B₂O₃ content in sintered magnesium oxide obtained from seawater

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The effect of TiO₂ concentration (1, 2, and 5 mass %) on the reduction of B₂O₃ content has been studied during isothermal and activated sintering of seawater-derived magnesium oxide at 1550, 1650 and 1750°C for 1, 3 and 5 h. Magnesium oxide is obtained from seawater by precipitation with 80% and 120% of the stoichiometric quantity of the dolomite lime as the precipitation agent. The results indicate that the addition of TiO₂ has a significant effect and it also greatly affects the evaporation of B₂O₃. The thermodynamic analysis of experimental results, based on Onsager phenomenological postulates, has established the relations of mutual influence of simultaneous irreversible processes, i.e., reactions of the formation of Ca₂B₂O₅ and CaTiO₃, during isothermal and activated sintering of seawater-derived magnesium oxide.

Keywords: Activated sintering, B₂O₃, Isothermal sintering, Seawater-derived magnesium oxide, Titanium oxide

More than 70% of the planet Earth is covered by seas and oceans. They contain great quantities of dissolved salts, which indicates the need for identification of new methods and the improvement of existing technological processes to obtain industrial raw materials from seawater.

Consequently, seas and oceans have become the unlimited deposit and main source of magnesium oxide, owing to high mass concentration of magnesium in seawater¹ which amounts to 1.35 g dm⁻³, i.e. 0.13% magnesium in the whole mass of seawater. A technological process, using procedures developed more than 50 years ago on the industrial scale²⁻⁸, yields magnesium hydroxide that turns to magnesium oxide during calcination and to refractory magnesium oxide during sintering at high temperatures.

Magnesium oxide from seawater contains boron (III) oxide as impurity, which has to be reduced to the minimum because the properties of high-temperature sintered magnesium oxide greatly depend on the content of B₂O₃ in the final product. According to Heasman² good quality sintered magnesium oxide contains ≤ 0.05 mass % of B₂O₃. The magnesium oxide used was derived from seawater by substoichiometric precipitation (precipitation of Mg(OH)₂ takes place with 80% of the stoichiometric quantity of dolomite lime) and by overstoichiometric precipitation (with 120% of the stoichiometric quantity of dolomite lime). It is found that the effect of TiO₂ on reduction of the B₂O₃ content in seawater-derived magnesium oxide during sintering at high temperatures of 1550, 1650, and 1750°C has not been examined yet. Therefore in this study, we have focused our attention on the favourable effect of the TiO₂ addition on the reduction of B₂O₃ content during sintering of magnesium oxide from seawater at temperatures 1550, 1650 and 1750°C for 1–5 h. We have studied the mutual relationship of two interdependent reactions, i.e., reactions of formation of Ca₂B₂O₅ and CaTiO₃, which take place simultaneously during sintering of seawater-derived magnesium oxide, as the final B₂O₃ content in sintered samples depends both on the content of CaO and of TiO₂.

Experimental Procedure

The composition of seawater used for precipitation of magnesium hydroxide was: MgO 2.5299 and CaO 0.6048 g dm⁻³. The composition of the dolomite lime used as the precipitation agent was: CaO 57.17, MgO 42.27, SiO₂ 0.099, Fe₂O₃ 0.079 and Al₂O₃ 0.051%.

The seawater was first acidified by sulphuric acid to lower its pH from the normal value of 8.2 to 4.0. It was then passed through the desorption tower packed with Rasching rings where it flowed downward against a rinsing stream of air. At low pH, the bicarbonates (HCO₃⁻) and carbonates (CO₃²⁻) were

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converted to CO$_2$ gas, which was stripped out of the falling water drops by the ascending airflow. The flow rate of the induced air was 120 dm$^3$ h$^{-1}$ and the volumetric flow rate of seawater through the desorption tower was 6 dm$^3$ h$^{-1}$.

The precipitation of magnesium hydroxide took place after the pre-treatment of seawater with 80% and 120% of the stoichiometric quantity of dolomite lime as the precipitation agent. The precipitation reaction took 30 min with stirring of the magnetic stirrer. 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 already been described$^9$. Magnesium hydroxide obtained from seawater was dried at 105°C after filtering and then calcined at 950°C for 5 h to form caustic magnesium. Its chemical composition is given below:

For magnesium oxide (80% precipitation):

MgO = 98.76%; CaO = 0.88%; B$_2$O$_3$ = 0.1934%.

