Thermal characteristics of Al$_2$O$_3$–MgO and Al$_2$O$_3$–spinel castables for steel ladles

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Abstract

The hot properties of the Al$_2$O$_3$–MgO castables containing 5.5 wt.% MgO and 1.36 wt.% CaO with and without the addition of 0.75 wt.% microsilica and the Al$_2$O$_3$–spinel castables containing 20 wt.% Al$_2$O$_3$–rich spinel of 90 wt.% Al$_2$O$_3$ and 1.70 wt.% CaO, respectively, were investigated. The thermal shock damage test using the prism quench into water technique indicated that the retained modulus of rupture of the Al$_2$O$_3$–MgO castables after three cycles was down to 5%, while that of the Al$_2$O$_3$–spinel castables was 51%. The combined test of slag and thermal shock attack on castables using the rotary slag test furnace showed that the Al$_2$O$_3$–MgO castables had 0% penetration and 24% erosion, while the Al$_2$O$_3$–spinel castables had 10% penetration and 30% erosion. The field trials confirmed that Al$_2$O$_3$–MgO castables have better slag resistance and a longer service life for use in steel ladles, compared to Al$_2$O$_3$–spinel castables. The importance of thermal shock damage resistance of castables for use in steel ladles should be de-emphasized, based on the lab and field tests. There is no correlation between hot strengths and slag resistance for castables. The magnitude of specific surface area of pores is more important than pore size and porosity for governing the slag resistance of Al$_2$O$_3$–MgO castables, with and without microsilica addition.

Keywords: C. Thermal shock resistance; RUL; HMOR; Slag resistance; Pore size; Specific surface area

1. Introduction

Both Al$_2$O$_3$–MgO and Al$_2$O$_3$–spinel castables have been widely used as steel ladle linings below the slag line because of increasing labor costs and the severe secondary steelmaking environment in the ladle. In Al$_2$O$_3$–MgO castables, MgO reacts with Al$_2$O$_3$ to form in situ spinel during the service, while in Al$_2$O$_3$–spinel castables spinel are added to the mixes as a grain phase. Al$_2$O$_3$–MgO castables are replacing Al$_2$O$_3$–spinel castables because of their superior slag resistant properties [1–3].

Currently Al$_2$O$_3$–MgO castables are used in the wall and bottom impact pad, while Al$_2$O$_3$–spinel castables are used in the bottom area other than the impact pad.

The addition of a small amount of microsilica to Al$_2$O$_3$–MgO castables is to promote hydration resistance and spinel formation [4,5]. The addition results in the deterioration of hot strength [2] and thermal shock damage resistance [4]. High hot strength and low deformation under load are highly preferred by refractories users. Al$_2$O$_3$–MgO castables show lower hot strength, higher deformation under load and poor thermal shock damage resistance, compared to Al$_2$O$_3$–spinel castables [2]. Yet Al$_2$O$_3$–MgO castables is superior to Al$_2$O$_3$–spinel castables in slag resistance.

The purpose of the present work is to further explore the characteristics of these castables.

2. Experimental procedures

2.1. Materials

The chemical composition of raw materials is listed in Table 1. The Al$_2$O$_3$–MgO castables contained 5.5 wt.% MgO and 1.36 wt.% CaO. The Al$_2$O$_3$–spinel castables contained 20 wt.% Al$_2$O$_3$–rich spinel of 90 or 95 wt.% Al$_2$O$_3$ and 1.70 wt.% CaO. The physical properties of these castables are given in Table 2.
2.2. Procedures

Castables were cast with water (6 wt.% for Al$_2$O$_3$–MgO castables and 6.5 wt.% for Al$_2$O$_3$–spinel castables) with the aid of a vibrating table. Castables were cured in air at ambient temperature for 24 h and then dried at 110°C for at least 16 h before firing. Specimens 160x40x40 mm were cast for measuring physical properties including hot modulus of rupture (HMOR). Physical properties such as apparent porosity, reheat linear change, and cold strengths of the castables fired at 1500°C for 3 h were measured based on JIS [6]. All physical properties were determined using three specimens with the average value taken.

The specimens for hot modulus of rupture measurements were heated at a rate of 10°C/min from ambient temperature to 1000°C and, for tests at higher temperatures, further on at a rate of 5°C/min from 1000 to 1250°C and 3°C/min from 1250°C up to the final testing temperature. The specimens were held at 1000, 1100, 1200, 1300, 1400 and 1500°C for 2 h 40 min before measurements at temperature were made. Hot strength was determined using a three-point bending method. The span and loading rate used in measuring the strength were 100 mm and 0.49 MPa/s, respectively. Hot strength at temperature was determined using three specimens with the average value taken.

