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Effect of TiO_2 Addition on the Sintering Process of Magnesium Oxide from Seawater

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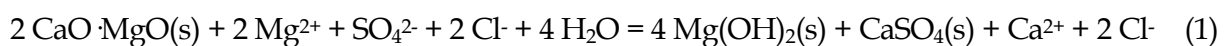
1. Introduction

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 $(2823 \pm 40)^\circ\text{C}$), 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 ($\text{CaCO}_3 \cdot \text{MgCO}_3$), hydromagnesite ($3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), brucite ($\text{Mg}(\text{OH})_2$) and serpentine ($\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$). 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 ($\geq 98\% \text{ MgO}$). 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, Rabadzhieva 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 magnesium produced in the western world, and today it still remains a major source of magnesium oxide 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 particularly 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_2O_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_2O_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:



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

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_2SO_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:



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 $120 \text{ dm}^3 \text{ h}^{-1}$, and the volumetric flow rate of the seawater through the desorption tower was $6 \text{ dm}^3 \text{ h}^{-1}$. 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 dm³ 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.

Sample	MgO / wt.-%	CaO / wt.-%	B ₂ O ₃ / wt.-%
MgO (80% precipitation)	99.20	0.59	0.193
MgO (120% precipitation)	98.25	1.32	0.056

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 Mg²⁺ 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 TiO₂ 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_2O , Al_2O_3 , Cr_2O_3 , Fe_2O_3 , SiO_2 , TiO_2 , ZrO_2 and V_2O_5) and some halides, such as LiF and LiCl . The effect of small additions of these 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 extent 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

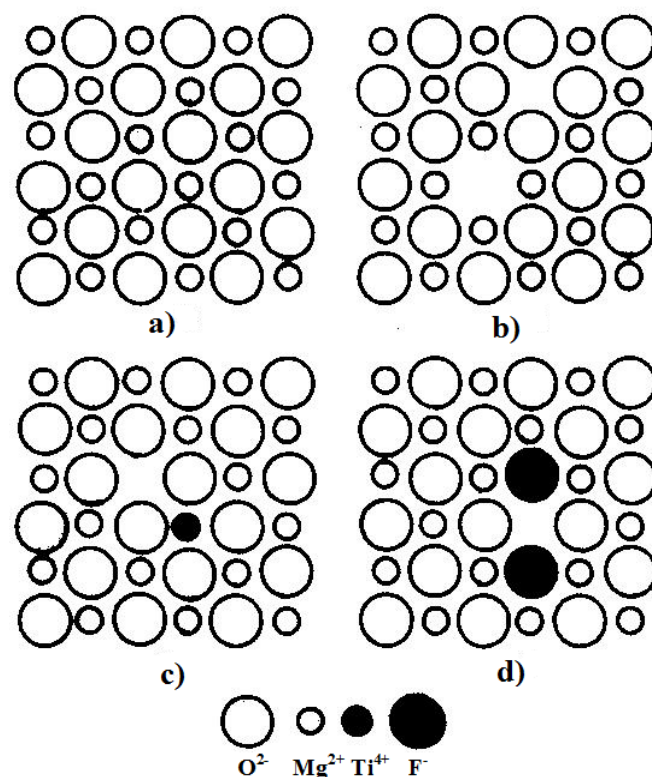
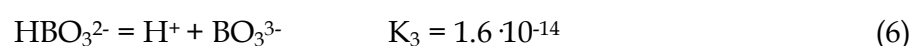
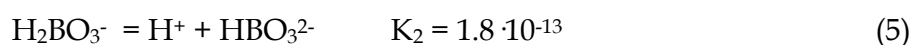
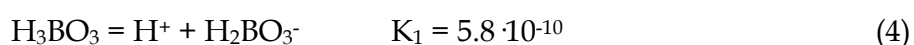


Fig. 1. Schematic representation of a small section of a periclase crystal (MgO), a) at low temperatures (intrinsic) and b) Schottky defect (anionic and cationic vacancies). The ions originally at the vacant lattice sites have been removed to the surface, c) The crystal has a Ti^{4+} ion that induces a cation vacancy, d) This crystal has a F^- ion inducing a cation vacancies.

