ACTIVATED SINTERING OF MAGNESIUM OXIDE OBTAINED FROM SEAWATER

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The process of isothermally sintering magnesium oxide obtained from seawater by substoichiometric (where precipitation of magnesium hydroxide took place with 80 % of the stoichiometric quantity of dolomite lime) and by overstoichiometric precipitation (which took place with 120 % of the stoichiometric quantity of dolomite lime) was examined, with the addition of mass fractions (1, 2 and 5) % TiO₂, at temperatures in the range 1550–1750 °C, with (1, 3 and 5) h of soaking at the maximum temperature. The process was followed by a determination of the product density, as well as of the B₂O₃ content in the sintered samples. The results indicate that, besides favorably affecting the density of the sintered samples, the addition of TiO₂, with increasing temperature and soaking time, also significantly reduces the B₂O₃ content in the sintered magnesium oxide obtained from seawater. A statistical analysis of the obtained data was performed with the “Statistica” package in order to obtain a model of the density (ρ) of sintered samples of magnesium oxide relative to the temperature (t), time of isothermal heating (υ), and the percentage of added TiO₂ (w).

Key words: substoichiometric precipitation, overstoichiometric precipitation, magnesium oxide from seawater, TiO₂ addition, activated sintering

1 INTRODUCTION

Magnesia₁ (MgO) is a very important material for the refractory industry. Due to its high refractory properties (MgO melts at (2823 ± 40) °C), MgO ceramics are chemically inert, resistant to the effect of metal melts, acid gases, alkali slag, neutral salts, and react with carbon only above 1800 °C. Raw magnesites for refractory use are obtained from natural ore or are synthetically processed from seawater. Magnesium oxide obtained from seawater²⁻⁹ is a high-quality refractory material, and its advantages lie not only in the huge reserves of seawater¹⁰ (1 m³ contains 0.945 kg of magnesium), but in the higher purity of the sintered magnesium oxide (> 98 % MgO). The magnesium oxide used here was obtained from seawater either by substoichiometric (MgO 80 % pptn – where pptn stands for precipitation) or overstoichiometric (MgO 120 % pptn) precipitation of magnesium hydroxide in seawater using dolomite lime.

The purpose of this work was to examine the effect of TiO₂ additions on the properties (density and the B₂O₃ content) of sintered samples of magnesium oxide obtained from seawater at elevated temperatures. The examinations described were carried out in order to obtain a model of the density of sintered samples of magnesium oxide relative to the temperature and the time of isothermal heating and the percent of added TiO₂.

2 EXPERIMENTAL

The composition of the seawater used for the precipitation of magnesium hydroxide was:

\[
\begin{align*}
\text{MgO} &= 2.124 \text{ g dm}^{-3} \\
\text{CaO} &= 0.5573 \text{ g dm}^{-3}
\end{align*}
\]

The composition of the dolomite lime used as the precipitation agent was as follows (mass fractions, w/\%):

\[
\begin{align*}
\text{CaO} &= 57.17 \% \\
\text{MgO} &= 42.27 \% \\
\text{SiO₂} &= 0.099 \% \\
\text{Al₂O₃} &= 0.051 \% \\
\text{Fe₂O₃} &= 0.079 \%
\end{align*}
\]

The experimental procedure used to obtain magnesium hydroxide from seawater was similar to that employed in our previous investigations⁸⁻⁹. The sedimentation rate was increased by the addition of the
optimum amount of the anionic 818A flocculent (polyacrylamide), produced by the Dutch firm Hercules. The experimental procedure used to determine the optimum quantity of the anionic 818A flocculent has been described in a previous study. The magnesium hydroxide obtained from seawater was dried at 105 °C and then calcined at 950 °C. The composition of the magnesium oxide obtained by precipitation with 80 % of the stoichiometric quantity of dolomite lime was (mass fractions, w%): 97.92 % MgO, 1.45 % CaO and 0.1055 % B2O3.

MgO, determined by the diffusion of O2¯ ions through the MgO lattice as the slower diffusion species. The MgO lattice as the slower diffusion species. The increased temperature leads to the increased mobility of the elements forming the crystal lattice, a contact surface is formed between the particles of compacted powder, the porosity is eliminated, and the whole system shrinks.

