

ACTIVATED SINTERING OF MAGNESIUM OXIDE OBTAINED FROM SEAWATER

AKTIVIRANO SINTRANJE MAGNEZIJEVEGA OKSIDA, DOBLJENEGA IZ MORSKE VODE

Vanja Martinac, Miroslav Labor, Meri Mirošević-Anzulović, Nedjeljka Petric

Faculty of Chemical Technology, Department of Thermodynamics, Teslina 10/V, 21000 Split, Croatia
martinac@ktf-split.hr

Prejem rokopisa – received: 2006-09-18; sprejem za objavo – accepted for publication: 2006-11-19

The process of isothermally sintering magnesium oxide obtained from seawater by substoichiometric (where precipitation of magnesium hydroxide took place with 80 % of the stoichiometric quantity of dolomite lime) and by overstoichiometric precipitation (which took place with 120 % of the stoichiometric quantity of dolomite lime) was examined, with the addition of mass fractions (1, 2 and 5) % TiO_2 , at temperatures in the range 1550–1750 °C, with (1, 3 and 5) h of soaking at the maximum temperature. The process was followed by a determination of the product density, as well as of the B_2O_3 content in the sintered samples. The results indicate that, besides favorably affecting the density of the sintered samples, the addition of TiO_2 , with increasing temperature and soaking time, also significantly reduces the B_2O_3 content in the sintered magnesium oxide obtained from seawater. A statistical analysis of the obtained data was performed with the “Statistica” package in order to obtain a model of the density (ρ) of sintered samples of magnesium oxide relative to the temperature (t), time of isothermal heating (τ), and the percentage of added TiO_2 (w).

Key words: substoichiometric precipitation, overstoichiometric precipitation, magnesium oxide from seawater, TiO_2 addition, activated sintering

Proučevan je proces izotermnoga sintranja magnezijevega oksida, dobljenega iz morske vode z nestehiometrijskim (dodatek dolomitnega apna je bil 80 % od stehiometrijske potrebne količine) in prestehiometrijskim usedanjem (z dodatkom 120 % od stehiometrijske količine dolomitnega apna) z dodatkom masnih deležev TiO_2 (1, 2 in 5) %, v temperaturnem intervalu 1550–1750 °C, v trajanju izotermnoga sintranja (1, 3 in 5) h. Proces je bil spremljan z določevanjem gostote in določevanjem vsebnosti B_2O_3 v sintranih vzorcih. Rezultati preučevanja kažejo, da dodatek TiO_2 pozitivno deluje na gostoto sintranih vzorcev, s povečanjem temperature in obdobjem izotermnoga sintranja pa občutno vpliva tudi na zmanjšanje B_2O_3 v sintranem magnezijevem oksidu, dobljenem iz morske vode. Da bi dobili model odvisnosti gostote (ρ) sintranih vzorcev magnezijevega oksida od temperature (t) in časa izotermnoga sinteriranja (τ), ter deleža dodanega TiO_2 (w) je bila narejena statistična obdelava dobljenih podatkov z uporabo paketa “Statistica”.

Ključne besede: nestehiometrijsko usedanje, prestehiometrijsko usedanje, magnezijev oksid iz morske vode, TiO_2 dodatek, aktivirano sintranje

1 INTRODUCTION

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

The purpose of this work was to examine the effect of TiO_2 additions on the properties (density and the B_2O_3

content) of sintered samples of magnesium oxide obtained from seawater at elevated temperatures. The examinations described were carried out in order to obtain a model of the density of sintered samples of magnesium oxide relative to the temperature and the time of isothermal heating and the percent of added TiO_2 .

2 EXPERIMENTAL

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

$$\text{MgO} = 2.124 \text{ g dm}^{-3}; \quad \text{CaO} = 0.5573 \text{ g dm}^{-3}$$

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

$$\text{CaO} = 57.17 \% \quad \text{MgO} = 42.27 \%$$

$$\text{SiO}_2 = 0.099 \% \quad \text{Al}_2\text{O}_3 = 0.051 \%$$

$$\text{Fe}_2\text{O}_3 = 0.079 \%$$

The experimental procedure used to obtain magnesium hydroxide from seawater was similar to that employed in our previous investigations^{8,9}. The sedimentation rate was increased by the addition of the

optimum amount of the anionic 818A flocculent (polyacrylamide), produced by the Dutch firm Hercules. The experimental procedure used to determine the optimum quantity of the anionic 818A flocculent has been described in a previous study¹¹. The magnesium hydroxide obtained from seawater was dried at 105 °C and then calcined at 950 °C. The composition of the magnesium oxide obtained by precipitation with 80 % of the stoichiometric quantity of dolomite lime was (mass fractions, w/w): 98.76 % MgO, 0.88 % CaO and 0.1934 % B₂O₃.

