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Sintering of Magnesium Oxide Obtained from Sea Water

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Abstract

The process of isothermal sintering of magnesium oxide obtained from sea water (by precipitation with 80% and 120% of the stoichiometric quantity of the precipitation agent respectively) and of reagent grade magnesium oxide was examined with addition of 0·5% TiO_2*, at a temperature of 1600°C, for different durations of isothermal sintering and for different pressures applied in the forming of compacts.*

Product density, shrinkage and porosity were examined, and the results obtained were analysed mathematically. The effect of the TiO_2 *in the magnesium oxide sample on the content of* B_2O_3 *was also determined. Coefficients have been calculated for associated reactions, namely those for the formation of* $Ca_2B_2O_5$ *and* $CaTiO_3$.

Der isothermische Sinterprozeß von Magnesiumoxid, das aus Seewasser gewonnen wurde (durch Fällung mit 80% bzw. 120% der stöchiometrischen Menge des Fällmittels) und von reinem Magnesiumoxid, wurde für Preßkörper bei 1600°C und einem Zusatz von 0·5% TiO_2 *für verschiedene Sinterzeiten und Drücke untersucht.*

Dabei wurden die Probendichte die Schrumpfung und die Porosität gemessen und die Daten analysiert. Weiterhin wurde der Effekt des TiO_2 *in den Magnesiumoxidproben, auf den Gehalt des* B_2O_3 *bestimmt, und es erfolgte die Berechnung der Koeffizienten für die damit verbundenen Reaktionen, in erster Linie die Bildung von* $Ca_2B_2O_5$ *bzw.* $CaTiO_3$

On a étudié le frittage iostherme d'un oxyde de magnésium obtenu à partir d'eau de mer (par précipitation avec 80% et 120% d'agent de précipitation), et d'un oxyde de magnésium de qualité commerciale, en ajoutant 0·5% de TiO_2*, à 1600°C pour différents temps de frittage et différentes pressions de compactage.*

On a mesuré la densité, la densification et la porosité, et les résultats obtenus ont été analysés de manière quantitative. On a aussi étudié l'effet de Ti_2O *sur le contenu en* B_2O_3 *de l'oxyde de magnésium. On a calculé les coefficients pour les réactions associées, c'est-à-dire pour la formation de* $Ca_2B_2O_5$ *et* $CaTiO_3$.

1 Introduction

The effect of TiO_2 on the properties of sintered magnesium oxide obtained from sea water has been determined;[1] even a small quantity (0·5%) of TiO_2 favourably affects the product density, even at 1300°C.

The magnesium oxide used was obtained from sea water by non-stoichiometric precipitation (precipitation of $Mg(OH)_2$ takes place with 80% of the stoichiometric quantity of dolomite lime; 80% pptn) and by over-stoichiometric precipitation (with 120% of the stoichiometric quantity of dolomite lime; 120% pptn).[2]

This paper presents the experimental results obtained for the effects of pressure applied in the production of compacts (62, 94, 156, 312, 469 and 625 MPa) and duration of isothermal heating (25, 60 and 75 min) at 1600°C, on properties (density, porosity and shrinkage) of sintered samples of magnesium oxide obtained from sea water, and on reagent grade magnesium oxide.

The effect of the quantity of TiO_2 (1%, 2% and 5%) on the content of B_2O_3 in the product was also examined.

