Microstructural features of alumina refractories with mullite-zirconia aggregates

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Refractory materials are often subjected to high temperatures and loads and their performance depends on their microstructural evolution during use. In this context, microstructural changes were monitored in alumina-based refractories containing mullite-zirconia aggregates and heat-treated at 1400°C and 1500°C for 2, 6, and 18 days. With the purpose of inducing in situ mullite formation, bricks containing microsilica were also prepared and heat-treated at 1500°C for 6 days for the sake of comparison. These heat treatments allowed for an evaluation of the use of refractories from the standpoint of temperature and time. In this work, scanning electron microscopy and X-ray diffraction analyses were made to identify the phases in the materials. The Rietveld method was also used for quantitative phase analyses. Interfacial reactions occurred between alumina and aggregates and between alumina and microsilica, causing the system to become mullitized. The effect of in situ-formed mullite was particularly evident in the results of the modulus of rupture of the materials containing microsilica. Creep tests revealed a reduction in the creep rate of materials treated at 1500°C for 18 days.

Key words: refractories, microstructure, aggregate, Rietveld, creep

1. INTRODUCTION

The steelmaking industry is the major consumer of refractories among the various industrial sectors. Changing metallurgical processes have influenced the demand for refractory products and the trend today is for high quality refractories with greater technological content. From this standpoint, therefore, microstructural design is particularly important.

Among the special refractories under development to meet the strict requirements of the metallurgical industry, carbon-bonded high-alumina refractories with added electrofused mullite-zirconia aggregates (MZ-aggregates) rank among the most important materials. These materials are used, for instance, in the production of plates for slide valves (1). The purpose of using MZ-aggregates to replace part of the coarse fraction of alumina is to promote a more intensive interaction between cracks and microstructure. Because the microstructure of this type of refractory is highly prone to microcracking and porosity, the addition of small zirconia particles, even partially-stabilized one, does not significantly affect the toughening mechanism through additional microcracking, as could be done in the case of normal technical ceramics. That is the underlying reason for the use of MZ-aggregates.

The technical literature (2-8) contains reports on many processing routes to produce mullite-zirconia and alumina-mullite-zirconia (AMZ) ceramics. However, owing to raw material availability and production-related costs, the most common routes are reaction sintering (4-6) and solid-state reaction between oxides (7,8). Be that as it may, control of the final microstructure is a determinant in limiting the severity of critical defects. Moreover, the microstructure must be capable of adjusting to phase transformations and microcracking (9).

An earlier publication (7) reported that high-alumina refractories containing MZ-aggregates did not present a balanced microstructure immediately after sintering, but that...
transformations towards equilibrium during the use of the refractory promoted improved creep resistance and thermal shock damage resistance, which are both qualities of major interest for technological applications. It was also observed (7) that, after electromelt cooling, the aggregates showed a small content of vitreous phase, which caused some degradation of the creep resistance of the as-received refractory. A 10-day heat treatment at 1400°C led to an increase in mechanical strength, which was attributed to the in situ formation of mullite. This increase was possible because, during heat treatments, the system tends toward equilibrium and a reaction occurs between the alumina matrix and the aggregate particles. In order to better understand the mechanical and thermomechanical behavior of this type of material, this study investigated the microstructural evolution of high-alumina refractories containing different MZ-aggregate contents, heat treated at distinct temperatures and for different durations.

The chemical composition of the chosen aggregate differed from those of previous studies (7). Therefore, its crystallization during fabrication also differed and, as a consequence, no vitreous phase was formed in the aggregate used. From the mechanical standpoint, greater creep resistance would be expected when using a more refractory aggregate.

2. EXPERIMENTAL

2.1. Preparation of the refractory bricks

A mixture of tabular alumina, Alcoa T-60, calcined alumina, Alcoa APC-2011SG, electromelted MZ-aggregate, Elfusa TP-35, and microsilica, Elkem 971D, was prepared in a planetary device. Water and dextrin (additive) were added to the mixture, at concentrations of 2 wt-% each. Table I shows the compositions of the bricks produced. Considering the granulometry of the raw materials, two types of bricks were prepared: the first, called GF, for the fine granule material and the second, called GG, for the coarse granule material. The idea was that, in the GF-type, the interfacial reaction between the different raw materials would be easier, facilitating observation of the phase transformation. On the other hand, the GG-type results in a real brick.