transfer, as in the case with pure magnesium oxide to be determined by diffusion of O₂⁻ 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.-% TiO₂ 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 TiO₂ also greatly affects the removal of boron from the sample into air, i.e., TiO₂ reduces the B₂O₃ content during isothermal sintering of magnesium oxide obtained from seawater (Martinac, 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 H₃BO₃ and partly as the borate ion H₂BO₃⁻. The concentration of the higher oxidation level ions HBO₃²⁻ and BO₃³⁻ is very low. The orthoborate acid is a weak acid with the following dissociation constants:



By calculating the dissociation rate, one can establish the molal concentration of H₂BO₃⁻, HBO₃²⁻, and BO₃³⁻, 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 B₂O₃ 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 B₂O₃ per 100 parts of magnesia. However, using specific reaction conditions as well as addition TiO₂, the boron contamination can be virtually eliminated. The addition of TiO₂ proved rather interesting since the content of B₂O₃ is reduced in a sintered samples by means of TiO₂. Mixtures of magnesium oxide were prepared in the above composition (Tab. 1), with 1, 2 and 5 wt.-% TiO₂, respectively. The dopant oxide used was an analytical reagent grade titania (TiO₂ p.a.), in rutile form, produced by Merck. The chemical analysis of TiO₂ p.a. is given in Tab.2.

	TiO ₂ (99 %)
Water soluble matter	0.3 %
Chloride (Cl)	0.01 %
Sulphate (SO ₄)	0.05 %
Heavy metals (such as Pb)	0.001 %
Iron (Fe)	0.005 %
Arsenic (As)	0.0002 %

Table 2. Chemical analysis (wt.-%) of TiO₂ p.a. (Merck).

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 $\tau = 1, 3$ 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: $\sigma_{\max} = 9.8 \cdot 10^{-3}$ and $\sigma_{\min} = 4.4 \cdot 10^{-3}$. The standard deviation for MgO (120 % precipitation) was: $\sigma_{\max} = 5.0 \cdot 10^{-3}$ and $\sigma_{\min} = 1.5 \cdot 10^{-3}$.

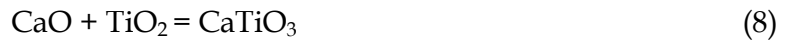
t / °C	τ / h	B ₂ O ₃ (wt.-%) in MgO without addition	B ₂ O ₃ (wt.-%) in MgO + 1 wt.-% TiO ₂	B ₂ O ₃ (wt.-%) in MgO + 2 wt.-% TiO ₂	B ₂ O ₃ (wt.-%) in MgO + 5 wt.-% TiO ₂
1300	1	0.1934	0.1395	0.0789	0.0652
	3	0.1655	0.1363	0.0752	0.0638
	5	0.1192	0.0852	0.0645	0.0587
1500	1	0.1265	0.0434	0.0396	0.0264
	3	0.0756	0.0184	0.0170	
	5	0.0689	0.0173	0.0159	0.0131

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

t / °C	τ / h	B ₂ O ₃ (wt.-%) in MgO without addition	B ₂ O ₃ (wt.-%) in MgO + 1 wt.-% TiO ₂	B ₂ O ₃ (wt.-%) in MgO + 2 wt.-% TiO ₂	B ₂ O ₃ (wt.-%) in MgO + 5 wt.-% TiO ₂
1300	1	0.0512	0.0428	0.0293	0.0165
	3	0.0459		0.0109	0.0086
	5	0.0376	0.0384	0.0096	0.0053
1500	1	0.0453	0.0431	0.0116	0.0062
	3	0.0400	0.0331	0.0100	0.0060
	5	0.0318	0.0204	0.0050	0.0035

Table 4. Effect of TiO₂ on the B₂O₃ content in the sintered magnesium oxide samples (120 % precipitation) at t = 1300 °C, 1500 °C, τ = 1, 3, 5 h, p = 625 MPa.

