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Effect of TiO_2 on properties of magnesium oxide obtained from seawater

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The effect has been examined of TiO_2 on B_2O_3 content in sintered magnesium oxide samples obtained by precipitation of magnesium hydroxide in seawater with 80 or 120% of the stoichiometrical quantity of the precipitation agent, i.e. the effect of TiO_2 on product properties has been examined. Coefficients were calculated for dependent reactions of $Ca_2B_2O_5$ and $CaTiO_3$ formation.

1. Introduction

It has been established that TiO_2 affects properties of magnesium oxide obtained from seawater; even a small addition of 0.5% TiO_2 significantly increases product density at 1300 °C [1].

This paper reports on the effects of the addition of 1, 2 and 5% TiO_2 on B_2O_3 content in the product.

The magnesium oxide used had been obtained from seawater, either by non-stoichiometrical overstoichiometrical precipitation, or (precipitation of magnesium hydroxide with 80 and 120% of the stoichiometrical quantity of dolomite lime [2].

2. Experimental procedure

Magnesium hydroxide obtained from seawater was calcined at 950 °C. The magnesium oxide obtained was of the following composition

For magnesium oxide (80% p.p.tn)

$$MgO = 99.2\% \quad CaO = 0.59\%$$

$$B_2O_3 = 0.1934\%$$

For magnesium oxide (120% p.p.tn)

$$MgO = 98.25\% \quad CaO = 1.32\%$$

$$B_2O_3 = 0.0562\%$$

Seawater, in which the magnesium hydroxide was precipitated, was of the following composition

$$MgO = 2.423\ g\,dm^{-3} \quad CaO = 0.604\ g\,dm^{-3}$$

and the composition of dolomite used was as follows

$$MgO = 42.51\% \quad CaO = 57.15\%$$

$$Fe_2O_3 = 0.248\% \quad Al_2O_3 = 0.093\%$$

$$SiO_2 = 0.001\%$$

Mixtures of magnesium oxide were prepared in the above composition, with 1, 2 and 5% TiO_2, respectively. TiO_2 p.a. powder Merck was used in the form of rutile. Samples were homogenized by manual stirring in absolute alcohol. Compacts were made in an hydraulic press at pressures of 62, 94, 156, 312, 469 and 625 MPa, respectively. The compacts were then sintered at 1300 and 1500 °C in an electric furnace: the duration of isothermal sintering was 1, 3 and 5 h, respectively. It took approximately 2 h to reach the maximum temperature in the furnace. Samples were left to cool in the furnace. The boron content in the samples was determined potentiometrically.

Table I shows the results obtained of the effect of TiO_2 on the boron content in samples sintered, relative to the method of obtaining magnesium oxide, for the operating conditions described above.

The results shown represent an average of a number of measurements. The standard deviation, σ, for MgO (80% p.p.tn) was

$$\sigma_{max} = 9.8\ 10^{-3} \quad \text{and} \quad \sigma_{min} = 4.4\ 10^{-3}$$

The standard deviation for MgO (120% p.p.tn) was

$$\sigma_{max} = 5.0\ 10^{-3} \quad \text{and} \quad \sigma_{min} = 1.5\ 10^{-3}$$

3. Results and discussion

Experimental data indicate that addition of TiO_2, as well as temperature and duration of isothermal heating, greatly affects the removal of boron from the sample into the air, i.e. TiO_2 reduces the B_2O_3 content during isothermal sintering of magnesium oxide.

Different behavioural patterns relative to B_2O_3 content are encountered in magnesium oxide obtained by means of 80% precipitation compared to that obtained by means of 120% precipitation of magnesium hydroxide in seawater; this is due to different CaO contents of the samples.

Earlier papers have determined the dicalcium borate ($Ca_2B_2O_5$) content in sintered samples by means of X-ray diffraction: it has been found that during sintering B_2O_3 reacts with CaO to form $Ca_2B_2O_5$. Therefore, the higher the CaO content, the more B_2O_3 is retained in the sample, i.e. sintered samples contain a greater quantity of B_2O_3. Thus, in MgO samples (120% p.p.tn) containing a greater quantity of CaO (1.32%), the B_2O_3 content is reduced less during

0022–2461

TABLE I Boron contents of sintered samples

Samples	T (°C)	t (h)	% B_2O_3 in MgO without admixture	% B_2O_3 in MgO + 1% TiO_2	% B_2O_3 in MgO + 2% TiO_2	% B_2O_3 in MgO + 5% TiO_2
MgO (80% p.p.tn)	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
MgO (120% p.p.tn)	1300	1	0.0512	0.0428	0.0293	0.0165
		3	0.0459	–	0.0109	0.00856
		5	0.0376	0.0384	0.00956	0.00534
	1500	1	0.0453	0.0431	0.0116	0.00617
		3	0.0400	0.0331	0.0100	0.00605
		5	0.0318	0.0204	0.0050	0.00351

isothermal sintering than is the case with MgO (80% p.p.tn) containing less CaO (0.59%).

With MgO (120% p.p.tn) CaO is in excess, and favours $Ca_2B_2O_5$ formation; in MgO (80% p.p.tn) a greater quantity of boron is removed from the sample.

Addition of TiO_2 reduces the B_2O_3 content during sintering because a part of the CaO is bound in calcium titanate ($CaTiO_3$) [3].

In MgO (80% p.p.tn) a smaller quantity of TiO_2 (1%) binds almost all of CaO present, while in MgO (120% p.p.tn) it takes approximately 2% TiO_2 to bind all of CaO present, so that only greater TiO_2 addition (5%) affects boron removal to a greater degree.