A cylindrical specimen, 50 mm in height and 50 mm in diameter, was cast for the refractoriness under load test. A differential technique was employed for measuring the deformation. The specimen was heated at a constant rate of 6°C/min below 1000°C and 3°C/min above 1000°C, at a fixed load of 0.2 MPa. Deformation under load vs. temperature was recorded from ambient temperature up to 1640°C. The high temperature load testing machine (model HW-10K, EKO, Japan) was used for carrying out the measurements.

The thermal shock damage test was conducted by quenching a specimen into 25°C water. Prior to quenching each specimen was heated at 1500°C for 3 h, followed by overnight furnace cooling. One prism quench cycle consisted of reheating a specimen at 1100°C for 1 h, followed by quenching into a 25°C water barrel. The combined test of slag attack and thermal shock on these castables was conducted in a gas-fired rotary slag test furnace; the test detail was reported elsewhere [7]. The furnace was rotated at 2 rpm and fired rapidly to reach 1650°C in 50 min. Block steel (800 g) were charged into the furnace as soon as the furnace temperature reached at 1200°C. Steel melted in 10 min. Eight hundred grams of lump BOF slag (CaO/SiO$_2$ = 3.8, 33.7% Fe$_2$O$_3$) were charged into the furnace when the steel started melting. Slag and steel melted in another 10 min. At the end of 60 min holding at 1650°C, the slag was drained by tilting the furnace to a 60° position, followed by quenching the lining using compressed air of 0.7 MPa for 10 min. One cycle consisted of adding 800 grams of steel and 800 g of slag to the rotary furnace and holding at 1650°C for 60 min, followed by quenching the lining. A total of six consecutive cycles was required for one run for the combined test of slag attack and thermal shock. After the completion of the

### Table 1

<table>
<thead>
<tr>
<th>Composition (wt.%)</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>Na$_2$O</th>
<th>MgO</th>
<th>CaO</th>
<th>K$_2$O</th>
<th>B$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>White fused Al$_2$O$_3$</td>
<td>99.7</td>
<td>0.016</td>
<td>0.013</td>
<td>0.004</td>
<td>0.15</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>94% Al$_2$O$_3$ spinel</td>
<td>94.1</td>
<td>0.05</td>
<td>0.05</td>
<td>–</td>
<td>–</td>
<td>5.41</td>
<td>0.29</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>90% Al$_2$O$_3$ spinel</td>
<td>89.04</td>
<td>0.11</td>
<td>0.03</td>
<td>0.04</td>
<td>0.21</td>
<td>10.51</td>
<td>0.15</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Calcined Al$_2$O$_3$</td>
<td>99.7</td>
<td>0.02</td>
<td>0.01</td>
<td>–</td>
<td>0.27</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Reactive Al$_2$O$_3$</td>
<td>99.6</td>
<td>0.02</td>
<td>0.01</td>
<td>–</td>
<td>0.26</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MgO fines</td>
<td>0.27</td>
<td>2.80</td>
<td>0.13</td>
<td>–</td>
<td>–</td>
<td>95.48</td>
<td>0.95</td>
<td>–</td>
<td>0.37</td>
</tr>
<tr>
<td>MgO powders</td>
<td>0.32</td>
<td>2.68</td>
<td>0.20</td>
<td>–</td>
<td>–</td>
<td>95.28</td>
<td>1.10</td>
<td>–</td>
<td>0.42</td>
</tr>
<tr>
<td>Cement</td>
<td>80.0</td>
<td>0.08</td>
<td>0.08</td>
<td>–</td>
<td>–</td>
<td>8.08</td>
<td>17.20</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Microsilica*</td>
<td>0.70</td>
<td>96.0</td>
<td>0.30</td>
<td>–</td>
<td>0.30</td>
<td>0.50</td>
<td>0.30</td>
<td>0.6</td>
<td>–</td>
</tr>
</tbody>
</table>

* pH 4.6–6.5.

