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SINTERING OF HIGH-PURITY MAGNESIUM OXIDE

The sintering of magnesium oxide of a high degree of purity—such as spectrally pure magnesium oxide—differs substantially from the sintering of the less pure grades of this oxide that have been studied earlier ([1]). A characteristic feature of the behavior of high-purity MgO is the attainment of a high relative density, exceeding 95% of the theoretical value, already at low firing temperatures and without strong recrystallization. This phenomenon is of both theoretical and practical interest, since such high-density and high-purity magnesium-oxide ceramics may find application in such cases, for example, as the melting of especially pure metals. It is also significant that, in its electrical-insulating properties at high temperatures, such ceramics do not differ from pure MgO single crystals ([2]). In the present work we studied the comparative activity of high-purity magnesium oxide obtained from hydroxide and carbonate, the influence of the calcination temperature of these compounds and of the firing temperature of the ceramics, as well as the kinetics and mechanism of sintering.

Experimental procedure

Magnesium oxide was prepared in an active form by calcining spectrally pure magnesium carbonate or hydroxide, the latter obtained by precipitation with ammonia from a 20% aqueous solution of spectrally pure magnesium chloride. In the latter case, after the introduction of a stoichiometric amount of 25% ammonia, the precipitate that formed was allowed to stand for 24 hours, filtered off, thoroughly washed, and dried at 110°. The yield of hydroxide under these conditions was 50%. After calcination at the required temperature for two hours, specimens were pressed from the powders without any binder, in the form of disks 11 mm in diameter and 2–3 mm thick or bars of size $3 \times 3 \times 25$ mm, and were fired in a silite furnace or in a furnace with a rhodium heating winding. The sintering of the specimens was monitored by the magnitude of their bulk density (by hydrostatic weighing in toluene with an accuracy of 0.1 mg) and, when required, by the shrinkage of the specimens and their microstructure. Every possible precaution was taken against accidental contamination of the specimens during their preparation and firing. Triply distilled water was used for preparing solutions and washing precipitates, and the firing of specimens was carried out on platinum supports. Steel chromium-plated dies were used for pressing. Control spectral analyses show that, when specimens are obtained by this procedure, no significant contamination occurs; however, when some batches of ammonia were used, traces (on the order of 0.001%) of calcium or silicon impurities were observed.

Results and discussion

Influence of the starting compound and calcination temperature

As the study of the sinterability of less pure types of magnesium oxide, obtained by thermal decomposition of hydroxide, carbonates, oxalate, and other compounds, has shown, their activity is to a signifi-

depends to a significant extent on the type of these starting compounds, and is especially high during the decomposition of hydroxide and carbonate ($^{3-4}$). In connection with this, a study was made of the comparative activity of spectrally pure magnesium oxide obtained from these two compounds. These experiments were carried out by the method described above. The results of measurements of the density of the specimens after pressing (by direct measurement of their volume and weight), the bulk density, and the shrinkage of the specimens in diameter after firing for two hours at the indicated temperatures are given in Table 1.

As follows from the value of the bulk density of the specimens after firing at 1400°, at one and the same calcination temperature the activity of magnesium oxide obtained from both of these compounds is approximately the same. At the same time, the density of compacts made from calcined magnesium carbonate is considerably lower, and the shrinkage during firing is almost twice as high as for MgO from hydroxide. Thus, other conditions being equal, it is more advantageous to use the latter. In the subsequent work only magnesium oxide obtained from hydroxide was used.

