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Effect of TiO$_2$ Addition on the Sintering Process of Magnesium Oxide from Seawater

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1. Introduction

Magnesium oxide is one of the most important materials used in the production of high-temperature-resistant ceramics. Due to its high refractory properties (MgO melts at (2823 ± 40) °C), MgO ceramic is non-toxic and chemically inert in basic environments at elevated temperatures, resistant to the effect of metal melts, acid gases, alkali slag, neutral salts, and react with carbon only above 1800 °C. Today, in large-scale technical processes, magnesia (MgO) for refractories is produced from two sources: natural and synthetic. Magnesia from natural sources constitutes 82% of the world’s magnesia installed capacity. The dominant source is magnesite (MgCO$_3$) which occurs in both a macro and a cryptocrystalline forms. Less significant are dolomite (CaCO$_3$·MgCO$_3$), hydromagnesite (3MgCO$_3$·Mg(OH)$_2$·3H$_2$O), brucite (Mg(OH)$_2$) and serpentine (Mg$_3$(Si$_2$O$_5$)(OH)$_4$). Synthetic materials are manufactured either from seawater or from magnesia rich brines. Magnesium oxide obtained from seawater is a high-quality refractory material, and its advantages lie not only in the huge reserves of seawater (1 m$^3$ contains 0.945 kg of magnesium), but in the higher purity of the sintered magnesium oxide (≥ 98% MgO). The production of magnesium oxide from seawater is a well-known industrial process (Bocanegra-Bernal, 2008; Bonney, 1982; Gilpin & Heasman, 1977; Heasman, 1979; Maddan, 2001; Martinac, 1994; Petric & Petric, 1980, Rabadžhieva et al., 1997) and has been studied all over the world for a number of years. For most of the second half of the twentieth century, seawater provided almost 50% of the magnesia produced in the western world, and today it still remains a major source of magnesia in many countries. The process involves the extraction of dissolved magnesium, which has a concentration of around 1.3 g dm$^{-3}$ in seawater (Brown et al., 1997), and 3 to 40 times this values for brines, and the reaction of magnesium salts (chloride and sulphate) with lime or dolomite lime to produce a magnesium hydroxide precipitate. The precipitate is washed and calcined to form caustic magnesia. The apparently simple chemistry of the process is unfortunately complicated in practice because seawater is not a pure solution of magnesium salts and dolomite or limestone, although abundant, are never found free of impurities. Boron is a particular problematic impurity for the magnesia used as a high quality refractory material. Thus, boron can be a problem in refractory magnesia for specialized refractory applications where a high hot strength is required. Taking into consideration that B$_2$O$_3$ is common impurity in seawater derived magnesia, the aim of this study was to examine the possibility of adding TiO$_2$ in quantities of 1, 2 and 5 wt.-% for
reducing the boron content in the product, i.e. sintered magnesium oxide obtained from seawater. The purpose of this paper was, first, to reduce the B$_2$O$_3$ content in magnesium oxide from seawater as much as possible in ensure a high-purity product, because the hot-strength properties of certain refractory products are significantly affected by their boron content, and, second to sinter the individual products and determine the properties of samples sintered depending on the precipitation method and the boron content in the magnesium oxide.

2. MgO from seawater

Processing of seawater magnesium involves precipitation of magnesium hydroxide in seawater reacting with an alkaline base, such as calcined dolomite or calcined limestone. If dolomite lime is used as precipitation agent, the chemical reaction is as follows:

$$2 \text{CaO} \cdot \text{MgO}(s) + 2 \text{Mg}^{2+} + \text{SO}_4^{2-} + 2 \text{Cl}^- + 4 \text{H}_2\text{O} = 4 \text{Mg(OH)}_2(s) + \text{CaSO}_4(s) + \text{Ca}^{2+} + 2 \text{Cl}^- \tag{1}$$

The composition of the dolomite lime (from the location Dipalo near the town of Sinj, Croatia) used for precipitating the magnesium hydroxide from seawater was as follows (wt.-%): MgO = 42.27%, CaO = 57.55 %, SiO$_2$ = 0.076%, Al$_2$O$_3$ = 0.042%, Fe$_2$O$_3$ = 0.064%, and the composition of the seawater (from the location at the promontory of the Hill Marjan near the Oceanographic Institute in Split, Croatia) was as follows: MgO = 2.423 g dm$^{-3}$ and CaO = 0.604 g dm$^{-3}$.

