Thermomechanical properties of refractories from natural dead burnt magnesites.

THERMOMECHANICAL PROPERTIES OF REFRACTORIES FROM
NATURAL DEAD BURNT MAGNESITES.

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1. Abstract

Thermomechanical properties of magnesite bricks manufactured from three natural dead burnt magnesites having more than 90% MgO and different CaO/SiO₂ ratios were studied. Hot modulus of rupture at 1400°C, 1500°C and 1600°C were evaluated. The alteration of hot strength due to increase of brick firing temperature from 1600°C to 1700°C is explained from their microscopic and X ray diffraction studies.

2. Introduction

Magnesite from natural sources accounts for about 67% of refractory grade and from synthetic sources about 33% on world basis(1). Different countries producing natural magnesites are Austria, Czechoslovakia, Greece, Spain, Turkey, USSR, Yugoslavia, China, Brazil, India(2).

Thermomechanical properties of natural magnesite have been studied by various workers. Jones and Melford(3) studied the high temperature behaviour of Grecian magnesite and found superior to American Sea Water Magnesite. Jackson and Laming(4) studied the thermomechanical properties of magnesite bricks manufactured from Grecian natural dead burnt magnesite after firing the bricks at 1400°C, 1550°C and 1700°C. According to them the hot modulus of rupture at 1400°C, increases with the increase of brick firing temperature.

The evaluation or thermomechanical properties at elevated temperatures i.e. more than 1400°C is of great importance as the magnesite bricks are used in steel melting furnaces operating above 1600°C. Hence a scheme of work was undertaken in the authors' Institute to study the thermomechanical properties of natural dead burnt magnesites having different CaO/SiO₂ ratio at elevated temperatures.

3. Experiment

The physical and chemical properties of dead burnt magnesites taken for studies are mentioned in Table-1.

TABLE—1.

<table>
<thead>
<tr>
<th></th>
<th>Magnesite-A</th>
<th>Magnesite-B</th>
<th>Magnesite-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO%</td>
<td>94.5</td>
<td>94.0</td>
<td>91.3</td>
</tr>
<tr>
<td>CaO%</td>
<td>2.25</td>
<td>2.0</td>
<td>1.12</td>
</tr>
<tr>
<td>SiO₂%</td>
<td>1.40</td>
<td>1.8</td>
<td>5.0</td>
</tr>
<tr>
<td>Fe₂O₃%</td>
<td>0.80</td>
<td>1.10</td>
<td>1.0</td>
</tr>
<tr>
<td>Al₂O₃%</td>
<td>0.40</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>CaO/SiO₂</td>
<td>1.60</td>
<td>1.11</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Grain Bulk Density (gm/cc) 3.38 3.33 3.25
Specific Gravity 3.560 3.515 3.510
True Porosity (%) 5.05 5.26 7.48

Magnesite-A and magnesite-B has MgO content around 95.0%, while the MgO content of Magnesite-C is about 90%. The R₂O₃ content in three cases are more or less similar. The silica content of magnesite-A, B and C are 1.4, 1.8 and 5.0 respectively. The CaO/SiO₂ ratio of magnesite A, B, C are 1.60, 1.11 and 0.22 respectively. Magnesite bricks were manufactured from these magnesites having similar granulometric compositions, moulding pressure, drying and firing schedule. Thermomechanical and mineralogical properties of bricks fired at 1600°C and 1700°C were evaluated. Apparent porosity, bulk

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density were evaluated as per Indian Standard Test Procedures. Hot modulus of rupture at 1400°C, 1500°C and 1600°C were evaluated as per ASTM C-583-80 test method. Polished section of the brick samples were examined under optical microscope. X-ray diffraction studies were conducted on powdered samples of the bricks in a Philips X-Ray diffractometer PW-1730 using Cu-Kα radiation and silicon as internal standard.

4. Results
The physical, thermomechanical and mineralogical properties of the bricks are mentioned in Table-2. Refractory bricks manufactured from magnesite-A, B and C are termed as brick-A, brick-B and brick-C respectively.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Brick fired at 1600°C Brick-A; Brick-B; Brick-C</th>
<th>Brick fired at 1700°C Brick-A; Brick-B; Brick-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Apparent porosity%</td>
<td>18.2 14.8 15.5</td>
<td>17.9 14.2 13.7</td>
</tr>
<tr>
<td>2. Bulk density gm/cc</td>
<td>2.91 3.01 2.96</td>
<td>2.92 3.02 3.01</td>
</tr>
<tr>
<td>3. Hot modulus of rupture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(kg/cm²) at 1400°C</td>
<td>140 109 75.3</td>
<td>64 70 109.8</td>
</tr>
<tr>
<td>1500°C</td>
<td>129 25 37.0</td>
<td>19.3 14.1 63.8</td>
</tr>
<tr>
<td>1600°C</td>
<td>66.5 0 6.9</td>
<td>3.5 0 17.7</td>
</tr>
</tbody>
</table>