The GF-type material presented a granulometric distribution in which particle sizes varied from less than 45µm to 297µm and, in this case, the MZ-aggregates constituted the coarse part of the brick (particle sizes of less than 297µm). A granulometric range of less than 45µm up to 6300µm was imposed for the GG-type brick and, in this case, the coarse part of the brick consisted of tabular alumina (particle size smaller than 6300µm).

Considering the granulometric distribution, the GG-material was designed to provide the greatest possible particle compactness.

The mixed powder was pressed into 40 mm x 40 mm x 160 mm shapes and sintered at 1510°C for 12 hours. Several samples were then heat treated at 1400°C and 1500°C for 2, 6 and 18 days. The following notation will be applied to distinguish between the samples: n%(x/y)-z, where n% indicates the aggregate content, x is the duration and y the temperature of the heat treatment, and z the granulometry (GF or GG), e.g., 20%(6/1500)-GG. The letter “S” will replace “x/y” to designate a brick which has been sintered but not heat treated, such as 20%(S)-GG.

2.2. Characterization

Three different techniques were applied to quantitatively identify the phases. X-ray diffraction and Rietveld analysis were performed. The MOR was measured by subjecting unnotched samples to the 3-point bending test and measuring the maximum load at the point of catastrophic fracture. The mechanical behavior at high temperature was characterized by creep test. The longest and shortest heat-treated samples were chosen for this test in order to reveal the effect of the microstructure. 30 mm x 30 mm x 40 mm samples having 40%(S)-GF and 40%(18/1500)-GF were tested at 1400°C under 1 MPa and 3 MPa compressive stress.

Porosity was characterized by immersion in water and pore size distribution by quicksilver intrusion (Micromeritics Porosizer 9320) to physically characterize the samples.

3. RESULTS AND DISCUSSION

3.1. Quantitative phase analysis of MZ-aggregates

A Rietveld analysis of the as-received MZ-aggregates showed the following composition: 70.3 wt-% mullite; 26.1 wt-% zirconia, and 3.5 wt-% alumina (11).

Figure 1 shows the liquidus-projection of the alumina-silica-zirconia equilibrium phase diagram, where point A represents the composition calculated as described in the previous paragraph. That diagram is based on propositions of Sorrell and Sorrell, Aramaki and Roy, Butterman and Foster, and Alper. It is supposed that the eutectic temperature of the invariant reaction inside the alumina-mullite-zirconia compatible triangle is between 1700 °C and 1710 °C. The nominal composition given by producer (60 wt-% mullite, 38 wt-% zirconia and 2 wt-% impurities), which is represented by point B, is also shown in Figure 1 for comparison. Point C indicates the composition of the aggregate studied in reference 7 (nominal composition: 67 wt-% mullite and 33 wt-% zirconia). The last composition is apparently a two-phase one, but is located inside the compatible zirconia-mullite-silica triangle, as shown and discussed by Pandolfelli et al. (12).
sufficiently sensitive to detect them.

We are of the opinion that no reaction took place during the heat treatments and that the aggregate actually contained no free silica, corroborating our earlier analysis. Thus, the aggregate used in this study actually belongs to the zirconia-mullite-alumina compatibility triangle and is more refractory than that of the composition shown at point C in Figure 1. In the same figure, points D and E represent the complete composition of the refractories with 20 and 40 wt-% aggregate, respectively.

3.3. Quantitative phase analysis of complete refractories containing microsilica

To promote the mullite formation reaction, a composition was prepared with 75 wt-% alumina, 20 wt-% MZ-aggregate, and 5 wt-% amorphous microsilica. This refractory was of the GG-type.

Table IV shows the quantitative phase analysis of complete refractories containing 20 and 40 wt-% aggregate, respectively. As for heat treatment after sintering, tables II and III show, from left to right, the effect of treatment duration and temperature. It was impossible to identify a trend for the reactions between different pre-existing phases in the bricks or between these phases and impurities. This means that either no thermally activated reaction took place during the heat treatments or that the Rietveld method was not sufficiently sensitive to detect them.

We are of the opinion that no reaction took place during the heat treatments and that the aggregate actually contained no free silica, corroborating our earlier analysis. Thus, the aggregate used in this study actually belongs to the zirconia-mullite-alumina compatibility triangle and is more refractory than that of the composition shown at point C in Figure 1. In the same figure, points D and E represent the complete composition of the refractories with 20 and 40 wt-% aggregate, respectively.