For magnesium oxide (120% precipitation):

MgO = 97.92%; CaO = 1.45%; B$_2$O$_3$ = 0.1055%.

Mixtures of magnesium oxide of the above composition were prepared with the addition of a mass fraction of 1, 2 and 5% TiO$_2$. The doping oxide used was analytical reagent grade titania (TiO$_2$ p.a.) in the rutile form, produced by Merck. The chemical composition of TiO$_2$ p.a. (99 mass %) is given below:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water soluble matter</td>
<td>0.3</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.01</td>
</tr>
<tr>
<td>Sulphate</td>
<td>0.05</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>0.001</td>
</tr>
<tr>
<td>Iron</td>
<td>0.005</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

Samples were homogenized by manual stirring in absolute ethanol (C$_6$H$_5$O p.a.) for 30 min. The mixtures were then dried at 80°C until all the alcohol was evaporated. The mixtures were cold pressed into compacts in a hydraulic press at a pressure of 625 MPa. The compacts were then sintered in a gas furnace (Mecker, type 553) with zirconium (IV) oxide lining at 1550, 1650 and 1750°C for 1, 3 and 5 h of soaking at the maximum temperature respectively.

It took approximately 2 h to reach the maximum temperature in the furnace. After sintering, the samples were left to cool in the furnace. The boron content in the magnesium oxide samples examined was determined potentiometrically. The variation coefficient for the method applied$^{10}$ is $\pm$ 1%. The results obtained are the average of a number of measurements (5 analyses in each case).

**Results and Discussion**

Table 1 shows the effect of TiO$_2$ addition on the quantity of B$_2$O$_3$ in sintered samples, relative to the method of obtaining magnesium oxide from seawater, for the operating conditions indicated. It is observed that the addition of TiO$_2$ in the process of activated sintering of seawater-derived magnesium oxide has a significant effect on evaporation of B$_2$O$_3$. Magnesium oxide obtained by 80% precipitation behaves differently from that obtained by 120% precipitation, which is related to the CaO content in samples examined. CaO leads to retention of B$_2$O$_3$ in samples during sintering. MgO samples (120% precipitation) have a significantly higher CaO content ($\omega_\text{CaO} = 1.45\%$) than the MgO samples obtained at 80% precipitation ($\omega_\text{CaO} = 0.88\%$), which favours the dicalcium borate formation reaction (Ca$_2$B$_2$O$_5$).

In his study, Green$^{11}$ specified that Ca$_2$B$_2$O$_5$ forms during sintering of magnesium oxide if the sample contains CaO and B$_2$O$_3$. In our previous study$^{12}$, the X-ray diffraction (XRD) method was used to prove the dicalcium borate content (Ca$_2$B$_2$O$_5$) in sintered seawater-derived magnesium oxide sample. Thus, it is found that during sintering, B$_2$O$_3$ reacts with CaO to form Ca$_2$B$_2$O$_5$.

Examinations$^{13-16}$ performed using the X-ray diffraction (XRD) method and Energy Dispersive X-ray analysis (EDAX analysis) indicate that the TiO$_2$ reacts with CaO from the MgO-CaO solid solution in the sintering process and forms calcium titanate (CaTiO$_3$).

Consequently, the TiO$_2$ addition reduces the B$_2$O$_3$ fraction in sintered samples, because a part of CaO binds into calcium titanate (CaTiO$_3$) during sintering. This reduces the fraction of CaO that reacts with B$_2$O$_3$, i.e. a higher quantity of B$_2$O$_3$ evaporates. In samples of MgO (120% precipitation) where CaO is in great surplus, significant quantities of Ca$_2$B$_2$O$_5$ are formed, while in samples of MgO (80% precipitation) that contain a much lower quantity of CaO, a greater part of B$_2$O$_3$ evaporates during sintering. The favourable effect of TiO$_2$ addition on the reduction of the B$_2$O$_3$ content in seawater-derived
magnesium oxide contributes to high purity products, as the properties of special-purpose refractory magnesium oxide, i.e. high strengths (hot test) and slag action resistance, required by the modern steel industry significantly depend on the B$_2$O$_3$ content. Therefore, following two reactions determine the B$_2$O$_3$ fraction in the process of sintering of seawater-derived magnesium oxide:

$$2\text{CaO} + \text{B}_2\text{O}_3 = \text{Ca}_3\text{B}_2\text{O}_5$$

$$\text{CaO} + \text{TiO}_2 = \text{CaTiO}_3.$$ 

It is of interest to consider these reactions together, as the final B$_2$O$_3$ content in sintered samples depends both on the content of CaO and of TiO$_2$. The system of these two interdependent reactions has therefore been analysed by the open systems thermodynamics$^{17-19}$, based on an important theorem due to Onsager.