The composition of the magnesium oxide obtained by precipitation with 120 % of the stoichiometric quantity of dolomite lime was (mass fractions, w/w): 97.92 % MgO, 1.45 % CaO and 0.1055 % B₂O₃.

Mixtures of magnesium oxide were then prepared with the addition of a mass fraction of 1 %, 2 % and 5 % TiO₂. The doping oxide used was analytical reagent grade titanium (TiO₂ p. a.) in the rutile form, produced by Merck. The samples were homogenized by manual stirring in absolute ethanol (C₆H₅O p. a.). 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, made by a French firm Mecker (type 553), with a zirconium (IV)-oxide lining, at 1550 °C, 1650 °C and 1750 °C with 1h, 3h and 5h of soaking at the maximum temperature.

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 sample density after sintering (ρ) was determined from the volume of water displaced from a calibrated cylinder. The boron content in the magnesium oxide samples examined was determined potentiometrically. The variation coefficient for the method used was ± 1 %¹². The results shown represent the average of a number of measurements.

3 RESULTS AND DISCUSSION

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

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

Tabela 1: Gostota (ρ) za sintrane vzorce magnezijevega oksida (80-odstotno usedanje) z masnimi deleži TiO₂ in 1, 2 in 5 %, in brez dodatka TiO₂, $t = 1550$ °C, 1650 °C, 1750 °C, $\tau = 1$ h, 3 h, 5 h, $p = 625$ MPa

| sample | $t/^\circ\text{C}$ | τ/h | $\rho/(\text{g cm}^{-3})$ | | | |
|-----------|--------------------|-----------------|--------------------------------|--------|--------|--------|
| | | | TiO ₂ addition, w/w | | | |
| | | | no sint. aid | 1 % | 2 % | 5 % |
| 80 % pptn | 1550 | 1 | 3.2401 | 3.2691 | 3.3243 | 3.3361 |
| | | 3 | 3.3181 | 3.3498 | 3.3439 | 3.3744 |
| | | 5 | 3.3514 | 3.3643 | 3.3953 | 3.4017 |
| | 1650 | 1 | 3.3463 | 3.3798 | 3.4115 | 3.4257 |
| | | 3 | 3.3513 | 3.3803 | 3.4245 | 3.4351 |
| | | 5 | 3.4230 | 3.4128 | 3.4385 | 3.4510 |
| | 1750 | 1 | 3.3522 | 3.4007 | 3.4199 | 3.4391 |
| | | 3 | 3.3660 | 3.4593 | 3.4513 | 3.4719 |
| | | 5 | 3.4244 | 3.4881 | 3.4933 | 3.5289 |

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

Tabela 2: Gostota (ρ) za sintrane vzorce magnezijevega oksida (120-odstotno usedanje) z masnimi deleži TiO₂ in 1, 2 in 5 %, in brez dodatka TiO₂, $t = 1550$ °C, 1650 °C, 1750 °C, $\tau = 1$ h, 3 h, 5 h, $p = 625$ MPa

| sample | $t/^\circ\text{C}$ | τ/h | $\rho/(\text{g cm}^{-3})$ | | | |
|------------|--------------------|-----------------|--------------------------------|--------|--------|--------|
| | | | TiO ₂ addition, w/w | | | |
| | | | no sint. aid | 1 % | 2 % | 5 % |
| 120 % pptn | 1550 | 1 | 3.2880 | 3.3088 | 3.3980 | 3.4036 |
| | | 3 | 3.3179 | 3.3557 | 3.4156 | 3.4383 |
| | | 5 | 3.3739 | 3.3887 | 3.4409 | 3.4619 |
| | 1650 | 1 | 3.3350 | 3.3726 | 3.4253 | 3.4357 |
| | | 3 | 3.3570 | 3.4029 | 3.4378 | 3.4603 |
| | | 5 | 3.4244 | 3.4412 | 3.4662 | 3.5047 |
| | 1750 | 1 | 3.3711 | 3.4033 | 3.4292 | 3.4473 |
| | | 3 | 3.4153 | 3.4516 | 3.4860 | 3.5180 |
| | | 5 | 3.4591 | 3.4786 | 3.5018 | 3.5434 |