3.4. Mechanical characterization

Table IV also indicates that, even taking experimental errors into account, the heat treatment at 1500°C for 6 days did not contribute towards increased mullite content in comparison to the content already formed during sintering. A certain amount of silica failed to react and ended up becoming crystallized, indicating that the local fine alumina did not suffice to react with silica.

Boletín de la Sociedad Española de Cerámica y Vidrio. Vol. 42 Núm. 1 Enero-Febrero 2003

Table II: Phase contents (wt-%) in refractories containing 20 wt-% aggregate, determined by the Rietveld method

<table>
<thead>
<tr>
<th>Phases</th>
<th>Composition, heat treatment, and granulometry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20% (S)-GF</td>
</tr>
<tr>
<td>Alumina</td>
<td>66.8 (5.50)</td>
</tr>
<tr>
<td>Mullite</td>
<td>8.3 (18.71)</td>
</tr>
<tr>
<td>Zirconia</td>
<td>4.8 (6.06)</td>
</tr>
<tr>
<td>Silica</td>
<td>0.2 (29.06)</td>
</tr>
</tbody>
</table>

# R-Bragg values not expected.

Table III: Phase content (wt-%) in refractories containing 40 wt-% aggregate, determined by the Rietveld method

<table>
<thead>
<tr>
<th>Phases</th>
<th>Composition, heat treatment and granulometry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40% (S)-GF</td>
</tr>
<tr>
<td>Alumina</td>
<td>63.6 (3.377)</td>
</tr>
<tr>
<td>Mullite</td>
<td>24.9 (4.65)</td>
</tr>
<tr>
<td>Zirconia</td>
<td>11.3 (5.63)</td>
</tr>
<tr>
<td>Silica</td>
<td>0.2* (1.67)</td>
</tr>
</tbody>
</table>

* R-Bragg values not expected. Average values based on the measurement of 3 samples of the same material.

Table IV: Quantitative phase analysis of (20+5)%-GG refractory subjected to sintering and heat treatment. Units in wt%.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Composition, heat treatment and granulometry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial nominal composition</td>
</tr>
<tr>
<td>Alumina</td>
<td>75.7</td>
</tr>
<tr>
<td>Mullite</td>
<td>14.1</td>
</tr>
<tr>
<td>Zirconia</td>
<td>5.2</td>
</tr>
<tr>
<td>Silica</td>
<td>5.0</td>
</tr>
</tbody>
</table>

R-Bragg values are shown in parentheses.

Figure 1: ZrO$_2$-Al$_2$O$_3$-SiO$_2$ phase equilibrium diagram (liquidus projection). MZ-aggregate composition quantitatively determined in this work (point A), nominal composition of the aggregate (point B), and composition of the material of reference 7 (point C) are shown in the diagram. See the text for points D, E, and F.
The room temperature modulus of rupture was measured in GG-type refractories with 20 wt-% of aggregate and without aggregate. These measurements were taken from only sintered materials and from sintered and heat-treated materials. To observe the effect of in situ mullite formation, samples with 5 wt-% of microsilica ((20+5)%-(S)-GG and (20+5)%-(6/1500)-GG) were also characterized.

Figure 2 shows the results of the corrected modulus of rupture. For the sake of comparison, the results for materials containing 0 wt-% and 20 wt-% of aggregate from reference 7 are also shown. These materials were only in the sintered state and were produced with raw materials having particle sizes ranging from less than 10 µm to 2000 µm. The correction for different porosity-values was made according to equation 1 (13), using the porosity values shown in figure 3. The (20+5)%-(S)-GG-refractory was taken as reference and all the MOR-values were normalized based on the porosity of this reference.

\[
\sigma = \sigma_0 \cdot \exp(-b \cdot P)
\]

In equation 1, P is the porosity, b is a non-dimensional constant, and \( \sigma_0 \) represents the MOR value of non-porous material. The value adopted for b was taken as 4 (14), which is the same value as that of alumina.

Figure 2 shows that the addition of 20 wt-% of MZ-aggregate to the alumina matrix increased the strength of the material of reference 7. However, the same addition produced a deleterious effect in the materials studied here. This comparison is reliable, since the materials made of only alumina in both studies presented very similar MOR-values, i.e., approximately 14 MPa.