The experimental data indicate that the TiO₂ addition together with the temperature and duration of isothermal heating significantly reduces the B₂O₃ content during sintering. Different behaviour patterns relative to the B₂O₃ 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 Ca₂B₂O₅ formation reaction. Namely, based on a previous paper (Petric et al., 1987) the presence of dicalcium borate (Ca₂B₂O₅) was proved in sintered samples by the method of X-ray diffraction, that is, it was established that B₂O₃ transforms into Ca₂B₂O₅ through the reaction with CaO. Also the studies (Chaudhuri et al., 1992, 1999; Ćosić et al., 1989; Čeh & Kolar, 1994) show that the method of X-ray diffraction and EDAX analysis indicate that in the sintering process the TiO₂ added reacts with CaO from the MgO-CaO solid solution and transforms into calcium titanate CaTiO₃. Therefore, TiO₂ binds a part of CaO in CaTiO₃ and thus reduces the CaO content which reacts with B₂O₃. So a smaller quantity of Ca₂B₂O₅ is formed which remains in the sintered samples while a greater part of B₂O₃ evaporates. This is the way in which the TiO₂ reduces the quantity of B₂O₃ in a sample. The higher the CaO content, the more B₂O₃ is retained in the sintered samples. With MgO (80% precipitation) already a small amount of TiO₂ (wt. = 1%) binds almost all of CaO present. With MgO (120 % precipitation) CaO is in excess and favors Ca₂B₂O₅ formation; in MgO (80 % precipitation) a greater part of B₂O₃ evaporates from the sample into the atmosphere. In the magnesium oxide (120 % precipitation) it can be seen that a higher quantity of TiO₂ (2 – 5 wt.-%) binds almost all of CaO and effects boron removal significantly. Therefore, the final content of B₂O₃ in the sintered samples depends both on the CaO and TiO₂ content. These two mutually dependent reactions of formation of Ca₂B₂O₅ and CaTiO₃ which cause B₂O₃ content reduction during sintering, are:



In order to examine the effect of TiO_2 on the reduction of the B_2O_3 content in samples sintered, experimental results on the fraction of evaporated boron and the degree of reaction CaO with TiO_2 has 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:

$$J_i = \sum L_{ij} X_j \quad (9)$$

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:

$$J_1 = L_{11} X_1 + L_{12} X_2 \quad (10)$$

$$J_2 = L_{21} X_1 + L_{22} X_2 \quad (11)$$

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:

$$L_{ij} = L_{ji} \quad (ij = 1, \dots, n; i \neq j) \quad (12)$$

or

$$\left(\frac{\partial J_i}{\partial X_j} \right)_{X_{i=0}, i \neq j} = \left(\frac{\partial J_j}{\partial X_i} \right)_{X_{j=0}, j \neq i} \quad (13)$$

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:

$$L_{11} \geq 0; \quad L_{22} \geq 0$$

(14)

$$(L_{12} + L_{21})^2 \leq 4 L_{11} L_{22}$$

(15)

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

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

(16)

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 $\text{Ca}_2\text{B}_2\text{O}_5$ and CaTiO_3 formation reactions, which are interdependent, we assume the linear relations:

$$J_1 = L_{11} t' + L_{12} \tau$$

(17)

$$J_2 = L_{21} t' + L_{22} \tau$$

(18)

where J_1 is the percent of B_2O_3 removed during sintering, and calculated from experimental data on the B_2O_3 content in sintered samples and on the content B_2O_3 in calcined magnesium oxide, i.e. the sample before sintering, J_2 is the percent of CaO which reacted with TiO_2 , τ is the duration of isothermal heating (h), and t' is the themperature at 10^{-2} ($^{\circ}\text{C}$), i.e., $t' = t \cdot 10^{-2}$ ($^{\circ}\text{C}$). From this we see that we may regard t' and τ 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 duratin of isothermal heating (τ) for sintered magnesium oxide samples (80 % and 120 % precipitation), with different quantities of sintering