is formed between the particles of compacted powder, the porosity is eliminated, and the whole system shrinks¹³⁻¹⁵. **Tables 3 and 4** show the results of the examination of the effect of TiO₂ on the boron content in the sintered magnesium oxide samples (80 % and 120 % precipitation) for the operating conditions described. The results indicate that the TiO₂ addition significantly influences the reduction of the B₂O₃ content in the process of the isothermal sintering of magnesium oxide from seawater, even at higher temperatures. The different behavior of the magnesium oxide obtained by 80 % from that obtained by 120 % precipitation of magnesium hydroxide in seawater is due to the different contents of CaO in these samples. CaO retains the B₂O₃ in the samples during sintering. With MgO (120 % precipitation) the CaO content is much higher ($w = 1.45$ %) than with MgO (80 % precipitation) ($w = 0.88$ %),

Table 3: Effect of TiO₂ on B₂O₃ content in the sintered magnesium oxide samples (80 % precipitation) at $t = 1550\text{ }^{\circ}\text{C}$, $1650\text{ }^{\circ}\text{C}$, $1750\text{ }^{\circ}\text{C}$, $\tau = 1\text{ h}$, 3 h , 5 h , $p = 625\text{ MPa}$

Tabela 3: Vpliv TiO₂ na vsebnost B₂O₃ v sintranih vzorcih magnezijevega oksida (80-odstotno usedanje) pri $t = 1550\text{ }^{\circ}\text{C}$, $1650\text{ }^{\circ}\text{C}$, $1750\text{ }^{\circ}\text{C}$, $\tau = 1\text{ h}$, 3 h , 5 h , $p = 625\text{ MPa}$

| sample | $t/^{\circ}\text{C}$ | τ/h | B ₂ O ₃ , w/% | | | |
|-----------|----------------------|-----------------|-------------------------------------|--------|--------|--------|
| | | | TiO ₂ addition, w/% | | | |
| | | | no sint. aid | 1 % | 2 % | 5 % |
| 80 % pptn | 1550 | 1 | 0.1894 | 0.1249 | 0.0913 | 0.0245 |
| | | 3 | 0.1337 | 0.1075 | 0.0193 | 0.0174 |
| | | 5 | 0.0759 | 0.0637 | 0.0145 | 0.0132 |
| | 1650 | 1 | 0.1445 | 0.0750 | 0.0272 | 0.0216 |
| | | 3 | 0.1020 | 0.0640 | 0.0161 | 0.0096 |
| | | 5 | 0.0589 | 0.0257 | 0.0138 | 0.0085 |
| | 1750 | 1 | 0.0862 | 0.0594 | 0.0193 | 0.0158 |
| | | 3 | 0.0415 | 0.0261 | 0.0116 | 0.0074 |
| | | 5 | 0.0319 | 0.0126 | 0.0090 | 0.0055 |

and favors the Ca₂B₂O₅ formation reaction. In a previous paper¹⁶ the X-ray diffraction method was used to prove the content of di-calcium borate (Ca₂B₂O₅) in sintered samples of magnesium oxide from seawater. Therefore, in the process of sintering, B₂O₃ reacts with CaO to form Ca₂B₂O₅. In papers¹⁷⁻²⁰ the X-ray diffraction method and EDAX analysis have helped determine that during the sintering process the added TiO₂ reacts with CaO from the solid MgO-CaO solution and forms calcium titanate CaTiO₃. Thus, TiO₂ binds a part of the CaO in the CaTiO₃ and as a result reduces the content of CaO that reacts with B₂O₃. In this way a smaller quantity of Ca₂B₂O₅ remains in the sintered sample, i.e., a higher quantity of B₂O₃ evaporates.

With MgO (120 % precipitation) there is an excess of CaO, which favors the formation of Ca₂B₂O₅, while with MgO (80 % precipitation) a larger part of the B₂O₃ evaporates from the sample into the air during sintering. A positive effect of the TiO₂ addition on the reduction of the B₂O₃ content in the magnesium oxide obtained from seawater makes it possible to achieve a high-purity product, because the hot-strength properties of certain refractory products are significantly affected by their boron content.

