Magnesia-Zircon Brick: Evolution of Microstructure, Properties and Performance with Increasing Sintering Temperature

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Abstract:
Depending on phase components and densification, Magnesia-Zircon brick varies in appearance from white to veined and then brown with increasing sintering temperature. Properties including bulk density, apparent porosity and hot modulus of rupture as well as performance embodied with creep resistance and refractoriness continue to improve with sustaining enhancement of sintering temperature. Exceptionally, cold crushing strength first increases then decreases with rising sintering temperature and a peak exists at 1550°C. Microstructural evolution suffers zircon decomposition companied by silica escape, forsterite formation, matrix solidification and zirconia coagulation, until a zirconia/forsterite composites belt tightly coating on magnesia aggregates. Excessive coagulation of zirconia caused by oversintering probably results in microcracks formation and defects enlargement thereby degrades cold crushing strength.

Keywords: Magnesia-Zircon; Microstructure; Properties; Performance.

1. Introduction
The glass-melting process involves large amounts of energy due to relatively high processing temperatures. In order to use the energy as efficient as possible, glass tank regenerators are developed to achieve heat recovery through preheating the combustion air and thereby provide better heat transfer via a high flame temperature [1]. With modern regenerators, 50-75% of the enthalpy contained in the hot exhaust gases is returned to the system and thus energy is saved [2].

However, refractories installed in regenerator checker are chronically exposed to erosive and corrosive working conditions. Specially, the top courses are attacked by high temperature load and deposition of external oxides whilst the middle courses by condensation of alkali oxides and alkali sulfates mainly [3-4]. Therefore, common refractories are very hard to meet the rigorous requirement of regenerator, such as Magnesia brick with poor corrosion resistance, Forsterite brick with insufficient thermal resistance, and Magnesia-Chrome brick with hazardous Cr⁶⁺ contamination to environment [5-6]. Until 1986, these existing corrosion and negative effect problems were solved by the development of Magnesia-Zircon brick [5]. Nowadays, Magnesia-Zircon checker brick has been widely used as regenerator lining.

As known, during firing a series of transformation occurs, which determines the final quality of Magnesia-Zircon brick [7]. The objective of this research is to study the effect of the
change of firing temperature on microstructure, physical/mechanical properties and performance of Magnesia-Zircon brick.

2. Experimental procedure

In this investigation, Magnesia-Zircon brick was prepared based on 77.5% sintered magnesia (0-5mm), 21% zircon (0-0.1mm) and 1.5% fumed silica. The starting materials were compounded together with binder in an intensive mixer for 10 minutes. Then, the mixture was pressed into cuboid specimens (240×115×53mm) under a pressure of 150MPa. After dried at 130°C for 24 hours, the specimens were sintered in an elevator furnace in separate batches. Sintering was carried out at temperatures of 1400°C, 1450°C, 1500°C, 1550°C and 1600°C respectively and with soaking time of 6 hours.

Tab. I. Chemical composition of starting materials (wt%).

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>ZrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesia</td>
<td>95.27</td>
<td>1.62</td>
<td>2.11</td>
<td>1.04</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>Zircon</td>
<td>-</td>
<td>-</td>
<td>29.15</td>
<td>1.74</td>
<td>0.19</td>
<td>67.10</td>
</tr>
</tbody>
</table>

Chemical composition of magnesia and zircon was analyzed by XRF (Bruker S4, Germany) and the results were listed in Tab. I. Bulk density (BD) and apparent porosity (AP) of the sintered specimens was measured by means of Archimedes method with deionized water as immersion medium. Cold crushing strength (CCS) at room temperature was tested using Universal Testing Machine (Instron-5566, UK). Measurement of hot modulus of rupture (HMOR) was performed by using HMOR Tester (03AP, Precondar, China) at 1500°C with residence time of 30 minutes in air. High temperature performance of the sintered specimens was assessed in terms of creep in compression (CIC) at 1400°C and refractoriness under load (RUL) on 50 mm high by 50 mm diameter cylindrical samples under a 0.2 MPa load. The phase components of sintered specimens were identified by using XRD with CuKα radiation (D/max 2500V, Rigaku, JP). Microstructural observation on the mechanically polished samples was performed with optical microscope (STM6, Olympus, JP). The elemental composition of the matrix of sintered specimens was determined by electron probe microanalyser (EPMA-8705QH2, Shimadzu, Japan).