2 Experimental

Magnesium hydroxide obtained from sea water was calcined at 950°C. Its chemical composition was as follows:

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Table 1. Chemical analysis of reagent grade MgO (Kemika, Zagreb, Croatia) and TiO_2 (Merck)

	MgO (min 97%)	*TiO_2 (93%)*
Water soluble matter	max 0·5%	0·3%
Matter not soluble in HCl	max 0·005%	—
Chloride (Cl)	max 0·01%	0·01%
Sulphate (SO_4)	max 0·001%	0·05%
Total nitrogen (N)	max 0·002%	—
Heavy metals (like Pb)	max 0·005%	0·001%
Iron (Fe)	max 0·005%	0·005%
Zinc (Zn)	max 0·005%	—
Barium and strontium (like Ba)	max 0·005%	—
Calcium (Ca)	max 0·02%	—
Sodium (Na)	max 0·2%	—
Potassium (K)	max 0·005%	—
Arsenic (As)	—	0·0 002%
Loss weight	max 3%	—

For magnesium oxide (80% pptn):
MgO = 99·20%; CaO = 0·59%; B_2O_3 = 0·1934%.
For magnesium oxide (120% pptn):
MgO = 98·25%; CaO = 1·32%; B_2O_3 = 0·0562%.

The reagent grade magnesium oxide used contained a minimum of 97% MgO (produced by Kemika, Zagreb, Croatia). An analysis is given in Table 1.

The sea water in which the precipitation of magnesium hydroxide took place was of the following composition:

MgO = 2·423 g dm^{-3}; CaO = 0·604 g dm^{-3}; and the dolomite lime contained:

0·001% SiO_2; 57·15% CaO; 42·51% MgO; 0·248% Fe_2O_3; 0·093% Al_2O_3.

Mixtures of magnesium oxide of the composition listed were then prepared with 05%, 1%, 2% and 5% TiO_2 added respectively. TiO_2 reagent grade powder (Merck; Table 1) in the form of rutile was used in the experiments. Samples were homogenized by manual stirring in absolute alcohol for 30 min. The mixture was cold pressed into compacts in a hydraulic press at pressures of 62, 94, 156, 312, 469 and 625 MPa respectively.

The compacts produced were sintered at 1600°C in a gas furnace; duration of isothermal heating was τ = 25, 60 and 75 min respectively. It took approximately 2 h to reach the maximum temperature in the furnace. The samples were left to cool in the furnace. The boron content in the samples was determined potentiometrically. The density ρ and sample shrinkage during sintering were determined from the volume of water displaced from a calibrated cylinder; before sintering, they had been determined from the dimensions of the compact. The results represent an average value of a series of measurements.

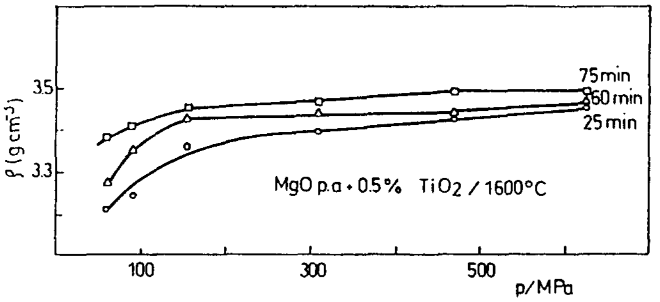

Fig. 1. The density ρ of sintered samples of reagent grade magnesium oxide with 0·5% TiO_2 added as a function of the forming pressure (p) and the duration of isothermal heating τ = 25, 60 and 75 min at 1600°C.

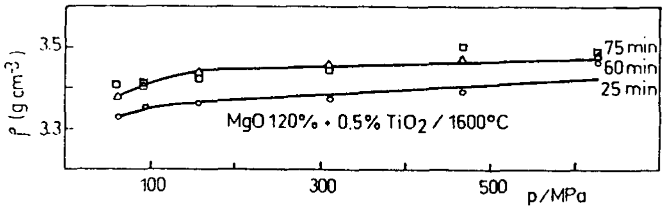

Fig. 2. The density ρ of sintered samples of magnesium oxide (120% pptn) with 0·5% TiO_2 added as a function of the forming pressure (p) and the duration of isothermal heating τ = 25, 60 and 75 min at 1600°C.

3 Results

Figures 1, 2 and 3 show experimentally obtained values for density under the operating conditions described.