Impurities from seawater and from precipitation agent get into the magnesium hydroxide precipitate, so that special attention has to be paid to precipitate purity, depending on the product application. Thus, seawater is pretreated by acidifying with H$_2$SO$_4$ to lower its pH from the normal 8.2 to 4.0, in order to remove bicarbonate (HCO$_3^-$) and carbonate (CO$_3^{2-}$) ions. The chemical reaction are:

$$\text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}^+ + \text{HSO}_4^- = \text{Ca}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O} + \text{CO}_2(aq) \tag{2}$$

$$\text{Ca}^{2+} + 2 \text{HCO}_3^- + \text{H}^+ + \text{HSO}_4^- = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2 \text{H}_2\text{O} + \text{CO}_2(aq) \tag{3}$$

The calcium sulphate formed remained in the solution. Seawater was then passed through the desorption tower packed with Rasching rings where it flowed downward against a rinsing stream of air. The liberated carbon dioxide (CO$_2$) gas was removed from falling water drops by the ascending airflow. In this way seawater derived lime contamination of the magnesia can be minimised. The flow rate of the induced air was 120 dm$^3$ h$^{-1}$, and the volumetric flow rate of the seawater through the desorption tower was 6 dm$^3$ h$^{-1}$. After the pretreatment of the seawater, a calculated amount of dolomite lime was added to precipitate the magnesium hydroxide. The magnesium oxide used was obtained from seawater by substoichiometric precipitation (where precipitation of magnesium hydroxide took place with 80% of the stoichiometric quantity of the dolomite lime) and by overstoichiometric precipitation (which took place with 120% of the stoichiometric quantity of the dolomite lime). The precipitation reaction lasted for 30 min; a magnetic stirrer was used. After magnesium hydroxide precipitation, settling took place. The sedimentation rate was increased by addition of the optimum amount of the anionic Flokal-B flocculent (polyacrilamide) (produced by Župa-Kruševac, Serbia). The precipitate obtained was then
decanted and rinsed. The rinsing and decantation procedure was repeated five times with approximately 1 dm$^3$ of distilled water as rinsing agent. After that, the magnesium hydroxide precipitate was filtered through a number of funnels. The rinsing agent used with the Mg(OH)$_2$ precipitate on the filter paper was the same as the one used for rinsing by decantation. This procedure was also repeated five times, i.e. until rinsing was completely carried out. The magnesium hydroxide thus obtained was dried at 105 °C and then calcined at 950 °C for 5 h to form caustic magnesia. The boron content was determined potentiometrically. The variation coefficient for the potentiometric method employed in boron determination is ± 1% (Culkin, 1975). The results listed represent an average value of a number of measurements (an average of five analyses in each case). Table 1 shows the chemical composition of magnesium oxide obtained from seawater with regard to magnesium oxide, calcium oxide, and boron(III) oxide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgO / wt.-%</th>
<th>CaO / wt.-%</th>
<th>B$_2$O$_3$ / wt.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO (80% precipitation)</td>
<td>99.20</td>
<td>0.59</td>
<td>0.193</td>
</tr>
<tr>
<td>MgO (120% precipitation)</td>
<td>98.25</td>
<td>1.32</td>
<td>0.056</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition of magnesium oxide obtained from seawater.

The substoichiometric precipitation of magnesium hydroxide from seawater is a very convenient precipitation method in the so-called «wet phase» (Petric & Petric, 1980), as it significantly increases the thickener capacity, i.e. the magnesium hydroxide settling rate which is the «bottleneck» of this technology. This is very important for the design of the thickener as its construction is the time-controlling factor in plants of this type. At precipitation of 80% the capacity of the thickener (calculated according to Kynch) increases by 71% in relation to complete precipitation (Martinac et al., 1997). Substoichiometric precipitation significantly increases the sedimentation rate of the magnesium hydroxide precipitate formed, due to the decreased thickness of the double electrical layer around the magnesium hydroxide particle. A consequence of the increased adsorption of Mg$^{2+}$ ions onto Mg(OH)$_2$ particles is a decrease in the zeta-potential. Therefore, substoichiometric precipitation increases the coagulation stability of the given Mg(OH)$_2$-seawater system. Also, one of the advantages of substoichiometric (80%) precipitation lies in the reduced quantity of concentrated HCl needed to neutralize waste seawater after sedimentation. This quantity amounts to only 1.1 g of concentrated HCl per kg of magnesium oxide, while it is 210.5 of concentrated HCl per kg of magnesium oxide with the overstoichiometric (120%) precipitation (Petric et al., 1991). In such a case, i.e. when this precipitation method is employed, the boron content adsorbed onto the magnesium hydroxide during the precipitation process is somewhat higher than during overstoichiometric precipitation, and should therefore be reduced. Boron oxide is a common impurity in magnesia obtained from seawater; it is capable of acting as a powerful fluxing agent for the calcium silicate phases which can be present in refractory grades of magnesia.

