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Abstract

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CHEMISTRY

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THE EFFECT OF IMPURITIES OF CERTAIN CATIONS ON THE SINTERING OF SPECTRALLY PURE MAGNESIUM OXIDE

The sintering of magnesium oxide and the influence of additives on the course of sintering have previously been studied in detail ([1],[2]). It should be noted, however, that both these works and most other investigations of this kind were carried out on materials containing, in some cases, up to 0.5% and more of various impurities.

Since the specific influence of small impurities on the properties of ceramic oxides, and in particular magnesium oxide, has not been studied, it is not possible to regard the conclusions of these works as entirely reliable; all the more so because, theoretically, one may expect that the presence of very small impurities of certain elements should have a considerable effect on diffusion processes and thus on the course of sintering of ceramics made from pure oxides. The possible role of very small amounts of impurities during sintering is also indicated by the divergence among the data of various authors who have studied sintering ([3]).

In the present work, the sintering of spectrally pure magnesium oxide and the influence on the course of sintering of small impurities of cations with different crystal-chemical characteristics were studied. The use of spectrally pure magnesium oxide makes it possible to study the influence of additives in a "pure" form, i.e., under conditions in which their amount greatly exceeds the total content of impurities already present in the initial base oxide and at the same time is sufficiently small to make it possible to be confident that these additives dissolve completely in the base oxide and do not remain in the form of inert mechanical inclusions.

For these reasons, the cations Fe^{3+}, Zr^{4+}, Sc^{3+}, and Ni^{2+}, whose radius is close to that of Mg^{2+}, were chosen as additives.

Table 1

Fig. 1. Shrinkage after firing of samples of sp. p. and c. p. magnesium oxide as a function of the amount of Fe^{3+} cation additives

Figure 1: Fig. 1. Shrinkage after firing of samples of sp. p. and c. p. magnesium oxide as a function of the amount of Fe^{3+} cation additives

Dependence of the shrinkage $\Delta D/D_0$ and the bulk density γ of specimens made from active spectrally pure magnesium oxide during firing at 1320 and 1600° on impurities

Impurity	C, %	1320° $\Delta D/D_0$, %	1320° γ, g/cm^3	1600° $\Delta D/D_0$, %	1600° γ, g/cm^3	Impurity	C, %	1320° $\Delta D/D_0$, %	1320° γ, g/cm^3	1600° $\Delta D/D_0$, %	1600° γ, g/cm^3
Without impurities	–	9.0	1.73	26	3.45	Fe^{3+}	0.1	22	2.80	28	3.52
Zr^{4+}	0.1	20	2.25	29	3.54	Fe^{3+}	0.2	27	3.29	29	3.53
Zr^{4+}	0.2	31	3.48	32	3.57	Fe^{3+}	0.3	30	3.45	30	3.51
Zr^{4+}	0.4	28	3.56	29	3.59	Fe^{3+}	0.6	30	3.38	31	3.53
Zr^{4+}	0.5	26	3.61	26	3.58	Fe^{3+}	1.0	30	3.48	30	3.60
Ni^{2+}	0.1	17*	–	26**	3.05	Fe^{3+}	1.8	24**	3.55	–	–
Ni^{2+}	0.2	22*	–	28**	3.09	Sc	0.1	17	–	29	3.52
Ni^{2+}	0.5	17*	–	26**	3.03	Sc	0.2	28	–	29	3.54

* Firing of specimens with Ni^{2+} was carried out at 1250 and 1600°.
** The specimens cracked.

In order to minimize the influence of the dissolution kinetics of additives in magnesium oxide and to equalize their distribution over the surface and volume of periclase grains, all additives were introduced by coprecipitation in the form of hydroxides from a mixture of solutions of magnesium chloride (20%) and the corresponding additive. The concentration of additive cations, taking into account the yield of MgO, is given in Table 1 in atomic percent; hereafter atomic percent is used throughout. The precipitates obtained by coprecipitation were filtered, thoroughly washed, dried at 110°, calcined in platinum crucibles at 625°, and ground. Calcination at 625° ensured the production of magnesium oxide in an active form. The effect of the calcination temperature was not specially investigated.

Fig. 1. Shrinkage after firing of samples of sp. p. and c. p. magnesium oxide as a function of the amount of the cation additive Fe^{3+}.

Next, in a steel die at a pressure of 1350 kg/cm^2, specimens in the form of disks 11 mm in diameter and 1-2 mm thick were pressed without binder.

In order to obtain data on both the initial and subsequent stages of sintering, the specimens were fired twice—at 1320 and 1600°. Firing at $1320 \pm 10^\circ$ with a hold of 1.5 hours was carried out in a silite furnace with a temperature-rise rate of about 300° per hour. Firing at $1600 \pm 10^\circ$ with a hold of 1 hour was carried out in a furnace with a heater made of platinum-rhodium wire wound on a cylinder of beryllium oxide; the rate of temperature rise at the end of firing was about 500° per hour. During firing, the specimens were placed on platinum-foil supports; only specimens of identical composition were fired simultaneously.