Mathematical analysis was then used to determine the most appropriate functions which would describe the dependence of density ρ (z) on pressure p (x) and duration of isothermal sintering τ (y), with r = mean relative error:

$z = e^{6\cdot9009\times10^{-5}}x + 6\cdot3539 \times 10^{-4}y + 1\cdot1684$
$r = 0\cdot29\%$; for reagent grade MgO + 0·5% TiO_2
$z = e^{4\cdot4697\times10^{-5}}x + 5\cdot6341 \times 10^{-4}y + 1\cdot1875$
$r = 0\cdot13\%$; for MgO (80% pptn) + 0·5% TiO_2
$z = e^{5\cdot2016\times10^{-5}}x + 4\cdot1268 \times 10^{-4}y + 1\cdot1936$
$r = 0\cdot11\%$; for MgO (120% pptn) + 0·5% TiO_2

Other equation forms were also examined, but the ones presented here had the lowest relative error in terms of the deviation of calculated values from the experimental ones.

Total porosity in the samples examined was determined according to the standard method. The results are shown in Table 2.

Open (apparent) porosity in the samples exam-

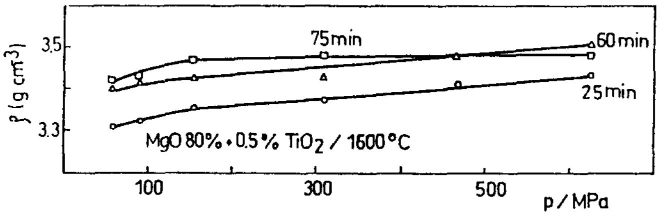

Fig. 3. The density ρ of sintered samples of magnesium oxide (80% pptn) with 0·5% TiO_2 added as a function of the forming pressure (p) and the duration of isothermal heating τ = 25, 60 and 75 min at 1600°C.

Table 2. Total porosity in sintered samples of magnesium oxide with 0·5% TiO_2 added, t = 1600°C

Sample	*τ (min)*	*p(MPa)*					
		62	*94*	*156*	*312*	*469*	*625*
Reagent grade MgO + 0·5% TiO_2	25	11·02	8·99	6·15	5·56	4·64	3·69
	60	9·35	6·61	4·23	4·15	3·86	3·41
	75	5·94	4·88	3·72	3·18	2·25	2·54
MgO (80% pptn) + 0·5% TiO_2	25	8·02	7·67	6·69	6·04	4·99	4·26
	60	5·17	4·41	4·31	4·20	2·74	1·81
	75	4·49	4·38	3·12	2·55	3·69	2·82
MgO (120% pptn) + 0·5% TiO_2	25	7·37	6·52	6·36	6·09	5·24	3·14
	60	5·62	5·16	3·95	3·16	2·95	2·79
	75	5·08	4·93	4·46	3·65	2·14	2·44

ined ranges from 0·3% to 0·7%. Accordingly, total porosity is almost identical to closed porosity.

Sample shrinkage during isothermal heating is defined by the expression

$$u = \frac{\Delta V}{V_0} - \left(\frac{\Delta V}{V_0}\right)_{\tau=0}$$

where V_0 = volume of the compact before heating started, ΔV = change in volume during heating, τ = duration of isothermal heating, $(\Delta V/V_0)_{\tau=0}$ = change in volume (%) before reaching the maximum sintering temperature.

Therefore, shrinkage (u) represents the change in volume (%) from the moment of reaching the maximum sintering temperature to the end of the process.

The relation between the shrinkage of magnesium oxide compacts and pore removal during isothermal sintering is shown in dependence on the exponent, according to the expression:

$$u = \tau^{\alpha}$$

Previous examinations[3,4] have shown that the process is well described by a function of that form. Values for the exponent α have been claimed to make it possible to draw conclusions about the pore removal mechanism in the isothermal sintering of magnesium oxide.[5–7]

Values obtained in those examinations for the exponent α, depending on the pressing pressure and the duration of isothermal sintering at 1600°C, range from 0·15 to 0·30.