2.1 TiO$_2$ addition as sintering aid

The use of sintering aids – small additions of various compounds that enhance densification, or allow it to occur at a lower temperature during sintering – is quite common in the
production of ceramic bodies. The most commonly used additives are oxides (Li$_2$O, Al$_2$O$_3$, Cr$_2$O$_3$, Fe$_2$O$_3$, SiO$_2$, TiO$_2$, ZrO$_2$ and V$_2$O$_5$) and some halides, such as LiF and LiCl. The effect of small additions of this compounds on the sintering of magnesium oxide has been studied in detail (Chaudhuri, 1990, 1992, 1999; Ćosić et al., 1987; Lee, 1998; Lucion, 2004; Martinac et al., 1996; Petric et al., 1987, 1989, 1994, 1999) and has received wide attention. Additions of tetravalent Si, Ti and Zr enhance sintering. There is a general consensus regarding the way in which many of these additives operate, based on a mechanism where intergranular liquid phase are formed which can restrict grain growth, assist the grain-boundary sliding and accelerate mass transport during sintering. It has been established that the addition of TiO$_2$ greatly affect properties of magnesium oxide obtained from seawater; even a small addition of 0.5 wt.-% TiO$_2$ significantly increases product density at 1300 °C (Petric et al., 1989). The densities amount to 94% of the theoretical density ($\rho_t = 3.576 \text{ g cm}^{-3}$) for duration of isothermal heating 5 h. The addition of TiO$_2$ promotes low-temperature densification of magnesium oxide, proportional to the extend of solid solution formation and vacancy formation. In that case the sintering was intensified in the presence of the liquid phase in the MgO-TiO$_2$ system. It is evident that TiO$_2$ addition is more efficient at lower temperatures than at the higher ones. The effect of ultravalent ions (such as Ti$^{4+}$) in the periclase crystal structure creates lattice defects in the form of cation vacancies (Fig. 1) which promote material transport and sintering at relatively low temperatures. At higher temperatures, such as 1600 °C and 1700 °C, the effect of this aid is less prominent. We can assume the mass

![Fig. 1. Schematic representation of a small section of a periclase crystal (MgO), a) at low temperatures (intrinsic) and b) Schottky defect (anionic and cationic vacancies). The ions originally at the vacant lattice sites have been removed to the surface, c) The crystal has a Ti$^{4+}$ ion that induces a cation vacancy, d) This crystalstal has a F$^-$ ion inducing a cation vacancies.](https://www.intechopen.com)
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Transfer, as in the case with pure magnesium oxide to be determined by diffusion of O\textsubscript{2} ions through the MgO lattice as the slower diffusion species. Higher temperatures improve mobility in elements forming the crystal lattice, due to which an interface is formed between particles of compact powder, porosity is eliminated and the whole system shrinks. The densities amount to 94-97\% of the theoretical densities at 1600 °C, and 96-98\% at 1700 °C, for duration of isothermal heating 1-5 h, and with 1, 2 and 5 wt.-\% TiO\textsubscript{2} added. Data on apparent porosity in sintered samples point to a very low presence of open pores in the system. The pores present are mainly the closed ones. Accordingly, total porosity is almost identical to closed porosity. An apparent porosity ranges from 0.15-0.10\% at 1600 °C and 0.05-0.03\% at 1700 °C, for soaking time 1-5 h for sintered magnesium oxide samples (80\% precipitation) and 0.16-0.11\% at 1600 °C and 0.04-0.01\% at 1700 °C for sintering magnesium oxide samples (120\% precipitation) under the same operating conditions (Petric et al., 1999). The low values obtained for the densification during isothermal heating in the samples examined indicate that a great part of densification process takes place during heating, i.e. before the maximum sintering temperature is reached.

The addition of TiO\textsubscript{2} also greatly affects the removal of boron from the sample into air, i.e., TiO\textsubscript{2} reduces the B\textsubscript{2}O\textsubscript{3} content during isothermal sintering of magnesium oxide obtained from seawater (Martinc, 1994). The boron content of seawater presents a problem because the hot-strength properties of certain specialized magnesia refractory products are markedly affected by their boron content. Boron is present in seawater in part as the non-dissociated orthoborate acid H\textsubscript{3}BO\textsubscript{3} and partly as the borate ion H\textsubscript{2}BO\textsubscript{3}\textsuperscript{-}. The concentration of the higher oxidation level ions HBO\textsubscript{2}\textsuperscript{2-} and BO\textsubscript{3}\textsuperscript{3-} is very low. The orthoborate acid is a weak acid with the following dissociation constants:

\[
\begin{align*}
H_2BO_3 &= H^+ + H_2BO_3^- & K_1 = 5.8 \times 10^{-10} \\
H_2BO_3^- &= H^+ + HBO_2\textsuperscript{2-} & K_2 = 1.8 \times 10^{-13} \\
HBO_2\textsuperscript{2-} &= H^+ + BO_3\textsuperscript{3-} & K_3 = 1.6 \times 10^{-14}
\end{align*}
\]