The purpose of the thermodynamic analysis performed is to connect all factors affecting boron (B$_2$O$_3$) removal during isothermal sintering. The irreversible process can generally be expressed by the following phenomenological relation:

$$J_i = \sum_{j=1}^{n} L_{ij} \ X_j \ (i = 1, 2, \ldots, n; \ i \neq j) \quad \ldots (1)$$

where $J_i$ denotes streams or flows; $X_j$ represents thermodynamic driving forces, and $L_{ij}$ is phenomenological coefficient.

For a system with two flows caused by two driving forces, i.e. with two simultaneous irreversible processes ($n = 2$), phenomenological relations can be written in the following form:

$$J_1 = L_{11} \ X_1 + L_{12} \ X_2 \quad \ldots (2)$$

$$J_2 = L_{21} \ X_1 + L_{22} \ X_2 \quad \ldots (3)$$

where $J_1$ and $J_2$ denote the flows; and $X_1$ and $X_2$ denote the forces causing these flows. These relations define the linear range of irreversible processes. It is evident that the $J_1$ flow is connected with its conjugated force $X_1$ through the phenomenological coefficient $L_{11}$. However, the $J_1$ flow can be affected by force $X_2$ ($j \neq i$) through the process conjugation coefficient $L_{12}$. Phenomenological coefficients $L_{ij}$ ($i \neq j$) describe the interference, i.e. characterize the mutual effect of the two irreversible processes $i'$ and $j'$.

Onsager has applied the principle of microscopic reversibility to the definition of phenomenological coefficients, and postulated that:

$$L_{ij} = L_{ji} \quad (i, j = 1, 2, \ldots, n; \ i \neq j) \quad \ldots (4)$$

i.e.

$$\left( \frac{\partial J_i}{\partial X_j} \right)_{x_{\neq 0, i \neq j}} = \left( \frac{\partial J_j}{\partial X_i} \right)_{x_{\neq 0, i \neq j}}$$

These Onsager reciprocity relations (symmetry relations) express that when the flux, corresponding to the irreversible process $i$ is influenced by the force $X_i$ of the irreversible process $j'$, then the flux $j'$ is also influenced by the force $X_i$ through the same interference coefficient $L_{ij}$. It implies that the matrix $L_{ij}$ is symmetrical.

As mutual coefficients $L_{ij}$ are equal according to Eq. (4), the number of phenomenological coefficients is reduced. Phenomenological coefficients have to satisfy the following conditions:

$$L_{11} \geq 0, \ L_{22} \geq 0 \quad \ldots (5)$$

$$L_{11} \times L_{22} - \frac{1}{4} \times (L_{12} + L_{21})^2 \geq 0 \quad \ldots (6)$$

Sign $> 0$ applies to irreversible processes.

Hence, as entropy production can never be negative, the “proper” phenomenological coefficients ($L_{11}, L_{22}$) are always positive. On the other hand, the “mutual” coefficients ($L_{12}, L_{21}$) do not have a defined sign. They may be positive or negative, their magnitude being limited only by Eq. (6). If phenomenological relations (2) and (3) are applied to interdependent Ca$_3$B$_2$O$_5$ and CaTiO$_3$, formation reactions, it follows:

$$J_1 = L_{11} \cdot t' + L_{12} \cdot \tau \quad \ldots (7)$$

$$J_2 = L_{21} \cdot t' + L_{22} \cdot \tau \quad \ldots (8)$$

This examines the functional dependence of the fraction of B$_2$O$_3$ evaporated ($J_1$), on the fraction of CaO that reacts with TiO$_2$ ($J_2$) at the temperature of isothermal sintering ($t'$) and the duration of isothermal sintering ($\tau$).

