Improved Corrosion Resistance of Alumina-Spinel Castable by Colloidal Alumina Addition


Alumina-spinel castables are usually applied as a refractory lining of steel ladles in regions where both volumetric stability and corrosion resistance are required. However, the addition of the traditional calcium aluminate cement as a binder agent in those refractories leads to residual expansion and reduces the basic slag resistance, mainly due to the CA$_6$ (CaO·6Al$_2$O$_3$) formation. In this work, a novel approach was designed in order to improve the performance of these materials, by using alumina-based binder agents: hydratable alumina and colloidal alumina. The results highlighted a reduced corroded area after the slag tests for the latter, which was most likely associated with the decrease in the average pore size. Therefore, the use of these nano-scaled alumina particles points out a promising technique to produce alumina-spinel castables for key regions in the steel ladle.

1 Introduction

Different classes of refractories are usually applied as a lining material for steel ladles due to the distinct applications requirements of the secondary steel treatment [1]. For the impact pad, for instance, a material with suitable hot mechanical strength must be selected, as this region withstands most of the mechanical load during the steel tapping [2]. In addition, the refractory in this area is subjected to thermal cycling and occasional contacts with the slag after casting [3]. Therefore, basic slag resistance and thermal-stress relaxation should also be considered.

In order to fulfill all these needs, alumina-spinel (spinel-containing) castables are preferred instead of alumina-magnesia (spinel-forming) ones for application as impact pad material. The presence of pre-reacted spinel grains ensures the volumetric stability desired for the ladle bottom materials [2, 4, 5]. Nonetheless, as calcium aluminate cement (CAC) is the traditional binder for this sort of castables, the expansive CA$_6$ (CaO·6Al$_2$O$_3$) formation takes place during the heat treatment [6]. According to previous investigations by the authors [7, 8], even alumina-spinel castables present relevant values of residual expansion after firing due to the calcium hexaluminate formation, which may lead to cracks and reduce its service life. Moreover, Braulio, et al. [9] pointed out that cement-bonded alumina-spinel castables presented poor corrosion resistance when in contact with basic molten slag.

Considering these aspects, an alternative binder has been required for a suitable performance of high-alumina castables containing pre-formed spinel. Hydratable alumina (HA) and a colloidal alumina suspension (ColAlu) were evaluated in the present work as two alumina-based binders with great potential to replace CAC. Although detecting eventual problems during the drying stages, some studies [10–12] showed interesting results regarding the use of such alumina particles as sintering additives, suggesting that this alternative might reduce the slag penetration level.

Tab. 1 Composition in weight percent of the evaluated castables with different binders

<table>
<thead>
<tr>
<th>Raw materials [mass-%]</th>
<th>CAC</th>
<th>HA</th>
<th>ColAlu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tabular alumina [d ≤ 6 mm]</td>
<td>72</td>
<td>72</td>
<td>72</td>
</tr>
<tr>
<td>Pre-formed spinel [d &lt;0.5 mm]</td>
<td>21</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>Fumed silica</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Fine tabular alumina [d &lt;45 µm]</td>
<td>–</td>
<td>–</td>
<td>6</td>
</tr>
<tr>
<td>CAC</td>
<td>6</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Hydratable alumina</td>
<td>–</td>
<td>6</td>
<td>–</td>
</tr>
<tr>
<td>Colloidal alumina [50 mass-% solids]</td>
<td>–</td>
<td>–</td>
<td>8</td>
</tr>
</tbody>
</table>

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2 Experimental procedures

Two alumina-spinel compositions containing colloidal alumina (ColAlu) or hydratable alumina (HA) as binders were formulated and compared with a traditional cement-bonded one. The compositions of the evaluated castables are presented in Tab. 1 and they comprised tabular alumina (d ≤ 6 mm, Almatis/DE) as the coarse aggregates, 21 mass-% of pre-reacted spinel (AR78, 78 mass-% Al₂O₃, Almatis), and 1 mass-% of fumed silica (971 U, Elkem/NO) in the matrix in order to attain a suitable workability. 6 mass-% of calcium aluminate cement (Secar 71, Kerneos/FR), 6 mass-% of hydratable alumina (Alphabond 300, Almatis) and 8 mass-% of colloidal alumina suspension (d < 80 nm, VP Disp 650 ZXP, Evonik Degussa/DE) were the binder contents analyzed in this work.

As the selected suspension comprised 50 mass-% of solids and 50 % of water, the actual solid content added to the ColAlu composition was 4 mass-%. Initially, samples containing 6 mass-% of nano-particles were prepared in order to compare them considering the same binder amount. However, due to gelling, large pores appeared in the castable’s microstructure after curing, which spoiled the properties evaluation. Thus, a composition with lower colloidal alumina content was designed and this problem was no longer detected.

For the corrosion experiments, the cup-test technique was applied and the samples were prepared in a 50 mm × 50 mm cylindrical shape with a 20 mm diameter × 25 mm depth internal hole. After curing at 50 °C for 1 day, drying at 110 °C for additional 24 h and pre-firing the samples at 1500 °C for 5 h, their internal holes were filled with 10 g of a high-iron steel ladle slag in order to perform the tests. The chemical composition of the industrial slag used in this work is presented in Tab. 2. The corrosion experiment was conducted at 1500 °C for 2 h in a vertical tube furnace (HTRV100-250/18 GERO/DE) in air. After the test, the corroded samples were cut and the cross-sections were used for further microstructural analyses (SEM, JEOL JSM – 5900 LV). SEM images of the castables before the slag attack were also attained and pore size distribution measurements were carried out analyzing these micrographs using the Noran NSS 2.2 analyzer software (Thermo Fisher Scientific/USA).