By calculating the dissociation rate, one can establish the molal concentration of H\textsubscript{2}BO\textsubscript{3}, HBO\textsubscript{2}\textsuperscript{2-}, and BO\textsubscript{3}\textsuperscript{3-}, as well as the molal dissociation rate for every degree of dissociation of the orthoborate acid. For 80\% precipitation of magnesium hydroxide from seawater by dolomite lime, the pH value is 9.6 during reaction precipitation and settling of the precipitate formed. In that case the orthoborate acid dissociation in the first degree is 69.78\%, which contributes to a significant increase of the B\textsubscript{2}O\textsubscript{3} content in the product, i.e. in magnesium oxide obtained from seawater (0.193 wt.-\%). Under the conditions more favorable to coprecipitation, the boron contamination of the magnesium hydroxide can be as high as the equivalent of 0.5 parts B\textsubscript{2}O\textsubscript{3} per 100 parts of magnesia. However, using specific reaction conditions as well as addition TiO\textsubscript{2}, the boron contamination can be virtually eliminated. The addition of TiO\textsubscript{2} proved rather interesting since the content of B\textsubscript{2}O\textsubscript{3} is reduced in a sintered samples by means of TiO\textsubscript{2}. Mixtures of magnesium oxide were prepared in the above composition (Tab. 1), with 1, 2 and 5 wt.-\% TiO\textsubscript{2}, respectively. The dopant oxide used was an analytical reagent grade titania (TiO\textsubscript{2} p.a.), in rutile form, produced by Merck. The chemical analysis of TiO\textsubscript{2} p.a. is given in Tab.2.
Samples were homogenized by manual stirring in ethanol absolute (C₂H₆O p.a.) for 30 min. After drying (at 80 °C) the mixture was crushed into fine powder and the powders were mixed well again. The mixtures were compacted by a cold-pressing process. The process was carried out in a hydraulic press at pressure of 625 MPa. The compacts were sintered at temperatures of 1300 °C and 1500 °C, with an isothermal heating duration of τ = 1, 3 and 5 h. The sintering at 1300 °C was carried out in an electric furnace. A gas furnace, made by a French firm, Mecker, (Type 553) with zirconium(IV) oxide lining, was used for sintering at 1500 °C. The furnace was heated by burning a mixture of propane-butane in the air, with oxygen added to achieve high temperature. It took approximately 2 h to reach the maximum temperature in the furnaces. In both cases, after sintering, the samples were left to cool in the furnace. Tabs. 3 and 4 show the results obtained for the effect of TiO₂ on the content of B₂O₃ in magnesium oxide samples after sintering at 1300 °C and 1500 °C, taking into account the method of obtaining magnesium hydroxide from seawater as well as the operating conditions listed. The results shown represent an average of a number of measurements. The standard deviation, σ, for MgO (80 % precipitation) was: σₘₐₓ = 9.8·10⁻³ and σₘᵢₙ = 4.4·10⁻³. The standard deviation for MgO (120 % precipitation) was: σₘₐₓ = 5.0·10⁻³ and σₘᵢₙ = 1.5·10⁻³.

Table 3. Effect of TiO₂ on the B₂O₃ content in the sintered magnesium oxide samples (80 % precipitation) at t = 1300 °C, 1500 °C, τ = 1, 3, 5 h, p = 625 MPa.

<table>
<thead>
<tr>
<th>t / °C</th>
<th>τ/h</th>
<th>B₂O₃ (wt.-%) in MgO without addition</th>
<th>B₂O₃ (wt.-%) in MgO + 1 wt.-% TiO₂</th>
<th>B₂O₃ (wt.-%) in MgO + 2 wt.-% TiO₂</th>
<th>B₂O₃ (wt.-%) in MgO + 5 wt.-% TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300</td>
<td>1</td>
<td>0.1934</td>
<td>0.1395</td>
<td>0.0789</td>
<td>0.0652</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.1655</td>
<td>0.1363</td>
<td>0.0752</td>
<td>0.0638</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.1192</td>
<td>0.0852</td>
<td>0.0645</td>
<td>0.0587</td>
</tr>
<tr>
<td>1500</td>
<td>1</td>
<td>0.1265</td>
<td>0.0434</td>
<td>0.0396</td>
<td>0.0264</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0756</td>
<td>0.0184</td>
<td>0.0170</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.0689</td>
<td>0.0173</td>
<td>0.0159</td>
<td>0.0131</td>
</tr>
</tbody>
</table>
### Table 4. Effect of TiO$_2$ on the B$_2$O$_3$ content in the sintered magnesium oxide samples (120 % precipitation) at $t = 1300$ °C, 1500 °C, $\tau = 1, 3, 5$ h, $p = 625$ MPa.