Table 1

Sintering of magnesium oxide obtained by thermal decomposition of $Mg(OH)_2$ *and carbonate*

Calcination temperature, °C	Density of compacts, g/cm^3	Firing at 1400°: γ, g/cm^3	Firing at 1400°: $\Delta D/D_0$, %	Firing at 1600°: γ, g/cm^3	Firing at 1600°: $\Delta D/D_0$, %
Decomposition of $Mg(OH)_2$	**Decomposition of** $Mg(OH)_2$	**Decomposition of** $Mg(OH)_2$	**Decomposition of** $Mg(OH)_2$	**Decomposition of** $Mg(OH)_2$	**Decomposition of** $Mg(OH)_2$
400	2.0	2.88	12	3.46	15
600	2.1	2.82	10	3.55	14
800	1.9	2.57	10	3.51	16

Calcination temperature, °C	Density of compacts, g/cm^3	Firing at 1400°: γ, g/cm^3	Firing at 1400°: $\Delta D/D_0$, %	Firing at 1600°: γ, g/cm^3	Firing at 1600°: $\Delta D/D_0$, %
1000	1.9	2.32	7	2.85	12
Decomposition of carbonate	**Decomposition of carbonate**	**Decomposition of carbonate**	**Decomposition of carbonate**	**Decomposition of carbonate**	**Decomposition of carbonate**
600	1.4	2.75	20	–	–
800	1.5	2.60	16	–	–
1000	1.5	2.25	12	–	–
1200	1.6	1.84	5	–	–
1400	1.6	1.79	3	–	–

From the data of Table 1 it is evident that the optimum calcination temperature of magnesium hydroxide is close to 600°. Under these conditions of preliminary calcination, the bulk density of the specimens after firing at 1600° proves to be maximal, and their shrinkage minimal. Calcination for two hours at 400° is insufficient for complete decomposition of the hydroxide, while after calcination at 1000° the activity of the magnesium oxide proves to be too low.

Effect of firing temperature. The dependence of the bulk density of specimens made of MgO obtained by calcining the hydroxide at 600, 800, and 1000°, on their firing temperature with a holding time of two hours is shown in Fig. 1. Sintering of these specimens, depending on the calcination temperature, begins at 1100° and below, changes slowly with further increase in firing temperature up to 1400—1500°, and then rapidly accelerates.

At all firing temperatures, the densest specimens are those made from material calcined at 600°, and at 1600° their sintering is already completed and the density approaches the theoretical value (3.60 g/cm^3). (In the course of other series of experiments it was found that, at a calcination temperature of 500—600°, the bulk density of the specimens after firing at 1500° is on the average 3.44 g/cm^3, and at 1600°, 3.56 g/cm^3, or 99% of the theoretically possible value.)

For comparison it should be noted that, according to data available in the literature, when less pure active magnesium oxide is sintered, the bulk density of the ceramic after firing at 1600° has never exceeded 3.40 g/cm^3 (95% of the theoretical value), and a higher density could be obtained only by hot pressing.

The grain size in specimens made from material calcined at 600°, after firing at 1400°, does not exceed 1 μ; at 1500° it is about 3 μ, and at 1600°, 10 μ. Thus, sintering at these temperatures is not accompanied by significant collective recrystallization.

Kinetics and mechanism of sintering. As is known, the kinetics of sintering depends on which of the possible mechanisms of mass transport takes place in a given system, and in general form can be described by the relation (5, 6)

$$\Delta l/l_0 = kt^n \tag{1}$$

or, for a small amount of shrinkage, for which this relation is valid and which pertains to the initial stages of sintering,

$$\gamma = k't^n. \tag{2}$$

The value of the exponent n in these relations is 0.5 for bulk diffusion of matter, 1 for viscous flow under the action of surface-tension forces, etc. The value of n can be found experimentally from the dependence of the bulk density or the shrinkage of specimens on their sintering time at constant temperature.

Such a dependence of the density of specimens of high-purity magnesium oxide on sintering time is shown in Fig. 2. In the course of these experiments, specimens pressed from a mass calcined at 800° were placed for the required period of time in a furnace that had been preheated to the corresponding temperature, and then their bulk density and shrinkage were measured. It was found that the results of bulk-density measurements were reproduced considerably better than the shrinkage measurements, and the former are presented here. The time required to heat the specimens to the equilibrium temperature was 1-1.5 min and was not taken into account.

