplied by Krosaki Harima Co. After melting and cooling, the solidified slag was pulverized. The chemical composition was analyzed by X-ray fluorescence analysis (XRF, Rigaku Co. Ltd., Simultix 14). Al₂O₃ 32.0%, CaO 55.7%, SiO₂ 8.9%, MgO 2.0%, FeO 0.8%, Fe₂O₃ 0.1%, MnO 0.5% in mass. The basicity defined as C/S (CaO/SiO₂) was 6.3.

The Corrosion test was carried out by a crucible method. The castables were prepared in a size of 50 mm in diameter and 50 mm in height. After firing at 1500°C for 3 h, the castables were machined to make a hole in a size of 20 mm in inner diameter and 30 mm in depth. The 12.5 g of pulverized slag was charged into the test crucible and heated at 1675°C for 12 h. After testing, the cooled slag and crucible were cross-sectioned and the appearance of slag penetration and damage of crucible wall was recorded with a digital camera. The corrosion index was determined by image analysis of the cross-section, in which the final cross-sectioned area of crucible hole was evaluated and normalized by that of Case 1. The microstructure was observed by EPMA, and the Al₂O₃/MgO molar ratio of spinel was analyzed by EDS.

### 2.3 Thermodynamic simulation

The stable phases after firing of alumina-magnesia castables and after reaction of slag with castables and their stable oxide components (CA6, alumina, spinel) were thermodynamically simulated under the condition of chemical equilibrium by using the FactSage program. In the calculation, ChemSheet was used as software and FACT database as data source. The data of pure solids were selected for the compound species, and FACT-MULL, FACT-Mel, FACT-SLAG, FACT-WOLL, FACT-MeO and FACT-CORU were selected for the solution species. The simulation was compared with the results of immersion tests to evaluate the corrosion resistance of alumina-magnesia castable against molten slag.

### 3. Results and discussion

#### 3.1 Stable phases of alumina-magnesia castable after firing

The stable phases after firing of alumina-magnesia castable were thermodynamically simulated in the temperature range of 1000–1800°C. The thermodynamic simulation of change in stable phase of Cast 1 and Cast 4 with temperature is shown in Fig. 1. The formation of gehlenite (Ca₃Al₂Si₂O₇), anorthite (CaAl₂Si₂O₈) and CA6 is expected as reaction product among alumina, calcia and silica, and the formation of spinel as reaction product between alumina and magnesia. The stability of the Ca-compound is in the order of Ca₃Al₂Si₂O₇ < CaAl₂Si₂O₈ < CA6. The Ca-compounds decompose with a rise of temperature, leading to the formation of liquid. Spinel is stable and remains at a relatively high temperature. Although alumina is consumed by reaction with calcia, silica and magnesia, corundum is more stable phase than the Ca-compounds at a high temperature. At the firing temperature of 1500°C, CA6, alumina and spinel are expected as stable solid phase. MgO/CaO ratio is high in the order of Cast 1 < Cast 2 < Cast 3 < Cast 4. With increasing MgO/CaO ratio, the contents of CA6, alumina and liquid decrease, whereas the spinel content increases.

The backscattered electron image of the microstructure of Cast 1 after firing at 1500°C is shown in Fig. 2. The image demonstrates the microstructure of fine-grain matrix. The distribution of Ca, Al, Mg and Si of each grain was measured by EDS spot analysis to distinguish CA6 and spinel grains. Acicular grains were assigned to CA6 and tiny grains to spinel. With an increase in MgO/CaO ratio from Cast 1 to Cast 4, the number of CA6 grains decreased and the number of spinel grains increased. The XRD patterns of fired castables are shown in Fig. 3. Since the castables included a large amount of alumina, strong XRD peaks
CA6. and alumina are more stable than spinel. The formation of CA2 and CA6 is not observed at 1800°C. The change in the amount of liquid formed from the oxide component by addition of slag is shown in Fig. 5. At 1600°C, the amount of liquid slightly decreases by addition of slag because of the formation of Ca-compounds, and increases at a large amount of added slag because of the dissolution of Ca-compounds. Because of the formation of large amounts of Ca-compounds, the sequence of solubility is expected in MgAl2O4 > CA6 > Al2O3 at 1600°C. The amount of liquid significantly increases at 1800°C, and CA2 and CA6 disappear on CA6 and alumina. Therefore, the sequence of solubility is expected in the order of CA6 > Al2O3 > MgAl2O4. As seen here, there is a possibility that CA2 and CA6 work as protective layer on CA6 and alumina at a low temperature, but spinel is essentially stable at a high temperature.