Mathematical processing of experimental data shown in Table 1, according to the Eqs (7) and (8), yields the required phenomenological coefficients $L_{ij}$ ($i, j = 1, 2$). Specifically, functional dependencies of the following form have been examined:
i.e. theoretical approximations $J_1$ and $J_2$ are sought for functions representing experimental results for the fraction of $B_2O_3$ evaporated ($J_1^o$) and the fraction of CaO that reacts with TiO$_2$ ($J_2^o$).

It has also been assumed that $t' = t \cdot 10^{-2}$, °C to achieve the appropriate adjustment of numeric expressions obtained. Table 2 shows the obtained values for $J_1^o$ and $J_2^o$ for sintered samples of magnesium oxide obtained by 80% and 120% precipitation respectively. Coefficients $L_{11}$, $L_{12}$ and $L_{22}$ have been calculated using the combination of mean values method with the least square method on a computer (using Mathcad 2000 Professional). Table 3 shows equations for $J_1$ and $J_2$ with coefficients calculated for respective fractions of TiO$_2$ added, for both samples of seawater-derived magnesium oxide.

The values of calculated coefficients $L_{11}$, $L_{12}$ and $L_{22}$, which provide an insight of interactions of the two reactions during sintering of seawater-derived...
magnesium oxide, depend on the mass fraction of added TiO$_2$. This dependence can be expressed by a second degree polynomial as shown below:

\[ Y = Ax^2 + Bx + C \]  

... (9)

where Y is the phenomenological coefficient; x, the mass fraction of added TiO$_2$; and A, B and C, the corresponding constants.

The coefficients have been calculated using the least square method and are shown by the following equations:

For samples of MgO (80% precipitation):

\[
L_{11} = -0.2219 \ x^2 + 1.6608 \ x + 2.0018 \\
L_{12} = -0.2048 \ x^2 + 1.4478 \ x + 2.6463 \\
L_{22} = -0.1820 \ x^2 + 1.3136 \ x + 2.3402
\]

For samples of MgO (120% precipitation):

\[
L_{11} = 0.0503 \ x^2 - 0.1227 \ x + 4.0041 \\
L_{12} = -0.5170 \ x^2 + 3.6908 \ x - 0.6178 \\
L_{22} = -0.7815 \ x^2 + 5.3922 \ x - 3.3412
\]

Examination of phenomenological coefficients established appropriate relations of interaction of simultaneous irreversible processes during isothermal and activated sintering of seawater-derived magnesium oxide in the wide temperature range 1550 – 1750°C, and duration of 1-5 h.

The thermodynamic analysis has established the relationship among all factors affecting boron evaporation during isothermal sintering and makes it possible to use a computer to predict the B$_2$O$_3$ content in sintered samples in dependence on temperature and duration of isothermal heating, and the chemical composition of the original magnesium oxide.

**Conclusion**

(i) In activated sintering of seawater-derived magnesium oxide, TiO$_2$ has a significant effect and greatly affects evaporation of B$_2$O$_3$ from the samples. Magnesium oxide obtained by 80% precipitation behaves differently than that obtained by 120% precipitation, which is attributed to the CaO content in samples examined.

(ii) The favourable effect of TiO$_2$ on reduction of the B$_2$O$_3$ content in sintered seawater-derived magnesium oxide is the consequence of two interdependent reactionship of formation of Ca$_2$B$_2$O$_5$ and CaTiO$_3$, which lead to the reduction of the B$_2$O$_3$ content during sintering.

(iii) Examination of phenomenological coefficients has established the appropriate relationship of interaction of simultaneous irreversible processes during isothermal and activated sintering of seawater-derived magnesium oxide in the temperature range 1550 – 1750°C for duration of 1-5 h.

(iv) The thermodynamic analysis of results establishes the relationship among all factors affecting boron evaporation during isothermal sintering. This has made it possible to use a computer to predict the B$_2$O$_3$ content in sintered samples in dependence on temperature and duration of isothermal heating, and the chemical composition of the original magnesium oxide.

(v) The study results extend the knowledge about the effect of the TiO$_2$ addition on the reduction of the B$_2$O$_3$ content during sintering at high temperatures, and the thermodynamic analysis also contributes to the development of process modelling under different process conditions.

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**References**