1 wt.-% TiO ₂							
t' / τ	J ₁			t' / τ	J ₂		
	1	3	5		1	3	5
13	27.87	-	55.95	13	61.19	-	76.46
15	77.56	90.49	91.05	15	85.54	93.25	93.54
2 wt.-% TiO ₂							
t' / τ	J ₁			t' / τ	J ₂		
	1	3	5		1	3	5
13	59.20	61.12	66.65	13	77.57	78.56	81.45
15	79.52	91.21	91.78	15	87.57	93.62	93.89
5 wt.-% TiO ₂							
t' / τ	J ₁			t' / τ	J ₂		
	1	3	5		1	3	5
13	66.29	67.01	69.70	13	81.26	81.62	83.04
15	86.35	-	93.23	15	91.10	-	94.66

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

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_1 , i.e. the percent of B_2O_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_2O_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.

1 wt.-% TiO_2							
t' / τ	J_1			t' / τ	J_2		
	1	3	5		1	3	5
13	23.81	-	31.69	13	52.52	-	52.52
15	23.31	41.16	63.70	15	93.06	94.26	95.76
2 wt.-% TiO_2							
t' / τ	J_1			t' / τ	J_2		
	1	3	5		1	3	5
13	47.85	80.64	83.02	13	95.32	95.57	97.73
15	96.84	97.01	97.64	15	79.36	82.21	91.10
5 wt.-% TiO_2							
t' / τ	J_1			t' / τ	J_2		
	1	3	5		1	3	5
13	70.64	84.75	90.50	13	96.89	97.85	98.24
15	89.02	89.23	93.75	15	97.47	97.50	97.81

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

For MgO (80 % precipitation)	For MgO (120 % precipitation)
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	
$J_1 = 4.3421 t' + 4.9044 \tau$	$J_1 = 4.9090 t' + 5.2364 \tau$
$J_2 = 4.9044 t' + 4.6067 \tau$	$J_2 = 5.2364 t' + 4.7514 \tau$
For 5 wt.-% TiO_2	
$J_1 = 4.4856 t' + 5.0239 \tau$	$J_1 = 4.9594 t' + 5.6129 \tau$
$J_2 = 5.0239 t' + 4.3569 \tau$	$J_2 = 5.6129 t' + 2.6914 \tau$

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.

The coefficient values L_{11} , L_{12} and L_{22} calculated depend on the quantity of TiO₂ added. Therefore, the dependence of the coefficients value L_{11} , L_{12} and L_{22} on percent TiO₂ was calculated. The relationship between the phenomenological coefficients and the percent of TiO₂ added can be expressed by the following equation:

$$Y = A x^2 + B x + C \quad (19)$$

where Y is the phenomenological coefficients L_{11} , L_{12} and L_{22} , x is the percent of TiO₂ 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):

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

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

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

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

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

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

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

where x is the percent of TiO₂. 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.-% TiO₂. As CaO simultaneously reacts with both B₂O₃ and TiO₂ 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 TiO₂ added. The analysis provides the opportunity to determine which percentage of TiO₂ should be added to the sample once to CaO and B₂O₃ contents are known. Thermodynamical analysis of the magnesium oxide sintering process with varying quantities of added TiO₂ has made possible to predict mathematically, without experiments, the B₂O₃ 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 TiO₂ addition on the B₂O₃ content of sintered samples, i.e. on product properties, has been examined. The addition of TiO₂ reduces the B₂O₃ content in the isothermal sintering process, as it binds a part of CaO in calcium titanate, CaTiO₃, so that a greater part of B₂O₃ 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 TiO₂ (1

wt.-%) binds almost all the CaO present (which has not reacted with B_2O_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_2O_3 is retained in the sintered samples. Two mutually dependent reactions of formation of $Ca_2B_2O_5$ and $CaTiO_3$ were analysed, and phenomenological coefficients calculated according to 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_2O_3) removed during the sintering process, i.e. the quantity of B_2O_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.

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