4. Mineralogical properties.
(a) Silicate phase
   major: 
   - CMS M’S
   minor: 
   - C₃S
   (b) Periclase grain (Min-max) micron
   - 30-100 10-50 30-50 30-100 30-50 50-100
   Average grain size (micron)
   - 40 30 40 70 40 70

C₃S —Dicalcium silicate (2CaO·SiO₂)
C₃MS₂—Merwinite (3CaO·MgO·2SiO₂)
CMS —Monticellite (CaO·MgO·SiO₂)
M₂S —Forsterite (2MgO·SiO₂)

The hot modulus of rupture of bricks fired at 1600°C are in the following order.
At 1400°C test temperature Brick-A > Brick-B > Brick-C
At 1500°C test temperature Brick-A > Brick-C > Brick-B
At 1600°C test temperature Brick-A > Brick-C > Brick-B

In each case the hot strength decreases as the test temperature increases from 1400°C to 1600°C. Similarly at 1700°C firing of the bricks the order of hot strength are in the following manner.

At 1400°C test temperature Brick-C > Brick-B > Brick-A
At 1500°C test temperature Brick-C > Brick-A > Brick-B
At 1600°C test temperature Brick-C > Brick-A > Brick-B

Microscopic Study
Examination under optical microscope was carried out to study the characteristic of periclase grains, and nature and distribution of silicate phases.

Brick-A Fired at 1600°C (Fig. 1)
The periclase grains are polygonal and size...
varies from 30 to 100 micron with an average grain size about 40 micron. The predominant silicate phases are merwinite (C₃M₂S₂) and dicalcium silicate (C₂S) which are present along the grain boundaries as thin film and occasionally as discrete patches. Silicate zones are observed containing merwinite in the centre and dicalcium silicate in the periphery of the zone which is in contact with periclase grains. In composite periclase grains occasional direct bonding occurs between periclase grains.

Brick-B Fired at 1600°C:—(Fig. 2)

The periclase grains are polygonal in size and ranges between 10 to 50 micron and 30 micron in average. The predominate silicate phase is monticellite and traces of merwinite is observed. Very thin film of silicate is present along the grain margin of polygonal grains. Silicate zones containing CMS are present along the grains occasional direct bonding occurs between periclase to periclase grains.

Brick-C Fired at 1600°C:—(Fig. 3)

The periclase grains are rounded to subrounded in shape and their size ranges from 30 to 50 micron with an average of 50 micron. The total quantity of silicate mineral is comparatively higher than Brick-A and Brick-B. The silicate are mostly M₂S with traces of CMS. The silicates are present along the grain boundaries and as discrete patches. The discrete patches are characterised by zoning-the centre being always a phase of higher calcium which is surrounded by silicates with lesser and lesser amount of calcium in sequence like C₃S, C₃M₂S₂, CMS and ultimately by the M₂S on the margin which is in contact with periclase grains. Occasionally direct bonding between periclase to periclase grains are also observed but comparatively less than Brick-A and Brick-B.

Brick-A Fired at 1700°C:—(Fig. 4 and 5)

The periclase grains are subrounded to rounded in shape with the variation of grain size from 30 to 100 micron and 70 micron in average. The silicates are present in the grain boundaries as thin film and as discrete patches. Discrete silicate patches are comparatively more than the bricks fired at 1600°C. The major silicate phases observed are C₃M₂S₂ and CMS.

The C₃M₂S₂ content has increased and CMS has appeared which was not found in the brick fired at 1600°C. The C₂S present in the periphery of silicate patches and in contact with periclase grains as observed in 1600°C firing brick is diminished in the brick fired at 1700°C.

Brick-B Fired at 1700°C:—(Fig. 6)

The periclase grains are polygonal, rounded to subrounded and varies from 30 to 50 micron and 40 micron in average. The silicate minerals observed were CMS with traces of C₃M₂S₂ present as thin film and discrete patches along the grain boundaries. The CMS phase is comparatively higher than the brick fired at 1700°C.

Brick-C Fired at 1700°C:—(Fig. 7 and 8)

The periclase grains are rounded to subrounded and varies from 50 to 100 micron with an average of 70 micron. The silicates are mostly M₂S with trace amount of CMS which are present along the grain boundaries as discrete patches. Direct bonding between the periclase grains are observed. Silicate zones are found to occur which are similar in nature of the brick-C fired at 1600°C.

X-Ray Diffraction Study:—

BRICK-A. (Fig. 9) Silicate phases such as C₃M₂S₂ and CMS were detected in brick-A fired at 1600°C. But in brick fired at 1700°C, the intensities of C₃M₂S₂ and CMS peaks were increased.