3 RESULTS AND DISCUSSION

Tables 1 and 2 show the experimentally obtained values for the density under the operating conditions described for sintered magnesium oxide samples (80 % precipitation) and magnesium oxide samples (120 % precipitation). The results indicate that at higher temperatures, such as 1550 °C, 1650 °C and 1750 °C, the increase in the density of the samples of magnesium oxide obtained from seawater is not very significant when compared to the undoped samples, even though they were sintered under the same thermal conditions. Therefore, at higher temperatures in the range 1550–1750 °C, the effect of the TiO2 addition is less evident because the concentration of the added ions is evenly distributed over the whole grain mass. One can assume that the mass transfer is the same as with pure MgO, determined by the diffusion of O2¯ ions through the MgO lattice as the slower diffusion species. The increased temperature leads to the increased mobility of the elements forming the crystal lattice, a contact surface

Table 1: Density (ρ) of sintered magnesium oxide samples (80 % precipitation) with the addition of a mass fraction of 1 %, 2 % and 5 % TiO2, and no sintering aid, t = 1550 °C, 1650 °C, 1750 °C, r = 1 h, 3 h, 5 h, p = 625 MPa

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO2 addition, w%</th>
<th>1%</th>
<th>2%</th>
<th>5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>No sint. aid</td>
<td>1550</td>
<td>1h</td>
<td>3.2401</td>
<td>3.2691</td>
</tr>
<tr>
<td></td>
<td>3h</td>
<td>3.3181</td>
<td>3.3498</td>
<td>3.3439</td>
</tr>
<tr>
<td></td>
<td>5h</td>
<td>3.3514</td>
<td>3.3643</td>
<td>3.3953</td>
</tr>
</tbody>
</table>

Table 2: Density (ρ) of sintered magnesium oxide samples (120 % precipitation) with the addition of a mass fraction of 1 %, 2 % and 5 % TiO2, and no sintering aid, t = 1550 °C, 1650 °C, 1750 °C, r = 1 h, 3 h, 5 h, p = 625 MPa

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO2 addition, w%</th>
<th>1%</th>
<th>2%</th>
<th>5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>No sint. aid</td>
<td>1550</td>
<td>1h</td>
<td>3.2880</td>
<td>3.3088</td>
</tr>
<tr>
<td></td>
<td>3h</td>
<td>3.3179</td>
<td>3.3557</td>
<td>3.4156</td>
</tr>
<tr>
<td></td>
<td>5h</td>
<td>3.3739</td>
<td>3.3887</td>
<td>3.4409</td>
</tr>
</tbody>
</table>

Assume that the mass transfer is the same as with pure MgO, determined by the diffusion of O2¯ ions through the MgO lattice as the slower diffusion species. The increased temperature leads to the increased mobility of the elements forming the crystal lattice, a contact surface is formed between the particles of compacted powder, the porosity is eliminated, and the whole system shrinks.

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and favors the Ca$_2$B$_2$O$_5$ formation reaction. In a previous paper the X-ray diffraction method was used to prove the content of di-calcium borate (Ca$_2$B$_2$O$_5$) in sintered samples of magnesium oxide from seawater. Therefore, in the process of sintering, B$_2$O$_3$ reacts with CaO to form Ca$_2$B$_2$O$_5$. In papers the X-ray diffraction method and EDAX analysis have helped determine that during the sintering process the added TiO$_2$ reacts with CaO from the solid MgO-CaO solution and forms calcium titanate CaTiO$_3$. Thus, TiO$_2$ binds a part of the CaO in the CaTiO$_3$ and as a result reduces the content of CaO that reacts with B$_2$O$_3$. In this way a smaller quantity of Ca$_2$B$_2$O$_5$ remains in the sintered sample, i.e., a higher quantity of B$_2$O$_3$ evaporates.

With MgO (120 % precipitation) there is an excess of CaO, which favors the formation of Ca$_2$B$_2$O$_5$, while with MgO (80 % precipitation) a larger part of the B$_2$O$_3$ evaporates from the sample into the air during sintering. A positive effect of the TiO$_2$ addition on the reduction of the B$_2$O$_3$ content in the magnesium oxide obtained from seawater makes it possible to achieve a high-purity product, because the hot-strength properties of certain refractory products are significantly affected by their boron content.

The results shown in Tables 1 and 2 have also been considered in a regression analysis. The "Statistica" package was used to analyze statistically the data obtained, in order to obtain a model of the density of the sintered samples of magnesium oxide relative to the temperature (t), the time of isothermal sintering (\( \tau \)), and the mass fraction of TiO$_2$ added (w).

A model of multiple regression has been proposed, 
\[
\hat{\rho} = \beta_0 + \beta_1 t + \beta_2 \tau + \beta_3 \ln(w+1) + \epsilon
\]
for MgO samples (80 % precipitation) and for MgO samples (120 % precipitation), where \( \rho \) is the density (g cm$^{-3}$), t is the temperature (°C), \( \tau \) is the time of isothermal sintering (h), w is the mass fraction (%) of added TiO$_2$, \( \beta_0, \beta_1, \beta_2, \beta_3 \) are unknown coefficients, and \( \epsilon \) is the random error in the model.