3.3 Reactivity of alumina-magnesia castable with slag

The stable phases of Cast 1–4 in slag were thermodynamically simulated by the similar method as in Section 3.2. Intermediate alumina aggregates and fine-grain matrix were considered for calculation, because coarse alumina aggregates seemed not to participate in the reaction. Figure 6 shows the thermodynamic simulation of change in stable phase on Cast 1 and Cast 4 in slag. Stable solid phases are CA6, alumina and spinel at 1600°C. CA6 is unstable in castables at this temperature according to Fig. 1. The existence of CA6 means that CA6 is stabilized by large amounts of calcia and alumina in slag. CA2 does not form in castables differently from CA6 and alumina in Fig. 4. This is because the amounts of CA6 and alumina are reduced by mixing with magnesia in castables and alumina is consumed to form spinel. With an increase in MgO/CaO ratio from Cast 1 to Cast 4, the amounts of CA6 and alumina decrease, whereas the amount of spinel increases. CA6 disappears at 1800°C, and the amount of alumina decreases and the amount of spinel increases with an increase in MgO/CaO ratio. The required amount of added slag for complete dissolution is raised owing to the formation of spinel at 1600 and 1800°C. The change in the amount of liquid formed from the castables by addition of slag is shown in Fig. 7. Even without added slag, the liquid exists because a liquid phase exists in castables as shown in Fig. 1. The change in the amount of liquid is divided into 4 stages at 1600°C. The direct dissolution of alumina takes place at Stage I. The dissolution is retarded by CA6 at Stage II. The CA6 dissolves at Stage III, and then spinel dissolves at Stage IV. There are Stage I and Stage IV at 1800°C because there is no CA6. The first slope is assigned to the dissolution of alumina and the second slope to the dissolution of spinel. The protective effect by CA6 is expected at a small amount of added slag and a low temperature. Under an ordinary operation condition, the solubility of castable is essentially in the order of Cast 1 > Cast 2 > Cast 3 > Cast 4, depending on the formation of spinel.

3.4 Corrosion resistance of alumina-magnesia castable in slag

The results of corrosion tests of Cast 1 to Cast 4 in slag at 1675°C are demonstrated in Fig. 8. Judging from the external view and the corrosion index, the erosion of crucible wall was
serious in the order of Cast 1 > Cast 2 > Cast 3 > Cast 4. This result agrees with the thermodynamic simulation, supporting the usefulness of spinel formation in castables. It was, further, found that the slag penetration was retarded at high MgO/CaO ratio. The apparent porosities of Cast 1, Cast 2, Cast 3 and Cast 4 after firing at 1500°C were 23.6, 22.4, 22.2 and 22.3 vol%, respectively. The porosity of Cast 1 was a little high, but those of other castables were identical. Hence, it was considered that the other factors rather than porosity affected the degree of slag penetration.

The backscattered electron images of microstructures of Cast 2 after corrosion test are shown in Fig. 9. The images demonstrate the microstructures of slag penetration layer immersed with molten slag and non-penetration layer inside. The Al/Mg atomic ratio of each grain was measured by EDS spot analysis to find spinel grains and calculate the Al2O3/MgO molar ratio. The results of spot analyses are described below Fig. 9. The Al2O3/MgO molar ratio of spinel was 1.0–1.1 in the slag penetration layer, whereas it was 1.5–1.6 in the non-penetration layer. Thus, the alumina-rich spinel formed in the castables and changed to stoichiometric one in the slag penetration layer. The authors reported in the previous paper4) that the alumina-rich spinel released the excessive alumina to molten slag, which led to the increase in viscosity of slag and the retardation of slag penetration. It should be also noted that, according to the thermodynamic simulation, CA6 in castables tends to disappear, meaning the dissolution of calcia into slag. The viscosity of molten slag is known to decrease with an increase in calcia content.11),12) The amount of dissolved calcia is low in high MgO/CaO castable. The dissolution of alumina from alumina-rich spinel and the decrease in the amount of dissolved calcia may cause the increase in viscosity of slag, leading to the retardation of slag penetration, in the front of penetrating molten-slag even though the slag contained large amounts of calcia and alumina.

As described above, there is a possibility that the corrosion of castable is suppressed by the formation of Ca-compounds at a small amount of added slag and a low temperature, which is also expected in the thermodynamic simulation of reactivity of oxide components. At a large amount of added slag and a high...
temperature, the Ca-compounds are useless and the corrosion resistance depends on spinel formation. The C/S of slag used in the present work is high, meaning that it is highly corrosive. Under such a corrosive condition, the magnesia-rich castable had a superior corrosion resistance against the molten slag because of the excellent stability of spinel generated in the castables.

Fig. 6. (Color online) Thermodynamic simulation of change in stable phase on castables in slag at 1600 and 1800°C.

Fig. 7. Thermodynamic simulation of change in the conversion of solid to liquid by addition of slag at 1600 and 1800°C.

Fig. 8. (Color online) Cross-sections of castable crucibles after corrosion test at 1675°C.
4. Conclusion

The corrosion resistance of alumina-magnesia castable against steel slag was evaluated thermodynamically and experimentally with emphasis on the MgO/CaO ratio of castables. The results are concluded as follows.

1) Stable oxide phases are CA6, alumina and spinel after firing of castables at 1500°C. The amount of CA6 decreases and the amount of spinel increases with an increase in MgO/CaO ratio.

2) The thermodynamic simulation of solubility of oxide component in slag exhibits the sequence of MgAl2O4 > CA6 > Al2O3 at 1600°C. This is attributed to the formation of CA2 and CA6 in CA6 and alumina owing to the large contents of calcia and alumina in slag. At 1800°C, however, the sequence of solubility changes to CA6 > Al2O3 > MgAl2O4 because the Ca-compounds are unstable at a high temperature.

3) The existence of CA6 is expected on castables in slag at 1600°C, similarly to the simulation of solubility of oxide component, suggesting the protection of castables by CA6. However, CA6 disappears at a large amount of added slag and a high temperature. Eventually, the corrosion resistance depends on the content of spinel. The high corrosion resistance of the high MgO/CaO castable was proved in the immersion test.

References