Table 3 shows results obtained for the effect of TiO_2 on boron content in sintered samples in dependence on the method of obtaining magnesium oxide, for the operating conditions listed.

The results represent averages for a number of measurements. The standard deviation is $\sigma_{max} = 9{\cdot}8 \times 10^{-3}$ and $\sigma_{min} = 4{\cdot}4 \times 10^{-3}$ for MgO (80% pptn) and $\sigma_{max} = 5{\cdot}0 \times 10^{-3}$ and $\sigma_{min} = 1{\cdot}5 \times 10^{-3}$ for MgO (120% pptn). The experimental data indicate that addition of TiO_2, as well as higher temperature and longer duration of isothermal heating (1, 3, 5 h) significantly promote boron disappearance from the samples into the air.

Different behaviour patterns relative to the B_2O_3 content were noticed in magnesium oxide obtained by 80% and 120% precipitation of magnesium hydroxide in sea water; this was due to different contents of CaO in those samples.

4 Discussion

Previous papers[8–10] have established the content of dicalcium borate ($Ca_2B_2O_5$) in sintered samples by

Table 3. Effects of TiO_2 on B_3O_3 content in sintered samples at 1300°C and 1500°C, at τ = 1, 3 and 5 h respectively

Sample	*t (°C)*	*τ (h)*	*B_2O_9 (%) in MgO without additions*	*B_2O_9 (%) in MgO + 1% TiO_2*	*B_2O_9 (%) in MgO + 2% TiO_2*	*B_2O_9 (%) in MgO + 5% TiO_2*
MgO (80% pptn)	1300	1	0·193 4	0·139 5	0·078 9	0·065 2
		3	0·165 5	0·136 3	0·075 2	0·063 8
		5	0·119 2	0·085 2	0·064 5	0·058 7
	1500	1	0·126 5	0·043 4	0·039 6	0·026 4
		3	0·075 6	0·018 4	0·017 0	—
		5	0·068 9	0·017 3	0·015 9	0·013 1
MgO (120% pptn)	1300	1	0·051 2	0·042 8	0·029 3	0·016 5
		3	0·045 9	—	0·010 9	0·008 56
		5	0·037 6	0·038 4	0·009 56	0·005 34
	1500	1	0·045 3	0·043 1	0·011 6	0·006 17
		3	0·040 0	0·033 1	0·010 0	0·006 05
		5	0·031 8	0·020 4	0·005 0	0·003 51

means of the X-ray diffraction method, i.e. it has been established that during sintering B_2O_3 reacts with CaO to form $Ca_2B_2O_5$. Therefore, the higher the quantity of CaO, the more B_2O_3 retained in the sample. Therefore, during isothermal heating, the B_2O_3 content in samples of magnesium oxide obtained by 120% precipitation, containing a higher quantity of CaO (1·32%), diminishes less than is the case with magnesium oxide obtained by 80% precipitation, containing a smaller quantity of CaO (0·59%).

Addition of TiO_2 reduces the B_2O_3 content in the sintering process, as it competes for the CaO by forming calcium titanate ($CaTiO_3$).[11]

In MgO (80% pptn) a smaller quantity of TiO_2 (1%) binds almost all the CaO present, while with MgO (120% pptn) it takes 2% TiO_2 to bind the CaO present; therefore only a higher quantity of TiO_2 (5%) affects boron removal significantly.

To summarize, two reactions influence boron (B_2O_3) content reduction in the sintering process. These are:

$$2\,CaO + B_2O_3 = Ca_2B_2O_5$$
$$CaO + TiO_2 = CaTiO_3$$

The final content of B_2O_3 in the sintered samples therefore depends both on the CaO and the TiO_2 content.