3. Results and discussion

Magnesia-Zircon brick varies in appearance with the variety of sintering temperature. As shown in Fig. 1., the appearance of the brick evolves from white to veined and then brown when the corresponding sintering temperature is 1400°C, 1500°C and 1600°C. This is probably related to a difference in densification degree and phase components of the specimens.

Fig. 2. presents the dependence of bulk density (BD) and apparent porosity (AP) on sintering temperature. Disparity of BD and AP among the specimens indicates different densification degree. The XRD patterns of the specimens are given in Fig. 3. and the phase components are tabulated in Tab. II. The following three reactions may occur in the mixture of magnesia and zircon during sintering, namely decomposition reaction of zircon (Equation 1), crystalline transformation reaction of zirconia from monolithic to tetragonal structure (Equation 2) and forsterite formation reaction between MgO and SiO₂ (Equation 3).

\[ ZrSiO_4 \rightarrow m - ZrO_2 + SiO_2 \]  

(1)
\[ m - ZrO_2 \rightarrow t - ZrO_2 \]  \hspace{1cm} (2)

\[ 2MgO + SiO_2 \rightarrow Mg_2SiO_4 \]  \hspace{1cm} (3)

Fig. 1. Variation of appearance with increasing sintering temperature.

Fig. 2. Temperature dependence of BD and AP.

Fig. 3. XRD patterns of specimens sintered at various temperatures.
Tab. II Phase components of the sintered specimens.

<table>
<thead>
<tr>
<th>Sintering temperature</th>
<th>Major phase component</th>
</tr>
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<tbody>
<tr>
<td>1400°C</td>
<td>Mg$_2$SiO$_4$, MgO, ZrSiO$_4$, m-ZrO$_2$, t-ZrO$_2$</td>
</tr>
<tr>
<td>1500°C</td>
<td>Mg$_2$SiO$_4$, MgO, t-ZrO$_2$</td>
</tr>
<tr>
<td>1600°C</td>
<td>Mg$_2$SiO$_4$, MgO, t-ZrO$_2$</td>
</tr>
</tbody>
</table>

The major phase components of the specimens sintered at 1500°C and 1600°C are the final Mg$_2$SiO$_4$, MgO and t-ZrO$_2$, indicating a full completion of the reactions. In contrary, the reactions are not completely finished in the specimen sintered at 1400°C because residual undecomposed zircon and unstabilized zirconia (m-ZrO$_2$) can be still identified. Optical microscopic observation displayed in Fig. 4.(a) confirms that undecomposed zircon is surrounded by a ring of zirconia, as marked by arrow. Moreover, the matrix of the specimen sintered at 1400°C looks still like compaction morphology rather than sintering texture. Fig. 4.(b) reveals zirconia skeleton in the specimen sintered at 1500°C, which basically remains the shape of zircon grain. Silica decomposed from zircon escapes and reacts with magnesia to form forsterite. There is a forsterite belt formed around magnesia grains. The micrographs of the specimen sintered at 1550°C and 1600°C are shown in Fig. 4.(c) and (d), respectively. Their typically common characterization is the zirconia/forsterite composite belt surrounding magnesia aggregate grains, which protects the grains from corrosion. However, the difference lies in the coagulation degree of zirconia.