<table>
<thead>
<tr>
<th>$t$ / °C</th>
<th>$\tau$ / h</th>
<th>B$_2$O$_3$ (wt.-%) in MgO without addition</th>
<th>B$_2$O$_3$ (wt.-%) in MgO + 1 wt.-% TiO$_2$</th>
<th>B$_2$O$_3$ (wt.-%) in MgO + 2 wt.-% TiO$_2$</th>
<th>B$_2$O$_3$ (wt.-%) in MgO + 5 wt.-% TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300</td>
<td>1</td>
<td>0.0512</td>
<td>0.0428</td>
<td>0.0293</td>
<td>0.0165</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0459</td>
<td></td>
<td>0.0109</td>
<td>0.0086</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.0376</td>
<td>0.0384</td>
<td>0.0096</td>
<td>0.0053</td>
</tr>
<tr>
<td>1500</td>
<td>1</td>
<td>0.0453</td>
<td>0.0431</td>
<td>0.0116</td>
<td>0.0062</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0400</td>
<td>0.0331</td>
<td>0.0100</td>
<td>0.0060</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.0318</td>
<td>0.0204</td>
<td>0.0050</td>
<td>0.0035</td>
</tr>
</tbody>
</table>

The experimental data indicate that the TiO$_2$ addition together with the temperature and duration of isothermal heating significantly reduces the B$_2$O$_3$ content during sintering. Different behaviour patterns relative to the B$_2$O$_3$ content were noticed in magnesium oxide obtained by 80 % or by 120 % precipitation of magnesium hydroxide in seawater; this is due to different contents of CaO in those samples. It was noted that the presence of calcium oxide caused the retention of boron in the samples during sintering. With the magnesium oxide (120 % precipitation) the content of CaO = 1.32 wt.-% is significantly higher than with the magnesium oxide (80 % precipitation) where CaO = 0.59 wt.-%, i.e. there is a significantly larger quantity of CaO than in case of 80 % precipitation which favors the Ca$_2$B$_2$O$_5$ formation reaction. Namely, based on a previous paper (Petric et al., 1987) the presence of dicalcium borate (Ca$_2$B$_2$O$_5$) was proved in sintered samples by the method of X-ray diffraction, that is, it was established that B$_2$O$_3$ transforms into Ca$_2$B$_2$O$_5$ through the reaction with CaO. Also the studies (Chaudhuri et al., 1992, 1999; Cosić et al., 1989; Čeh & Kolar, 1994) show that the method of X-ray diffraction and EDAX analysis indicate that in the sintering process the TiO$_2$ added reacts with CaO from the MgO-CaO solid solution and transforms into calcium titanate CaTiO$_3$. Therefore, TiO$_2$ binds a part of CaO in CaTiO$_3$ and thus reduces the CaO content which reacts with B$_2$O$_3$. So a smaller quantity of Ca$_2$B$_2$O$_5$ is formed which remains in the sintered samples while a greater part of B$_2$O$_3$ evaporates. This is the way in which the TiO$_2$ reduces the quantity of B$_2$O$_3$ in a sample. The higher the CaO content, the more B$_2$O$_3$ is retained in the sintered samples. With MgO (80 % precipitation) already a small amount of TiO$_2$ (wt. = 1%) binds almost all of CaO present. With MgO (120 % precipitation) CaO is in excess and favors Ca$_2$B$_2$O$_5$ formation; in MgO (80 % precipitation) a greater part of B$_2$O$_3$ evaporates from the sample into the atmosphere. In the magnesium oxide (120 % precipitation) it can be seen that a higher quantity of TiO$_2$ (2 - 5 wt.-%) binds almost all of CaO and effects boron removal significantly. Therefore, the final content of B$_2$O$_3$ in the sintered samples depends both on the CaO and TiO$_2$ content. These two mutually dependent reactions of formation of Ca$_2$B$_2$O$_5$ and CaTiO$_3$ which cause B$_2$O$_3$ content reduction during sintering, are:
In order to examine the effect of TiO$_2$ on the reduction of the B$_2$O$_3$ content in samples sintered, experimental results on the fraction of evaporated boron and the degree of reaction CaO with TiO$_2$ have been examined relative to the temperature and the duration of isothermal sintering for magnesium oxide samples obtained from seawater by 80% and 120% precipitation, with addition of wt. = 1, 2 and 5% TiO$_2$ respectively, according to expressions used in the open system thermodynamics (De Groot & Mazur, 1984; Haase, 1990; Lavenda, 1993; Prigogine, 1968). A system of equations dealt with the open system thermodynamics has therefore been considered, and coefficients $L_{11}$, $L_{12}$ and $L_{22}$ that describe the mutual effect of two simultaneous irreversible processes examined, have been calculated based on an important theorem due to Onsanger. Generally, the phenomenological relationship may be written in the following form:

$$ J_i = \sum L_{ij} X_j $$

For each force $X$, there is a corresponding conjugate primary flow $J$. These phenomena, and other like them, are called cross-effects. The coefficients $L_{ij}$ (with $i \neq j$) are called phenomenological coefficients. For the system with two flows caused by two driving forces, i.e., with two simultaneous irreversible processes, phenomenological dependencies can be expressed in the following way:

$$ J_1 = L_{11} X_1 + L_{12} X_2 $$
$$ J_2 = L_{21} X_1 + L_{22} X_2 $$

where $J_1$ and $J_2$ denote flows and $X_1$ and $X_2$ denote the forces causing these flows. Coefficients $L_{ij}$ (with $i \neq j$) describe the interference of the two irreversible processes $i$ and $j$. There exists a so-called Onsanger reciprocity ratio between cross coefficients $L_{ij}$ and $L_{ji}$ which can be expressed by following equations:

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

or

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

These Onsanger reciprocity relations state that when the flux, corresponding to the irreversible process $i$, is influenced by the force $X_j$ of the irreversible process $j$, then the flux $j$ is also influenced by the force $X_i$ through the same interference coefficient $L_{ij}$. Equation (12) allows a reduction in the number of phenomenological coefficients, i.e., the interaction coefficients $L_{12}$ and $L_{21}$ are equal. The coefficients $L_{ij}$ in the system of two equations, i.e., for $n = 2$, must satisfy the following conditions:

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

$$ \text{CaO} + \text{TiO}_2 = \text{CaTiO}_3 $$
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\[ L_{11} \geq 0; \quad L_{22} \geq 0 \]  
\[ (L_{12} + L_{21})^2 \leq 4 L_{11}L_{22} \]  

Using again the Onsanger relation \( L_{12} = L_{21} \), equation (15) now becomes

\[ L_{11}L_{22} - L_{12}^2 \geq 0 \]  

The conjugate coefficients (i.e. \( L_{11} \) and \( L_{22} \)) must be positive. Obviously, the crossed coefficients or interference coefficients (\( L_{12} \) and \( L_{21} \)) have no definite sign. They may be either positive or negative; their magnitude being limited only by equation (15). If the system of phenomenological Eqs. (10) and (11) is applied to the Ca$_2$B$_2$O$_5$ and CaTiO$_3$ formation reactions, which are interdependent, we assume the linear relations:

\[ J_1 = L_{11}t' + L_{12}\tau \]  
\[ J_2 = L_{21}t' + L_{22}\tau \]  

where \( J_1 \) is the percent of B$_2$O$_3$ removed during sintering, and calculated from experimental data on the B$_2$O$_3$ content in sintered samples and on the content B$_2$O$_3$ in calcined magnesium oxide, i.e. the sample before sintering. \( J_2 \) is the percent of CaO which reacted with TiO$_2$, \( \tau \) is the duration of isothermal heating (h), and \( t' \) is the temperature at \( 10^{-2} \) (°C), i.e., \( t' = t \cdot 10^{-2} \) (°C). From this we see that we may regard \( t' \) and \( \tau \) as driving forces corresponding to the fluxes \( J_1 \) and \( J_2 \), respectively. Tabs. 5 and 6 present the values obtained for dependence of \( J_1 \) and \( J_2 \) on the temperature (\( t' \)) and duration of isothermal heating (\( \tau \)) for sintered magnesium oxide samples (80 % and 120 % precipitation), with different quantities of sintering aid.

<table>
<thead>
<tr>
<th>( t'/\tau )</th>
<th>( J_1 )</th>
<th>( J_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>27.87</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>77.56</td>
<td>90.49</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( t'/\tau )</th>
<th>( J_1 )</th>
<th>( J_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>59.20</td>
<td>61.12</td>
</tr>
<tr>
<td>15</td>
<td>79.52</td>
<td>91.21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( t'/\tau )</th>
<th>( J_1 )</th>
<th>( J_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>66.29</td>
<td>67.01</td>
</tr>
<tr>
<td>15</td>
<td>86.35</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5. Dependence of \( J_1 \) and \( J_2 \) on temperature (\( t' \)) and duration of isothermal heating (\( \tau \)) for the sintered magnesium oxide samples (80 % precipitation) with different quantities of sintering aid.