A system of phenomenological equations describing the open system thermodynamics[12] was then considered, i.e.

$$J_1 = L_{11}t + L_{12}\tau \qquad (1)$$

$$J_2 = L_{21}t + L_{22}\tau \qquad (2)$$

where J, represents the percentage of boron lost and J_2 represents the percentage of CaO reacting with TiO_2.

These coefficients must meet the following requirements in the system of equations:

$$L_{11} \geq 0, \quad L_{22} \geq 0, \quad L_{12} = L_{21}$$
$$L_{11}L_{22} - L_{12}^2 = 0$$

The coefficients were calculated by a computer, using a combination of the mean values method with the least squares method.

Two examples of coefficients calculated from the experimental data are shown here: J_1 (percentage of B_2O_9 lost) and J_2 (percentage of CaO reacting with TiO_2).

(1) Magnesium oxide obtained by 80% precipitation of magnesium hydroxide with 5% of TiO_2 added; temperatures 1300°C and 1500°C; duration of isothermal sintering (τ) = 1, 3 and 5 h respectively (Tables 4 and 5).

(2) Magnesium oxide obtained by 120% precipitation of magnesium hydroxide with 5% of TiO_2 added; temperatures 1300°C and 1500°C; duration of isothermal sintering (τ) = 1, 3 and 5 h respectively (Tables 6 and 7).

After calculating the coefficients, the equations for these examples are:

$$(1)\quad J_1 = 4\cdot485\,6\,t + 5\cdot023\,9\,\tau$$
$$J_2 = 5\cdot023\,9\,t + 4\cdot356\,9\,\tau$$
$$(2)\quad J_1 = 4\cdot959\,4\,t + 5\cdot612\,9\,\tau$$
$$J_2 = 5\cdot612\,9\,t + 2\cdot691\,4\,\tau$$

where J_1 = % of B_2O_3 which disappeared, J_2 = % of CaO which reacted with TiO_2, τ = duration of isothermal sintering (h), and t = temperature (°C).

The average relative deviation errors (r) are 10·26 (for J_1) and 7·65% (for J_2) in the first case; they are 4·79% (for J_1) and 11·25% (for J_2) in the second case.

It is possible to trace the process of isothermal sintering of magnesium oxide by means of the experimental data for J_1, i.e. the percentage of B_2O_3 which was lost in the sintering process, which is of great importance for product quality, and for J_2, the percentage of CaO reacting with TiO_2, which also as described indirectly affects the content of B_2O_3.

The analysis offers the opportunity to determine which percentage of TiO_2 should be added to a sample once the CaO and B_2O_3 contents are known.

Table 4. J_1

	τ (h)		
t (°C)	1	3	5
130 0	66·29	67·01	69·70
150 0	86·35	—	93·23

Table 5. J_2

	τ (h)		
t (°C)	1	3	5
130 0	81·26	81·62	83·04
150 0	91·10	—	94·66

Table 6. J_1

t (°C)	1	3	5
130 0	70·64	84·75	90·50
150 0	89·02	89·23	93·75

Table 7. J_2

t (°C)	1	3	5
130 0	96·89	97·85	98·24
150 0	97·47	97·50	97·81

5 Conclusions

- —The properties of magnesium oxide obtained from sea water and reagent grade magnesium oxide were determined after sintering at 1600°C, with addition of 0·5% TiO_2. Density, porosity, and shrinkage and the exponent α (in τ^{α}) were determined.
- —The results achieved depended on the duration of isothermal heating and on the pressure applied in the production of compacts. Theoretical product densities were almost achieved.
- —Mathematical expressions were calculated for the dependence of density ρ on the pressing pressure and the duration of isothermal sintering.
- —The effect of TiO_2 addition to magnesium oxide on the content of B_2O_3 in samples after sintering was examined, taking into account the method of obtaining magnesium hydroxide from sea water. Two dependent reactions (those of formation of $Ca_2B_2O_5$ and of $CaTiO_3$) were analysed, according to expressions describing the open system thermodynamics.

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