BRICK-B. (Fig. 10) Brick-B fired at 1600°C and 1700°C, the only silicate phase detected was CMS. The silicate peak intensities in 1700°C fired brick was higher than the brick fired at 1600°C.

BRICK-C. (Fig. 11) Brick-C fired at 1600°C and 1700°C contains the silicate phase such as M₂S...
and CMS. The peak intensities are similar in both types of brick.

5. Discussion:
The nature and distribution of silicate phases and direct bonding between periclase to periclase mostly contribute towards the strength of magnesite brick at elevated temperatures. The types of silicate present in the magnesite bricks depend upon the CaO/SiO₂ ratio of the magnesite⁴. The silicates generally occur in magnesite are di-calcium silicate (C₂S), merwinite (C₃MS₂), monticelite (CMS), forsterite (M₂S) whose melting point are 2130°C, 1577°C, 1500°C and 1890°C respectively (⁴).

In 1600°C firing of the bricks, brick-A has highest hot strength at 1400°C, 1500°C and 1600°C test temperatures than brick-B and brick-C. The silicate in contact with the periclase grains is C₂S which has melting point around 2130°C and in composite periclase grains some direct bonding occurs between periclase to periclase. Brick-B has higher hot strength than brick-C up to test temperature of 1400°C. Brick-B has more direct bonding between periclase to periclase and contains less silicate than brick-C and the silicate phase is characterised as CMS which has melting point above 1400°C. But at 1500°C and 1600°C test temperature, hot strength of brick-B falls to a great extent and becomes lower than brick-C as the major silicate phase M₂S of brick-C has melting point about 1900°C and that of brick-B, CMS has melting temperature around 1500°C.

The increase of brick firing temperature from 1600°C to 1700°C alters the hot strength of bricks at elevated temperature. Brick-A and Brick-B show deterioration of hot strength while in case of brick-C the hot strength is improved. The alteration of hot strength is in accordance to the alteration of silicate phase as seen under optical microscope and confirmed by X-Ray diffraction studies. In brick-A the C₂S present in the periphery of the silicate patches and in contact with periclase grains as seen in case of 1600°C firing mostly disappears with the appearance of low melting silicate CMS and increase of C₃MS₂. This may be the reason of decrease of hot modulus of rupture values in brick-A. The hot modulus of rupture values of brick-B decreases considerably due to increase of CMS phase with the increase of brick-C the HMOR values are considerably higher than brick-A and brick-B. This is because of the fact that the average periclase grain size increases from 40 to 70 micron resulting more direct bonding between periclase to periclase and of the high melting silicate M₂S remains unaltered.

6. Conclusion
The evaluation of strength of magnesite bricks at elevated temperature is of great importance because:

1. Bricks are used in high temperature kilns and furnaces operating more than 1600°C.
2. At 1400°C test temperature the hot strength of different magnesite bricks are more or less similar but above 1400°C test temperature the strength of certain magnesite is decreased considerably.
3. The increase of firing temperature from 1600°C to 1700°C either increases or decreases the hot strength of magnesite brick at elevated temperature in accordance to the alteration of mineralogical phases.

Acknowledgement
The authors are pleased to acknowledge the aid of their colleagues Dr. G. Goswami and Mr. B. P. Padhi in mineralogical studies.

REFERENCES
Fig. 1 Photomicrograph of magnesite brick-A fired at 1600°C showing polygonal periclase grains. Thin film of silicate present along the grain boundaries. Fine pin holes containing silicate and present along the grain margin. 
Reflected light × 185

Fig. 2 Photomicrograph of magnesite brick-B fired at 1600°C showing polygonal periclase grains. Silicates are present as thin film and as small zones along the grain boundaries. 
Reflected light × 185

Fig. 3 Photomicrograph of magnesite brick-C fired at 1600°C showing rounded to subrounded grains. Silicates are present along the grain boundaries and are maximum around the spherical grains. 
Reflected light × 185

Fig. 4 Photomicrograph of magnesite brick-A fired at 1700°C showing subrounded periclase grains. Silicates are present as discrete patches and as thin film along the grain boundaries. 
Reflected light × 185
Fig. 5 Photomicrograph of magnesite brick-A fired at 1700°C at higher magnification showing silicate patches containing mostly $C_3M_2$ and CMS.

Reflected light $\times 850$

Fig. 6 Photomicrograph of magnesite brick-B fired at 1700°C showing polygonal and subrounded periclase grains. Silicate are observed as discrete patches and as thin film along the grain boundaries.

Reflected light $\times 185$

Fig. 7 Photomicrograph of magnesite brick-C fired at 1700°C showing subrounded periclase grains. Silicate minerals present along the grain boundaries and as discrete patches.

Reflected light $\times 185$

Fig. 8 Photomicrograph of magnesite brick-C fired at 1700°C showing the silicate zones at higher magnification.

Reflected light $\times 850$