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aid, respectively. The coefficients $L_{11}$, $L_{12}$ and $L_{22}$ in eqs. (17) and (18) were calculated by a computer using combination of the mean values method with the least squares method. After calculating the coefficients, the equations for $J_1$ and $J_2$ for each percent of TiO$_2$ added, for the magnesium oxide (80 % precipitation) and the magnesium oxide (120 % precipitation) are shown in Tab. 7. Thus, the experimental data $J_i$, i.e. the percent of B$_2$O$_3$ "removed" during sintering process, and $J_2$, i.e. the percent of CaO which reacted with TiO$_2$ which also indirectly affects the content of B$_2$O$_3$ were used to calculate the coefficients $L_{11}$, $L_{12}$ and $L_{22}$. The calculated phenomenological coefficients $L_{11}$, $L_{12}$ and $L_{22}$ describe simultaneous irreversible processes (reactions) and provide an insight into the interdependence of both reactions.

### Table 6. Dependence of $J_1$ and $J_2$ on temperature ($t'$) and duration of isothermal heating ($\tau$) for the sintered magnesium oxide samples (120 % precipitation) with different quantities of sintering aid.

<table>
<thead>
<tr>
<th>$t'/\tau$</th>
<th>$J_1$</th>
<th>$J_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t'$</td>
<td>$\tau$</td>
</tr>
<tr>
<td>13</td>
<td>23.81</td>
<td>13</td>
</tr>
<tr>
<td>15</td>
<td>23.31</td>
<td>41.16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$t'/\tau$</th>
<th>$J_1$</th>
<th>$J_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t'$</td>
<td>$\tau$</td>
</tr>
<tr>
<td>13</td>
<td>47.85</td>
<td>80.64</td>
</tr>
<tr>
<td>15</td>
<td>96.84</td>
<td>97.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$t'/\tau$</th>
<th>$J_1$</th>
<th>$J_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t'$</td>
<td>$\tau$</td>
</tr>
<tr>
<td>13</td>
<td>70.64</td>
<td>84.75</td>
</tr>
<tr>
<td>15</td>
<td>89.02</td>
<td>89.23</td>
</tr>
</tbody>
</table>

Table 6. Dependence of $J_1$ and $J_2$ on temperature ($t'$) and duration of isothermal heating ($\tau$) for the sintered magnesium oxide samples (120 % precipitation) with different quantities of sintering aid.

### Table 7. Equations for $J_1$ and $J_2$ with the calculated coefficients $L_{11}$, $L_{12}$ and $L_{22}$ for each percent of TiO$_2$ added, for the sintered magnesium oxide samples MgO (80 % precipitation) and MgO (120 % precipitation), respectively.

For MgO (80 % precipitation) | For MgO (120 % precipitation)
---|---
For 1 wt.-% TiO$_2$ | For 1 wt.-% TiO$_2$
$J_1 = 3.9411 t' + 4.6189 \tau$ | $J_1 = 1.8155 t' + 3.7793 \tau$
$J_2 = 4.6189 t' + 4.8140 \tau$ | $J_2 = 3.7793 t' + 5.9798 \tau$

For 2 wt.-% TiO$_2$ | For 2 wt.-% TiO$_2$
$J_1 = 4.3421 t' + 4.9044 \tau$ | $J_1 = 4.9090 t' + 5.2364 \tau$
$J_2 = 4.9044 t' + 4.6067 \tau$ | $J_2 = 5.2364 t' + 4.7514 \tau$

For 5 wt.-% TiO$_2$ | For 5 wt.-% TiO$_2$
$J_1 = 4.4856 t' + 5.0239 \tau$ | $J_1 = 4.9594 t' + 5.6129 \tau$
$J_2 = 5.0239 t' + 4.3569 \tau$ | $J_2 = 5.6129 t' + 2.6914 \tau$

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The coefficient values $L_{11}$, $L_{12}$ and $L_{22}$ calculated depend on the quantity of TiO$_2$ added. Therefore, the dependence of the coefficients value $L_{11}$, $L_{12}$ and $L_{22}$ on percent TiO$_2$ was calculated. The relationship between the phenomenological coefficients and the percent of TiO$_2$ added can be expressed by the following equation:

$$Y = A x^2 + B x + C$$  \hspace{1cm} (19)

where $Y$ is the phenomenological coefficients $L_{11}$, $L_{12}$ and $L_{22}$, $x$ is the percent of TiO$_2$ added and $A$, $B$ and $C$ are constants. The coefficients were calculated by the least squares method and are shown by the equations: For the sintered magnesium oxide samples (80 % precipitation):