Thus, there are two reactions which lead to a decrease in B_2O_3 content during sintering

$$2CaO + B_2O_3 = Ca_2B_2O_5$$

$$CaO + TiO_2 = CaTiO_3$$

The two reactions should be analysed together, as the final B_2O_3 content in sintered samples depends on the CaO and TiO_2 contents.

An equation system analysed in open system thermodynamics was then examined [4, 5]

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

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

These type of linearity laws are called phenomenological dependencies. Coefficients L_{ik} are so-called phenomenological coefficients characterizing the interdependence of two irreversible processes, "i" and "k".

The above coefficients in the system of equations must meet the following conditions

$$L_{11} \geq 0, L_{22} \geq 0, L_{12} = L_{21}$$

$$L_{11}L_{22} - L_{12}^2 = 0$$

J_1 is the per cent of B_2O_3 removed during sintering: it is calculated from experimental data on the B_2O_3 content of sintered samples and from the B_2O_3 content of calcined magnesium oxide, i.e. in the sample before sintering. J_2 is the per cent CaO which reacted with TiO_2; τ the duration of isothermal heating; and t the temperature at 10^{-2} (°C).

Table II presents the values for J_1 and J_2 at 80% p.p.tn, and Table III the values for J_1 and J_2 at 120% p.p.tn.

Coefficients L_{11}, L_{12}, and L_{22} in Equations 1 and 2 were computationally calculated by means of a combination of the mean value method and the least squares method.

TABLE II Values of J_1 and J_2 during sintering at 80% p.p.tn

J_1				J_2			
$t\backslash\tau$	1	3	5	$t\backslash\tau$	1	3	5
For 1% TiO_2							
13	27.87	–	55.95	13	61.19	–	76.46
15	77.56	90.49	91.05	15	85.54	93.25	93.54
For 2% TiO_2							
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
For 5% TiO_2							
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 III The values of J_1 and J_2 at 120% p.p.tn

J_1				J_2			
$t\backslash\tau$	1	3	5	$t\backslash\tau$	1	3	5
For 1% TiO_2							
13	23.81	–	31.69	13	52.52	–	52.52
15	23.31	41.16	63.70	15	93.06	94.26	95.76
For 2% TiO_2							
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
For 5% TiO_2							
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 IV 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 80% and 120% precipitation, respectively

For 80% p.p.tn	For 120% p.p.tn
For 1% 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% 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% 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 IV shows samples of magnesium oxide obtained from seawater by precipitation with 80% or 120% of the stoichiometrical quantity of dolomite lime.

Thus, the experimental data J_1, i.e. the percent of B_2O_3 "removed" during the 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 coefficient values L_{11}, L_{12} and L_{22} calculated depend on the quantity of TiO_2 added. Therefore, the dependence of the coefficient values L_{11}, L_{12} and L_{22} on per cent TiO_2 was calculated. This dependence, Y, can be expressed by the following equation

$$Y = Ax^2 + Bx + C$$

where

Y = the phenomenological coefficients L_{11}, L_{12} and L_{22}

x = the percent JiO_2

A,B,C = constants

The coefficients were calculated by the least squares method, and are shown by the equations

For 80% p.p.tn

$$L_{11} = -0.0833x^2 + 0.6659x + 3.3635$$

$$L_{12} = -0.0614x^2 + 0.4697x + 4.2106$$

$$L_{22} = 0.0310x^2 - 0.3003x + 5.0833$$

For 120% p.p.tn

$$L_{11} = -0.7692x^2 + 5.4010x - 2.8164$$

$$L_{12} = -0.3293x^2 + 2.4333x + 1.6803$$

$$L_{22} = 0.1354x^2 - 1.6347x + 7.4791$$

where x is the per cent TiO_2.

From these equations for dependence of L on x, coefficients L_{11}, L_{12} and L_{22} can be calculated for other values of x in the range 1–5% TiO_2 added.

As CaO reacts simultaneously with B_2O_3 and with TiO_2, the two reactions are interrelated, and it was a matter of interest to calculate coefficients for Equations 1 and 2 shown and their dependence on the quantity of TiO_2 added.

4. Conclusions

1. The effect of TiO_2 addition on the B_2O_3 content of sintered samples, i.e. on product properties, has been examined.
2. 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% p.p.tn) a lower quantity of TiO_2 (1%) binds almost all the CaO present (which has not reacted with B_2O_3).
3. In magnesium oxide (120% p.p.tn) it takes 2% TiO_2 to bind all the CaO present (which has not reacted), so that only a greater quantity (5%) of TiO_2 affects boron removal during sintering to a greater degree.
4. Two dependent reactions were analysed, these of formation of $Ca_2B_2O_5$ and $CaTiO_3$, respectively.
5. Phenomenological coefficients L_{11}, L_{12} and L_{22} were calculated; they describe the mutual influence of the two irreversible processes.

References

1. N. PETRIC, B. PETRIC, V. MARTINAC and M. MIROŠEVIĆ-AZULOVIĆ, in "Science of Sintering: New Directions for Materials Processing and Microstructural Control", edited by D. P. Uskoković, N. Palmour III and R. M. Springs (Plenum Press, New York, 1989) pp. 565–572.
2. B. PETRIC and N. PETRIC, *Ind. Eng. Chem. Process Des. Dev.* **19** (1980) 329.
3. M. ČOSIĆ, B. PAVLOVSKI and E. TKALČEC, *Sci. Sinter.* **21** (1989) 101.
4. I. PRIGOZIN, "An Introduction to Thermodynamics of Irreversible Processes" (Graotevinska Knjiga, Belgrade, 1977)
5. R. HAASE, "Thermodynamics of Irreversible Processes" Jzdateljstro "MIR", Moscow, 1987)
6. H. M. RICHARDSON, M. LESTER, F. T. PALIN and P. T. A. HODSON, (General reference) *Trans. Brit. Ceram. Soc.* **68** (1969) 29.

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