The results shown in **Tables 1 and 2** have also been considered in a regression analysis. The "Statistica" package was used to analyze statistically the data obtained, in order to obtain a model of the density of the sintered samples of magnesium oxide relative to the temperature (t), the time of isothermal sintering (τ), and the mass fraction of TiO₂ added (w).

A model of multiple regression has been proposed, $\rho = \beta_0 + \beta_1 t + \beta_2 \tau + \beta_3 \ln(w+1) + \varepsilon$ for MgO samples (80 % precipitation) and for MgO samples (120 % precipitation), where ρ is the density (g cm^{-3}), t is the temperature ($^{\circ}\text{C}$), τ is the time of isothermal sintering (h), w is the mass fraction (%) of added TiO₂, β_0 , β_1 , β_2 , β_3 are

unknown coefficients, and ε is the random error in the model.

Table 4: Effect of TiO₂ on B₂O₃ content in the sintered magnesium oxide samples (120 % precipitation) at $t = 1550\text{ }^{\circ}\text{C}$, $1650\text{ }^{\circ}\text{C}$, $1750\text{ }^{\circ}\text{C}$, $\tau = 1\text{ h}$, 3 h , 5 h , $p = 625\text{ MPa}$

Tabela 4: Vpliv TiO₂ na vsebnost B₂O₃ v sintranih vzorcih magnezijevega oksida (120-odstotno usedanje) pri $t = 1550\text{ }^{\circ}\text{C}$, $1650\text{ }^{\circ}\text{C}$, $1750\text{ }^{\circ}\text{C}$, $\tau = 1\text{ h}$, 3 h , 5 h , $p = 625\text{ MPa}$

| sample | $t/^{\circ}\text{C}$ | τ/h | B ₂ O ₃ , w/% | | | |
|------------|----------------------|-----------------|-------------------------------------|--------|--------|--------|
| | | | TiO ₂ addition, w/% | | | |
| | | | no sint. aid | 1 % | 2 % | 5 % |
| 120 % pptn | 1550 | 1 | 0.0705 | 0.0618 | 0.0360 | 0.0222 |
| | | 3 | 0.0582 | 0.0354 | 0.0264 | 0.0119 |
| | | 5 | 0.0312 | 0.0270 | 0.0245 | 0.0058 |
| | 1650 | 1 | 0.0592 | 0.0405 | 0.0331 | 0.0148 |
| | | 3 | 0.0315 | 0.0286 | 0.0254 | 0.0068 |
| | | 5 | 0.0180 | 0.0171 | 0.0106 | 0.0055 |
| | 1750 | 1 | 0.0331 | 0.0312 | 0.0216 | 0.0093 |
| | | 3 | 0.0177 | 0.0119 | 0.0106 | 0.0046 |
| | | 5 | 0.0148 | 0.0100 | 0.0084 | 0.0032 |

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

Tabela 5: Matrica korelacije za vzorce MgO (80 – odstotno usedanje)

| variable | correlations (MgO (80 % pptn) samples) | | | |
|------------------------------------|----------------------------------------|-----------------|--------------------------------|------------------------------------|
| | $t/^{\circ}\text{C}$ | τ/h | TiO ₂ addition, w/% | density, $\rho/(\text{g cm}^{-3})$ |
| $t/^{\circ}\text{C}$ | 1.00 | 0.00 | -0.00 | 0.69 |
| τ/h | 0.00 | 1.00 | -0.00 | 0.46 |
| TiO ₂ addition, w/% | -0.00 | -0.00 | 1.00 | 0.43 |
| density, $\rho/(\text{g cm}^{-3})$ | 0.69 | 0.46 | 0.43 | 1.00 |

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

Tabela 6: Matrica korelacije za vzorce MgO (120 – odstotno usedanje)

| variable | correlations (MgO (120 % pptn) samples) | | | |
|------------------------------------|-----------------------------------------|-----------------|--------------------------------|------------------------------------|
| | $t/^{\circ}\text{C}$ | τ/h | TiO ₂ addition, w/% | density, $\rho/(\text{g cm}^{-3})$ |
| $t/^{\circ}\text{C}$ | 1.00 | 0.00 | -0.00 | 0.53 |
| τ/h | 0.00 | 1.00 | -0.00 | 0.51 |
| TiO ₂ addition, w/% | -0.00 | -0.00 | 1.00 | 0.60 |
| density, $\rho/(\text{g cm}^{-3})$ | 0.53 | 0.51 | 0.60 | 1.00 |

Tables 5 and 6 show the correlation matrices for the examined samples. The results indicate that there is no correlation between the independent variables (temperature t , time τ and percentage of addition of TiO₂).