It is probable that the particle size distribution of the raw materials limited the mechanical strength of the materials in this work. Table V shows the pore size ranges, which indicate that major flaws were generated in the materials containing aggregates. 20%-GG-type samples have pores ranging from 20 to 30 µm for equivalent diameters. In contrast, samples containing only alumina (0%-GG) presented pores with equivalent diameters of only 2-3 µm.

Hence, assuming that pores are the critical flaws and taking into account Griffith’s equation (13), in its more general form,

\[
\sigma_f = \frac{1}{Y} \sqrt{\frac{2 \cdot \gamma_{eff}}{\pi \cdot a}}
\]

where Y is a geometrical factor, \( \gamma_{eff} \) is the effective surface energy, E is Young’s module, and a is half the length of the critical flaw, one can calculate that the strength of the complete refractory (containing aggregate) would be 0.3 of the one containing only alumina. This statement is confirmed by figure 2. In this evaluation, it was assumed that the ratio \( \gamma_{eff}/\gamma_{eff} = \psi_{eff}/\psi_{eff} \) is valid. It is implicit in this ratio that the changes in Y, E and \( \gamma_{eff} \) are small considering the material with and without aggregate particles.

A 74.7 % increase in the MOR was obtained with the addition of 5 wt-% of microsilica to the material, taking as comparison the complete sintered refractory without microsilica (see figure 2). An increase of 64.3% was obtained after a 6-day heat treatment at 1500°C considering the porosity correction, which is evidence that microsilica contributes toward microstructural cohesion through the in situ formation of mullite, corroborating the phases determined and presented in table IV.

\[
\gamma_{eff} - \gamma_{eff} - \gamma_{eff}
\]

Figures 4a and 4b show SEM micrographs of compositions with microsilica, (20+5)%-(6/1500)-GG, and without microsilica, 20%(2/1500)-GG, respectively. Figure 4a shows large particles of MZ-aggregate and tabular alumina immersed in a matrix of fine alumina (tabular alumina and calcined alumina) plus microsilica. On the other hand, figure 4b, which shows the microstructure of the material without microsilica, reveals that the fine alumina matrix of that material was lost during cutting and polishing, providing evidence of the bond weakness between the large grains and the matrix of this refractory.

Thus, the material containing microsilica clearly has a more strongly bonded microstructure, as depicted in figure 4, and hence, greater mechanical strength. The use of the MZ-aggregate, though more refractory than that reported in reference 7 (since it belongs to the mullite-zirconia-alumina compatibility triangle), caused the mechanical strength to...
deteriorate due to the formation of a less strongly bonded microstructure. However greater aggregate/matrix cohesion is favored by the addition of a small amount of microsilica, which promotes the in situ formation of mullite during sintering and post-heat treatments (or use), resulting in a microstructure with enhanced mechanical strength.

The materials containing 40 wt-% of MZ-aggregate were subjected to constant-load compression creep tests under 1 MPa and 3 MPa at 1400°C. Materials with the fine microstructure and with and without 18-day heat treatments at 1500°C were used in these tests. Creep rate values were calculated from the resulting creep curves. Under 1 MPa compression the creep curve did not reach the stationary creep stage. So, the creep rate was calculated at 2% and 4% creep strains. Those results are shown on table VI. Pore influence correction was applied to the creep rate to permit comparison between materials with different total porosity values.

Compression stress of 3 MPa was also applied with the aim to compare the creep rate of the materials of this work and equivalent results from reference 7. Those results are shown on table VII.

For comparison, the creep rate was corrected by the effect of the total porosity on the creep process, based on the following equation (14,15):

\[ \dot{\epsilon} = \dot{\epsilon}_0 \left( \frac{1}{(1 + p^{2/3})^n} \right) \]  

where \( n \) is equal to 1 and \( \dot{\epsilon}_0 \) denotes the creep rate for non-porous material.

From tables VI and VII it can be concluded that heat treatment exerted a remarkable influence on the creep rate of the fine-microstructure samples (type GF) of this work. Under 1 MPa compression, the creep rate reduction was of ninefold and twenty-twofold in comparison to the sample that was only sintered at 2% and 4% creep strain, respectively.