Fig. 4. Optical micrographs of specimens sintered at (a) 1400°C, (b) 1500°C, (c) 1550°C and (d) 1600°C.
Fig. 5. indicates that the cold crushing strength (CCS) rises firstly whereas then descends with increasing sintering temperature. The peak is achieved when the sintering temperature is 1550°C. This turn is probably attributed to the coagulation of zirconia in matrix. High sintering temperature, i.e. 1600°C, results in the excessive coagulation of zirconia in matrix. This induces the formation of microcracks due to the different coefficient of thermal expansion between zirconia and forsterite and thus deteriorates the cold crushing strength [8]. The speculation of excessive coagulation is supported by the result of elemental distribution analysis on matrix of the specimen sintered at 1600°C, as presented in Fig. 6.(a) and (b). There is almost no zirconia dispersed finely in the forsterite matrix. Defects enlargement caused by oversintering, as pointed by arrow in Fig. 6.(a), is also possible reason for degradation of CCS.

Fig. 5. Temperature dependence of CCS.

It is shown in Fig. 7. that the hot modulus of rupture (HMOR) continues to increase when raising the sintering temperature from 1400°C to 1600°C. This is attributed to the improved densification of matrix and enhanced bonding between matrix and aggregates with increasing sintering temperature. The inflection point of decelerated increase of HMOR
emerges roughly at 1550°C, implying microstructural evolution has generally completed under this temperature. This deduction is in good agreement with the performance of the specimens, which is embodied in terms of creep in compression (CIC) and refractoriness under load (RUL).

Fig. 7. Temperature dependence of HMOR.

Fig. 8. Relationship between CIC and sintering temperature.

Fig. 9. Relationship between RUL and sintering temperature.
As shown in Fig. 8., CIC expressed with the value of \((Z_{50}-Z_{25})\) tends to be generally small (\(\leq 0.05\%\)) and somewhat constant when the sintering temperature is above 1550\(^\circ\)C. This signals that the internal reactions and microstructural densification in the specimens has mostly completed. Temperature dependence of RUL plotted in Fig. 9. indicates similar refactoriness feature of specimens sintered above 1500\(^\circ\)C. Higher sintering temperature of 1600\(^\circ\)C has little improvement in performance of deformation resistance. Therefore, the sintering temperature of 1550\(^\circ\)C is thought to be suitable for Magnesia-Zircon brick because of its optimized combination of properties and performance obtained.

4. Conclusions

Based on the experimental results, the conclusions are drawn as follows.

1. Magnesia-Zircon brick is sensitive to its sintering temperature. The reaction completion and sinterability can be roughly evaluated by the brick's surface, which varies correspondingly with sintering temperature.

2. As a consequence of oversintering, excessive coagulation of zirconia deteriorates the cold crushing strength of Magnesia-Zircon brick due to the formation of microcracks and defects enlargement in matrix.

3. The appropriate temperature for sintering Magnesia-Zircon brick is 1550\(^\circ\)C. Optimized combination of properties and performance can be achieved at this temperature. Corresponding microstructural characterization is adhesive zirconia/forsterite composites belt around magnesia aggregates.

Acknowledgements

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5. References

Садржај: У зависности од састава фаза и денисификације, боја магнезијум-цирконске цигле варира од беле па све до броон са порастом температуре синтеровања. Својства као што су густина, порозност, модул прелома, као и својства везана за отпор при пузању и ватросталност побољшавају се са повећањем температуре синтеровања. Изузетак је снага дробљења која прво расте па опада са порастом температуре синтеровања и пик је на 1550 °C. Еволуција микроструктуре праћена је разлагањем цирконијума и нестанака силицијума, формацијом форстерита, згушивањем матрикса и коагулације циркона све до формирања композита цирконијум/форстерит преко агрегата магнезијума. Према извештају коагулација цирконијума условљена прекомерним синтеровањем вероватно резултира формирањем микропукотина и повећањем дефеката који даље деградирају и дробљења. 

Кључне речи: магнезијум-циркон; микроструктура; својства; карактеристике