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

The estimate for the regression function for MgO (120 % precipitation) is: $\hat{\rho} = 2.686 + 0.000382 T + 0.0181 \tau + 0.0567 \ln(w + 1)$ where $s = 0.01413$; $R^2 = 0.9433$; $F(3, 104) = 576.8233$; $p = 0.00$

The regression functions and the regression coefficients are significant at the level of $p = 0.00$ in both models. The statistical analysis indicates that these models are useful for an estimation of the density of the samples examined.

4 CONCLUSIONS

The statistical analysis using the Statistica package indicates that the proposed models are useful and acceptable for an estimation of the density of the sintered magnesium oxide samples relative to the temperature (t), the time of the isothermal heating (τ), and the percent of added TiO_2 (w).

The favorable effect of the TiO_2 addition on the reduction of the B_2O_3 content in the sintered magnesium oxide obtained from seawater is due to two interdependent reactions of the formation of $\text{Ca}_2\text{B}_2\text{O}_5$ and CaTiO_3 , which lead to a reduction in the B_2O_3 content during sintering.

5 LITERATURE

- ¹ Shand M. A., *The Chemistry and Technology of Magnesia*, Willey Interscience, N.York, 2006
- ² Frith M., Buttrey T., Strawbridge I., *Brit. Ceram. Trans.*, 97 (1998), 29
- ³ Sims C., *Industr. Minerals*, 7 (1997), 21
- ⁴ Gilpin W. C., Heasman N., *Chem. Ind.*, 16 (1977), 567
- ⁵ Heasman N., *Gas Wärme International*, 28 (1979), 392
- ⁶ Rabadžhieva D., Ivanova K., Balarev Hr., Trendafelov D., *Žurnal priklačnoji himii*, 70 (1997), 375
- ⁷ Bonney O. V., U. S. Patent 43 148 85 (to Amstar Corporation, New York) 9 Feb. 1982, *Chem. Abstr.* 96 (1982), 125549
- ⁸ Petric B., Petric N., *Ing. Eng. Chem. Des. Dev.*, 19 (1980), 329
- ⁹ Martinac V., Labor M., Petric N., *Mater. Chem. Phys.*, 46 (1996), 23
- ¹⁰ Brown E. et al., *Seawater: Its composition, properties and behaviour*, Butterworth Heinemann in association with The Open University, Walton Hall, Milton Keynes, 2nd Ed., 1997, 86
- ¹¹ Petric N., Martinac V., Labor M., Jurin O., *Kovine zlit. tehnol.*, 33 (1999), 475
- ¹² Culkin F., *The major constituents of seawater*, in: *Chemical Oceanography*, Ed. by Riley J. P., Skirrow G., Vol.1, Academic Press, London, 1975, 136–151
- ¹³ German R. M., *Sintering theory and practice*, Wiley, New York, 1996
- ¹⁴ Kang Suk-Joong L., *Sintering*, Elsevier, 2005
- ¹⁵ Lee Y. B., Park H. C., OH K. D., *J. Mat. Sci.*, 33 (1998), 4321
- ¹⁶ Petric N., Petric B., Tkalčec E., Martinac V., Bogdanić N., Mirošević-Anzulović M., *Sci. Sinter.*, 19 (1987), 81
- ¹⁷ Chaudhuri M. N., Kumar A., Bhadra A. K., Banerjee G., Sarkar S. L., *Ceram. Bull.*, 71 (1992), 345
- ¹⁸ Chaudhuri M. N., Kumar A., Bhadra A. K., Banerjee G., *Interceram.*, 39 (1990), 26
- ¹⁹ Čosić M., Pavlovski B., Tkalčec E., *Sci. Sinter.*, 21 (1989), 161
- ²⁰ Čeh M., Kolar D., *J. Mater. Sci.*, 29 (1994), 6295