3 Results and discussions

Fig. 1 shows the corrosion profiles and the respective penetration and wear indexes of the alumina-spinel castables with different binders after the corrosion experiments. The cement-bonded composition presented a poor corrosion resistance, which was already expected. Regarding the use of alumina-based binders, the HA sample was as corroded as the CAC one, but with a lower slag penetration index. Conversely, the ColAlu castable was barely infiltrated and the attained result for this spinel-containing castable was good and similar to those reported by Braulio et al. [9] for alumina-magnesia castables.

According to Mori, et al. [13], the corrosion mechanism related to these materials involves initial reactions between Al₂O₃ from the refractory and CaO from the slag (which is present in a high concentration, according to Tab. 2) leading to the precipitation of calcium aluminate phases. For the evaluated spinel refractory castables, three reactions involving Al₂O₃ and CaO are likely to take place during the interaction with the molten slag [15]:

\[
\text{CaO} + 6\text{Al}_2\text{O}_3 (s) + 2\text{CaO}_2 \rightarrow 3\text{[CaO-2Al}_2\text{O}_3 (s)} \quad \Delta G = -65.1 \text{ kJ/mol} \quad (1)
\]

\[
6\text{Al}_2\text{O}_3 (s) + \text{CaO}_2 \rightarrow \text{CaO-6Al}_2\text{O}_3 (s) \quad \Delta G = -261.1 \text{ kJ/mol} \quad (2)
\]

\[
2\text{Al}_2\text{O}_3 (s) + \text{CaO} \rightarrow \text{CaO-2Al}_2\text{O}_3 (s) \quad \Delta G = -152.2 \text{ kJ/mol} \quad (3)
\]

Reaction 1 can only be carried out in the cement-bonded composition, as CAC is an expected microstructural phase and, when in contact with the slag, leads to the formation of dense CA₂ layers. However, even in this case, the reaction only occurs in regions where the free alumina availability is low. When possible, the dissolution of Al₂O₃ in the molten slag and the precipitation of CA₂ (reaction 2) or CA₃ (reaction 3) is thermo-
dynamically more favorable (more negative ΔG values).

In order to better understand the corrosion mechanisms for the three compositions based on the above-described reactions, SEM micrographs of the samples’ corroded area were attained and presented in Fig. 2, highlighting the interaction between the liquid and the tabular alumina aggregates. Without any previous CA₆ formation during sintering, HA and ColAlu samples are more likely to be corroded according to reaction (2) (lowest value of Gibbs free energy). For the cement-bonded one, the tabular alumina aggregate availability is also high, as CA₆ crystals are usually generated in the castable matrix [8]. Therefore, as can be observed, the result was very similar for the three cases: a great needle-like CA₆ formation at the aggregates due to the reaction with slag (according to reaction 2).

As the chemical interactions between the alumina-spinel castables and the slag were ruled by the same mechanism, the differences observed in their corrosion resistance are most likely associated with the refractory contact to the liquid. In fact, the acicular calcium hexaluminate crystals formation is followed by a residual expansion [7–9]. Thus, if the infiltrated area is high, the amount of precipitated CA₆ will also increase, leading to crack generation and further penetration throughout the corrosion cycles.

Fig. 3 presents the permanent linear change and the apparent porosity values for the three castables at high temperatures. It can be noticed that the previous CA₆ formation in the cement-bonded sample led to expansion and then to an increase in the apparent porosity from 1300 to 1500 °C. On the other hand, due to the absence of expansive reactions, the values for the HA-bonded castable dropped at 1500 °C as a result of the sintering shrinkage. Finally, the colloidal alumina presence resulted in an even more densified structure due to its higher specific surface area and sinterability. Its low apparent porosity value at 1150 °C confirms that sintering initiated earlier in this composition. This different microstructural development during sintering can be observed in Fig. 4, which shows SEM micrographs before the slag attack after pre-firing at 1500 °C for 5 h. The castable’s average pore size (d₅₀) was also significantly affected by the addition of distinct binders, as observed in Fig. 5. Thus, although the corrosion mechanism was basically the same regardless of the binder agent, the better performance of the colloidal-alumina bonded-castable was associated with the lower physical infiltration degree. Due to a denser structure and higher amount of small pores, the chemical interaction between the molten slag and the refractory was restricted to the interface regions, decreasing the wearing rate. Conversely, for the CAC-bonded and HA-bonded
between the slag and the refractory during testing were restricted to the interface regions, leading to low penetration and wear indexes. Hence, the results pointed out a novel and promising technique to produce alumina-spinel castables suitable for key regions in the steel ladle.

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References


Fig. 5 Pore diameter distribution of the alumina-spinel castable containing CAC and colloidal alumina, based on SEM images measurements

castables, the slag penetration was deeper, increasing the corroded area and leading to the precipitation of a greater CA6 content. As a result, cracks were generated, acting as new paths for further cycles of penetration and chemical reactions.

4 Conclusions

Regardless of the selected binder agent, the chemical interaction between the alumina-spinel castables and the steel ladle slag was ruled by the same mechanism: alumina dissolution and CA6 precipitation as the main reaction product. Thus, the material corrosion resistance was defined by the physical infiltration degree and the amount of CA6 generated from the refractory-slag interaction. The colloidal alumina suspension provided the most efficient sintering process, reducing infiltration paths and the average pore size. As a result, unlike the other two compositions, the chemical reactions between the slag and the refractory during testing were restricted to the interface regions, leading to low penetration and wear indexes. Hence, the results pointed out a novel and promising technique to produce alumina-spinel castables suitable for key regions in the steel ladle.