From table VII it can be observed that the MZ-aggregate addition caused an increase in the minimum creep rate of materials from both, reference 7 and this work. But, the heat treatment of 18 hours at 1500 °C almost recuperated the original value of creep rate of alumina from reference 7. The reduction in the creep rate caused by heat-treatment in comparison to the sample that was only sintered, is of twenty-sevenfold.

Tables VI and VII clearly show the influence of the heat treatment on the creep rate, even considering the corrected porosity values of the creep rate. This illustrates very well how microstructural transformations that occur during heat treatments towards equilibrium effectively influence the creep behavior of this type of refractory.

4. CONCLUSIONS

(i) Mullite, zirconia and a small amount of alumina deduced from the quantitative phase analysis by the Rietveld method were the phases present in the aggregate used in this

Table VI: Corrected values of creep rate at 2% and 4% creep strain values for material with 40 wt-% aggregate. The least total porosity was taken as reference for rate’s correction. The creep test was carried out under 1 MPa at 1400°C.

<table>
<thead>
<tr>
<th>Composition, heat treatment and granularity</th>
<th>Total Porosity (%)</th>
<th>( \dot{\epsilon}_{at ; \epsilon = 2%} ) corrected value ( (\epsilon_v) )</th>
<th>( \dot{\epsilon}_{at ; \epsilon = 4%} ) corrected value ( (\epsilon_v) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>40%/G2-GF</td>
<td>34.95</td>
<td>4.0 x 10^{-6}</td>
<td>2.2 x 10^{-6}</td>
</tr>
<tr>
<td>40%/18%/1500-GF</td>
<td>25.16</td>
<td>4.5 x 10^{-6}</td>
<td>1.6 x 10^{-6}</td>
</tr>
</tbody>
</table>

Table VII: Values of \( \epsilon_{min} \) for 40 wt-% aggregate containing materials of this work and from reference 7, including 100% alumina material as reference. The creep test were carried out under 3 MPa at 1400 °C. It is also shown the range of particle size of alumina and aggregate for each material.

<table>
<thead>
<tr>
<th>Results’ origin</th>
<th>Composition and heat treatment</th>
<th>Range of alumina particle size (mm)</th>
<th>Range of aggregate particle size (mm)</th>
<th>( \epsilon_{min} ) (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ref. 7</td>
<td>100% alumina</td>
<td>0.04-2</td>
<td>0.02-1</td>
<td>1.1 x 10⁻⁵</td>
</tr>
<tr>
<td>ref. 7</td>
<td>60% alumina + 40% MZ-aggreg.</td>
<td>0.04-2</td>
<td>0.02-1</td>
<td>1.3 x 10⁻⁶</td>
</tr>
<tr>
<td>This work</td>
<td>40%/G2-GF</td>
<td>&lt; 0.045</td>
<td>&lt; 0.3</td>
<td>8.0 x 10⁻⁶</td>
</tr>
<tr>
<td>This work</td>
<td>40%/18%/1500-GF</td>
<td>&lt; 0.045</td>
<td>&lt; 0.3</td>
<td>3.0 x 10⁻⁶</td>
</tr>
</tbody>
</table>

Figure 4: Micrographs of cut and polished samples of composition (a) (20+5%)(6/1500)-GG and (b) 20%(2/1500)-GG obtained by SEM, using the secondary electron technique.
work. No vitreous phase was found. Therefore, the aggregate belongs to the zirconia-mullite-alumina compatibility triangle of the system \( \text{ZrO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2 \).

(ii) The MOR values highlighted the importance of adding small amounts of microsilica to the refractory formulation, since the \textit{in situ} formation of mullite results in improved microstructural characteristics. This microstructure possesses stronger interbonding among large tabular alumina grains and between the aggregate and the fine alumina matrix resulting, in turn, in a refractory with greater mechanical strength.

(iii) Densification, sintering, and microstructural accommodation are the transformation phenomena and microstructural evolution observed in the refractories containing only alumina and aggregate. In addition, a mullitization reaction was observed in the refractories containing microsilica.

(iv) The heat treatment applied effectively increased the refractory’s creep resistance, suggesting that the performance of these refractories tends to improve during their service life.

ACKNOWLEDGMENTS

The authors are grateful to FAPESP (96/2691-3 and 97/01114-5) and CNPq for their financial support of this work. The authors are also indebted to Dr. Carlos Paiva-Santos, Unesp-Araraquara, for his assistance with the Rietveld method.

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Recibido: 14.12.01
Aceptado: 25.09.02