[Figure 1 and Figure 2]

Fig. 1. Effect of firing temperature on the sintering of magnesium oxide obtained from hydroxide. Calcination temperature: 1 –600°, 2 –800°, 3 – 1000°.

Fig. 2. Sintering kinetics of active magnesium oxide. Calcination temperature 800°.

As is seen from Fig. 2, sintering of high-purity active magnesium oxide consists of two stages. In the intermediate stages of sintering, the density of the specimens changes in strict proportion to the square root of time ($n = 0.5$), and the mechanism of mass transport is bulk diffusion. The activation energy of this process, found from the slopes of the straight lines at 1500-1600°, is 3.7 eV (86 kcal/mole) and is close to the activation energy of the ionic electrical conductivity of magnesium oxide (3.8-3.2 eV) (2) and of magnesium diffusion in MgO single crystals (3.4 eV) (7).

In the initial stages of sintering, when the bulk density of the specimens practically already increases rapidly during their heating to the equilibrium temperature to a certain value depending on temperature, some other sintering mechanism apparently operates. This initial sintering corresponds to the low-temperature sintering observed in these specimens at temperatures below 1400° (see Fig. 1), and, as can be judged from the slow increase in the bulk density of the specimens with firing temperature in this region (Fig. 1), has a low activation energy. Possib-

but that the mechanism of mass transfer at this first stage of sintering of active magnesium oxide is surface diffusion. As can be seen from Fig. 1, the significance of this mechanism decreases with increasing temperature of the preliminary calcination.

A comparison of the bulk density of the specimens at the same firing temperature and duration (Figs. 1 and 2) shows that, after rapid heating of the specimens, their sinterability deteriorates markedly. For example, if during firing with the usual rate of temperature rise (of the order of 300° per hour), after two hours at 1600° the bulk density of the specimens is 3.50 g/cm^3, then after rapid heating of the specimens to this temperature in the course of studying the sintering kinetics, even after more than six hours' holding, the density of the specimens does not exceed 3.2 g/cm^3. This may be associated with the formation of a large number of microcracks, which disrupt contacts between grains and thereby impair sintering.

Conclusions. A study of the sintering of high-purity active magnesium oxide obtained by calcination of magnesium hydroxide and carbonate shows that it differs substantially from the sintering of less pure preparations of this oxide and makes it possible to obtain ceramics with a density of about 99% of theoretical at relatively low firing temperatures. In producing active magnesium oxide it is more advantageous to use the thermal decomposition of the hydroxide, which makes it possible to reduce shrinkage during firing. The optimum calcination temperature of the hydroxide, with a holding time of two hours, is close to 600°. At this calcination temperature, the bulk density of the ceramic after firing at 1600° (3.56 g/cm^3) is maximal, and its shrinkage (~15%) is minimal.

Sintering of active magnesium oxide obtained from $Mg(OH)_2$ occurs at intermediate stages due to volume diffusion with an activation energy of 3.7 eV. At low temperatures and at the initial stage of sintering at high temperatures, another mechanism of mass transfer operates, which ceases after a certain density —dependent on the calcination and firing temperatures—has been reached.

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REFERENCES CITED

1. P. P. Budnikov, T. N. Keshishyan, V. K. Yanovskii, DAN, 138, No. 2, 365 (1961).

2. P. P. Budnikov, V. K. Yanovskii, ZhPKh, 37, 6, 1247 (1964).

3. A. S. Berezhnoy, *Proceedings of the Third All-Union Conference on Refractory Materials.* Publishing House of the Academy of Sciences of the USSR, 1947, p. 161.

4. S. G. Tresvyatskii, P. L. Volodin, *Collected Works on the Chemistry and Technology of Silicates*, 1956, p. 248.

5. B. Ya. Pines, UFN, 52, 4, 501 (1954).

6. R. L. Coble, J. Am. Ceram. Soc., 41, No. 2, 55 (1958).

7. R. Lindner, G. P. Parfitt, J. Chem. Phys., 26, No. 1, 182 (1957).

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