### Table 2

<table>
<thead>
<tr>
<th>Type</th>
<th>Bulk density (kg/cm$^3$)</th>
<th>Apparent porosity (%)</th>
<th>Cold crushing strength (MPa)</th>
<th>Cold modulus of rupture (MPa)</th>
<th>Reheat linear change (%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$–MgO</td>
<td>2.86</td>
<td>23.7</td>
<td>87.2</td>
<td>23.1</td>
<td>+1.79</td>
<td>–</td>
</tr>
<tr>
<td>Al$_2$O$_3$–MgO</td>
<td>2.83</td>
<td>24.9</td>
<td>75.1</td>
<td>21.3</td>
<td>+1.92</td>
<td>–</td>
</tr>
<tr>
<td>Al$_2$O$_3$–spinel</td>
<td>2.97</td>
<td>21.6</td>
<td>74.6</td>
<td>20.3</td>
<td>–0.07</td>
<td>–</td>
</tr>
</tbody>
</table>

With the addition of 0.75 wt.% microsilica.
test, the furnace was cooled naturally overnight. The specimens were removed from the furnace and cut longitudinally at the center. Crack pattern and slag penetration of the tested specimens were examined visually.

Pore size distribution of the fired castables was measured using mercury penetration technique.

3. Results and discussion

3.1. Deformation under load

Fig. 1 demonstrates that the profiles of deformation under load of the unfired and prefired Al₂O₃–MgO castables are quite similar. Both started softening at 1200 °C, followed by the rapid subsidence. The unfired and prefired castables had a shrinkage of 1.22 and 1.45% at 1640 °C, respectively. The profiles suggest that during firing above 1400 °C a considerable amount of the liquid phase persisted and its viscosity probably greatly decreased at >1500 °C to accelerate densification, regardless of the unfired or prefired.

Fig. 2 shows that the unfired Al₂O₃–spinel castables started softening at 1300 °C, followed by the gentle subsidence with a shrinkage of 0.25% at 1640 °C, while the prefired castables started softening at 1530 °C, followed by the slight subsidence with an expansion of 0.88% at 1640 °C. The profiles of the deformation under load curves suggest that the amounts of liquid phases in the unfired and prefired castables during firing are very limited.

The S-type Al₂O₃–spinel castables contained 21.5 wt.% Al₂O₃–rich spinel of 73 wt.% Al₂O₃ and the K-type castables contained 20 wt.% of Al₂O₃–rich spinel of 95 wt.% Al₂O₃. The two commercial Al₂O₃–spinel castables contained almost the same amount of total fines (~0.075mm), but different kinds of Al₂O₃ for the grains above 8mm. Fig. 3 shows that the S-type castables had a shrinkage of ~2%, while the K-type castables had a shrinkage of ~0.25%, both at 1650 °C, respectively. Although there is a great disparity in the magnitudes of deformation under load, the two castables had the same degree of good performance in the field. Fig. 4 indicated that the deformation under load behavior of castables is probably mostly centered in the <1 mm fines portion in the mixes.

Two experimental Al₂O₃–spinel castables had almost the same chemical and mineralogical compositions but different total fines contents. One containing ~40 wt.% total fines (~0.075 mm) had a shrinkage of 0.4% and
the other containing $\approx 31.5$ wt.% total fines had an expansion of 0.67%, both at 1640 °C (Fig. 5). The former had a serious structural spalling problem and the latter showed a good performance in the field.

In summary, the profiles of Al$_2$O$_3$–MgO and Al$_2$O$_3$–spinel castables are the characteristics of castables and cannot be correlated to the slag resistance of castables for steel ladles.

3.2. Hot modulus of rupture and thermal shock damage resistance

Fig. 6 shows that hot modulus of rupture (HMOR) of Al$_2$O$_3$–MgO castables without the addition of microsilica increased from 1000 °C, reached a peak value at 1100 °C and then decreased with increasing temperature, while that of Al$_2$O$_3$–spinel castables remained constant from 1000 to 1300 °C and then increased rapidly with increasing temperature up to 1500 °C. The increase in hot modulus of rupture from 1300 to 1500 °C is due to the bond linkage between CA$_6$ and spinel in the bonding matrix [8,9].

Figs. 7 and 8 exhibit that Al$_2$O$_3$–spinel castables have much better thermal shock damage resistance than Al$_2$O$_3$–MgO castables, and the thermal shock damage resistance of Al$_2$O$_3$–MgO castables drastically decreases with the addition of 0.75 wt.% microsilica.

Figs. 7 and 8 show that thermal shock damage resistance of Al$_2$O$_3$–MgO castables with the addition of 0.75 wt.% microsilica is very poor, compared to Al$_2$O$_3$–spinel castables. Field performance indicated that Al$_2$O$_3$–MgO castables have better slag resistance and a longer service life in the wall below the slag line and the precast impact pad in the bottom of steel ladles, compared to Al$_2$O$_3$–spinel castables. Kienow [10] noted that thermal shock testing is a purely comparative procedure to differentiate the thermal shock damage resistance of different refractories, but it provides no guarantee of what refractories will behave in service.