### Table 3: Effect of TiO$_2$ on B$_2$O$_3$ content in the sintered magnesium oxide samples (80 % precipitation) at \( t = 1550 \) °C, 1650 °C, 1750 °C, \( \tau = 1 \) h, 3 h, 5 h, \( p = 625 \) MPa

<table>
<thead>
<tr>
<th>sample</th>
<th>( t/°C )</th>
<th>( \tau/h )</th>
<th>TiO$_2$, w%</th>
<th>B$_2$O$_3$, w%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>no sint. aid</td>
<td>1 %</td>
</tr>
<tr>
<td>80 % pptn</td>
<td>1550</td>
<td>1</td>
<td>0.1894</td>
<td>0.1249</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.1337</td>
<td>0.1075</td>
<td>0.0193</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.0759</td>
<td>0.0637</td>
<td>0.0145</td>
</tr>
<tr>
<td>1650</td>
<td>1</td>
<td>0.1445</td>
<td>0.0750</td>
<td>0.0272</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.1020</td>
<td>0.0640</td>
<td>0.0161</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.0589</td>
<td>0.0257</td>
<td>0.0138</td>
</tr>
<tr>
<td>1750</td>
<td>1</td>
<td>0.0862</td>
<td>0.0594</td>
<td>0.0193</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0415</td>
<td>0.0261</td>
<td>0.0116</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.0319</td>
<td>0.0126</td>
<td>0.0090</td>
</tr>
</tbody>
</table>

### Table 5: Correlation matrix for MgO (80 % precipitation) samples

<table>
<thead>
<tr>
<th>variable</th>
<th>correlations (MgO (80 % pptn) samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t/°C )</td>
<td>1.00 0.00 -0.00 0.69</td>
</tr>
<tr>
<td>( \tau/h )</td>
<td>0.00 1.00 -0.00 0.46</td>
</tr>
<tr>
<td>TiO$_2$ addition, w%</td>
<td>-0.00 -0.00 1.00 0.43</td>
</tr>
<tr>
<td>density, ( \rho (g \text{ cm}^{-3}) )</td>
<td>0.69 0.46 0.43 1.00</td>
</tr>
</tbody>
</table>

### Table 6: Correlation matrix for MgO (120 % precipitation) samples

<table>
<thead>
<tr>
<th>variable</th>
<th>correlations (MgO (120 % pptn) samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t/°C )</td>
<td>1.00 0.00 -0.00 0.53</td>
</tr>
<tr>
<td>( \tau/h )</td>
<td>0.00 1.00 -0.00 0.51</td>
</tr>
<tr>
<td>TiO$_2$ addition, w%</td>
<td>-0.00 -0.00 1.00 0.60</td>
</tr>
<tr>
<td>density, ( \rho (g \text{ cm}^{-3}) )</td>
<td>0.53 0.51 0.60 1.00</td>
</tr>
</tbody>
</table>

Tables 5 and 6 show the correlation matrices for the examined samples. The results indicate that there is no correlation between the independent variables (temperature \( t \), time \( \tau \) and percentage of addition of TiO$_2$).

The estimate for the regression function for MgO (80 % precipitation) is: 
\[
\hat{\rho} = 2.461 + 0.000512 T + 0.0173 \tau + 0.0434 \ln(w + 1) + 0.01899 R^2 = 0.9057; F(3, 104) = 333.2251; p = 0.00
\]

The estimate for the regression function for MgO (120 % precipitation) is: 
\[
\hat{\rho} = 2.686 + 0.000382 T + 0.0181 \tau + 0.0567 \ln(w + 1) + 0.01413; R^2 = 0.9433; F(3, 104) = 576.8233; p = 0.00
\]
The regression functions and the regression coefficients are significant at the level of $p = 0.00$ in both models. The statistical analysis indicates that these models are useful for an estimation of the density of the samples examined.

4 CONCLUSIONS

The statistical analysis using the Statistica package indicates that the proposed models are useful and acceptable for an estimation of the density of the sintered magnesium oxide samples relative to the temperature ($t$), the time of the isothermal heating ($T$), and the percent of added TiO$_2$ ($w$).

The favorable effect of the TiO$_2$ addition on the reduction of the B$_2$O$_3$ content in the sintered magnesium oxide obtained from seawater is due to two interdependent reactions of the formation of Ca$_2$B$_2$O$_5$ and CaTiO$_3$, which lead to a reduction in the B$_2$O$_3$ content during sintering.

5 LITERATURE

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