- $L_{11} = -0.0833 x^2 + 0.6659 x + 3.3635$  \hspace{1cm} (20)

- $L_{12} = -0.0614 x^2 + 0.4697 x + 4.2106$  \hspace{1cm} (21)

- $L_{22} = 0.0310 x^2 - 0.3003 x + 5.0833$  \hspace{1cm} (22)

For the sintered magnesium oxide samples (120 % precipitation):

- $L_{11} = -0.7692 x^2 + 5.4010 x - 2.8164$  \hspace{1cm} (23)

- $L_{12} = -0.3293 x^2 + 2.4333 x + 1.6803$  \hspace{1cm} (24)

- $L_{22} = 0.1354 x^2 - 1.6347 x + 7.4791$  \hspace{1cm} (25)

where $x$ is the percent of TiO$_2$. These equations describing dependence of $L$ to $x$ make it possible to calculate the coefficients $L_{11}$, $L_{12}$ and $L_{22}$ for other percentages of $x$ in the range from 1 wt.-% to 5 wt.-% TiO$_2$. As CaO simultaneously reacts with both B$_2$O$_3$ and TiO$_2$ two described reactions of formation of dicalcium borate and calcium titanate are related, and it was of interest to calculate the coefficients for Eqs. (17) and (18), as well as their dependence on the percentage of TiO$_2$ added. The analysis provides the opportunity to determine which percentage of TiO$_2$ should be added to the sample once to CaO and B$_2$O$_3$ contents are known. Thermodynamical analysis of the magnesium oxide sintering process with varying quantities of added TiO$_2$ has made possible to predict mathematically, without experiments, the B$_2$O$_3$ content in samples sintered relative to the temperature and the duration of isothermal sintering, as well as on the properties of initial magnesium oxide samples. The method of describing a system by application of equations studied in the open system thermodynamics can be used in some other cases when similar laws are involved, i.e. when due to a motive force in a system, a flow of mass or energy occurs.

3. Conclusion

The effect of TiO$_2$ addition on the B$_2$O$_3$ content of sintered samples, i.e. on product properties, has been examined. The addition of TiO$_2$ reduces the B$_2$O$_3$ content in the isothermal sintering process, as it binds a part of CaO in calcium titanate, CaTiO$_3$, so that a greater part of B$_2$O$_3$ evaporates from the system during sintering. Depending on the CaO content of the sample, i.e. the method of obtaining magnesium hydroxide from seawater, it has been found that in magnesium oxide (80 % precipitation) a lower quantity of TiO$_2$ (1
wt.-%) binds almost all the CaO present (which has not reacted with B$_2$O$_3$). In the magnesium oxide (120 % precipitation) it takes 2 wt.-% TiO$_2$ to bind all the CaO present (which has not reacted), so that only a greater quantity (5 wt.-%) TiO$_2$ affects boron removal during sintering to a greater degree. The higher the CaO content, the more B$_2$O$_3$ is retained in the sintered samples. Two mutually dependent reactions of formation of Ca$_2$B$_2$O$_5$ and CaTiO$_3$ were analysed, and phenomenological coefficients calculated using expressions used in the open system thermodynamics. Calculated phenomenological coefficients L$_{11}$, L$_{12}$ and L$_{22}$ describe the mutual interdependence of two simultaneous irreversible processes, based on an important theorem due to Onsanger. It is thus possible to calculate the quantity of boron (B$_2$O$_3$) removed during the sintering process, i.e. the quantity of B$_2$O$_3$ which remains in the sample sintered, for the area examined. Analogous consideration can be carried out for all the other cases when similar laws are involved, i.e. when mass or energy flows occur in the system due to a motive force.

4. Acknowledgment

The results shown arise from the research project «Activated sintering of magnesium oxide» which is financially supported by the Ministry of Science, Education and Sports of the Republic of Croatia.

5. References


Effect of TiO$_2$ Addition on the Sintering Process of Magnesium Oxide from Seawater


The chapters covered in this book include emerging new techniques on sintering. Major experts in this field contributed to this book and presented their research. Topics covered in this publication include Spark plasma sintering, Magnetic Pulsed compaction, Low Temperature Co-fired Ceramic technology for the preparation of 3-dimesinal circuits, Microwave sintering of thermistor ceramics, Synthesis of Bio-compatible ceramics, Sintering of Rare Earth Doped Bismuth Titanate Ceramics prepared by Soft Combustion, nanostructured ceramics, alternative solid-state reaction routes yielding densified bulk ceramics and nanopowders, Sintering of intermetallic superconductors such as MgB2, impurity doping in luminescence phosphors synthesized using soft techniques, etc. Other advanced sintering techniques such as radiation thermal sintering for the manufacture of thin film solid oxide fuel cells are also described.

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