The present work observed that a test combining the actions of slag and thermal shock on castables and using a gas-fired rotary slag test furnace for the assessment of thermal shock damage resistance [7] is much better than that using the prism quench into water technique. Fig. 9 shows the longitudinal sections of test specimens cut at center after the combined test.

Budnikov [11] noted that plastic deformation in refractories was observed above 800–1000 °C and hence
a thermal shock in the temperature range of plastic deformation cannot cause the same destruction as in the elastic deformation range alone, i.e. at low temperatures. The thermal shock using the prism quench into water technique is in the elastic deformation temperature range, while a thermal shock in the rotary slag test furnace is mostly in the plastic deformation temperature range.
range. This explains why there is a great disparity in the thermal shock test results using the prism quench in to water technique and a rotary slag test furnace.

3.3. Pore size distribution and microscopic studies on the fired castables

Pore size distribution and its characteristics of the Al$_2$O$_3$–MgO castables fired at 1500°C for 3 h, with and without microsilica addition, are shown in Figs. 10 and 11 and Table 3. As can be seen, castables with microsilica addition have larger pores with lower specific surface area and higher porosity, while castables without microsilica addition have smaller pores with higher specific surface area and lower porosity.

Fig. 12 shows that the well grown acicular CA$_6$ crystals only appeared in the matrix of the castables fired at 1500°C for 3 h with microsilica addition in a lower magnification scanning electron micrograph. The well grown CA$_6$ crystals suggest more glassy phase in the bonding matrix.

![Fig. 10. Typical pore size distribution of the Al$_2$O$_3$–MgO castables fired at 1500°C for 3 h with 0.75 wt.% microsilica addition.](image)

![Fig. 11. Typical pore size distribution of the Al$_2$O$_3$–MgO castables fired at 1500°C for 3 h without microsilica addition.](image)

![Fig. 12. Scanning electron micrographs of the bonding matrix of the Al$_2$O$_3$–MgO castables fired at 1500°C for 3 h, (a) with 0.75 wt.% microsilica addition and (b) without microsilica addition.](image)

<table>
<thead>
<tr>
<th>Castable Type</th>
<th>Mean pore size (µm)</th>
<th>Specific surface area (m$^2$g$^{-1}$)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With 0.75 wt.% microsilica addition</td>
<td>1.2–1.6</td>
<td>0.17–0.29</td>
<td>20.3–24.7</td>
</tr>
<tr>
<td>Without microsilica addition</td>
<td>0.9–1.0</td>
<td>0.24–0.30</td>
<td>18.2–19.9</td>
</tr>
</tbody>
</table>

*Four specimens were used for measuring pore size distribution for each castable.
The poorer thermal shock resistance of castables with microsilica addition is believed to be related to more glassy phase in the bonding matrix.

The better slag resistance of castables with microsilica addition (22.4% vs. 25.8% erosion) is most probably related to the lower specific surface area of pores. The smaller pores in castables without microsilica addition can be partly related to their better thermal shock resistance because finer pores could be more densely distributed to act as crack stoppers. It is believed that a material containing more smaller pores will be more resistant to crack propagation than a materials containing less larger pores.

In addition, Al₂O₃–spinel castables have the least amount of glassy phase in the bonding matrix evidenced by the increase in hot modulus of rupture from 1300 to 1500 °C, and hence have the best thermal shock resistance. The castables have poorer slag resistance, compared to Al₂O₃–MgO castables with and without microsilica addition, because a larger amount, as well as a smaller grain size, of in situ spinel in the matrix mostly accounts for the better slag resistance of Al₂O₃–MgO castables [12].

4. Summary and conclusions

1. The importance of thermal shock damage resistance of castables for use in steel ladles should be de-emphasized, based on the lab and field tests.
2. The thermal shock damage resistance of Al₂O₃–MgO castables drastically deteriorates with the addition of 0.75 wt.% microsilica, but the combined and field tests showed that the castables have better slag resistance and a longer service life in steel ladles, compared to Al₂O₃–spinel castables.
3. The combined test of slag and thermal shock attack on castables using the rotary slag test furnace is a better method for the assessment of castables performance in steel ladles.
4. There is no correlation between hot strengths and slag resistance for castables.
5. The deformation under load behavior of castables is probably mostly centered in the <1 mm portion in the mixes.
6. The magnitude of specific surface area of pores is more important than pore size and porosity for governing the slag resistance of Al₂O₃–MgO castables with and without microsilica addition.

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References