Sintering was monitored by the shrinkage of the specimens in diameter and by their bulk density. The bulk density of specimens with low porosity was determined by hydrostatic weighing in toluene on an analytical balance. For poorly sintered specimens, their dimensions were measured, their volume was calculated, and their bulk density was determined.

As is evident from the data given in Table 1, a small amount of introduced impurities has a decisive influence on the course of sintering of active magnesium oxide. All the additives used accelerated sintering starting already at a concentration of 0.1%.

Spectrally pure active magnesium oxide begins to sinter at a considerably higher temperature than chemically pure magnesium oxide. Thus, it was shown earlier(4) that MgO of the chemically pure analytical grade, prepared by approximately the same method, begins to sinter at 1000°, and at 1300° its sintering is already practically complete. Spectrally pure magnesium oxide only begins to densify at 1320°. When spectrally pure oxide is sintered at 1600°, a bulk density of 3.45 g/cm^3 is reached, whereas when less pure materials are sintered such densification cannot be obtained even at considerably higher temperatures(4). The usual values of γ in the sintering of active magnesium oxide from the hydrate at 1600° lie within the range 3.25–3.35 g/cm^3. Thus, it should be noted that spectrally pure magnesium oxide behaves during sintering in a qualitatively different way from chemically pure oxide.

For comparison, Fig. 1 gives data on the shrinkage of specimens of chemically pure magnesium oxide with impurities of Fe^{3+} cations. Specimens of chemically pure MgO were prepared by the method described above, with the only difference that no special precautions against contamination were taken and the specimens were fired at 1400° on a bed of MgO. Fig. 1 clearly illustrates the qualitative difference in the behavior of spectrally pure and chemically pure magnesium oxide.

As is evident from Table 1, when 0.2% Zr^{4+} is introduced, magnesium oxide sinters at 1320° almost to theoretical density; at 0.5% a bulk—

specific gravity of 3.61 g/cm^3, which, within the limits of error, coincides with the theoretical density if the specific gravity of magnesium oxide is taken as 3.58 g/cm^3 and it is assumed that the bulk density changes additively when Zr^{4+} cations are introduced into the MgO lattice. On firing at 1600°, the

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

shrinkage and bulk density of samples with 0.4 and 0.5% Zr^{4+} no longer changed appreciably.

Fig. 2. Microphotographs of the free surface of magnesium oxide samples with various additions of zirconium cations. *a*—without addition; *b*—0.1 at.% Zr^{4+}; *c* —0.4 at.% Zr^{4+}. 340×

Study of the microstructure of the samples shows that the practically complete sintering of magnesium oxide with an admixture of 0.2-0.5% Zr^{4+} cations at 1320° is not accompanied by noticeable recrystallization of magnesium oxide, as also occurs with the introduction of other impurities; the magnesium oxide grains are not visible under optical magnification. Firing at 1600° is accompanied by considerable recrystallization, and the growth of the grains depends to a large extent on the type and amount of impurity. In Fig. 2, as an example, microphotographs are given of the surface of MgO samples without additions and with additions of 0.1% and 0.4% Zr^{4+} after firing at 1600°. The introduction of 0.1% zirconium cations sharply enhances the recrystallization of magnesium oxide at 1600°; increasing the amount of the addition does not affect the size of the MgO crystallites, but leads to a noticeable increase in the amount of intercrystalline material.

Fig. 3. Dependence of the bulk density γ and apparent porosity B of magnesium oxide samples on the amount of impurity of Fe^{3+} cations

Figure 3 shows the dependence of the bulk density and apparent porosity of samples with an impurity of Fe^{3+} cations on the concentration of the latter. The character of the curve of the dependence of the bulk density of samples after firing at 1320° on the content of Fe^{3+} impurity differs noticeably from the character of the analogous dependence for Zr^{4+}. Apparently, the Zr^{4+} impurity is significantly less effective than the Fe^{3+} impurity in the initial stage of sintering of the samples (at a bulk density of less than 3.0 g/cm^3). The same also applies to the Sc^{3+} impurity. However, when Sc^{3+} and Zr^{4+} are introduced in large amounts and firing is carried out at 1600°, it is possible to obtain much stronger densification than with the introduction of Fe^{3+} or Ni^{2+}. This leads to the conclusion that the strongly polarizing cations Fe^{3+} and Ni^{2+}, which have a mobile 18-electron shell, exert a greater influence on the surface diffusion that predominates at the beginning of sintering in active, very fine-grained magnesium oxide, whereas the cations Zr^{4+} and Sc^{3+}, with the atomic structure of inert gases, have a stronger influence on volume diffusion, whose importance is greatest in the final stages of sintering, after the formation of closed pores.

It should be noted that the dependence of the bulk density and apparent porosity of the specimens on the concentration of the impurity of Fe^{3+} cations is not monotonic and has a maximum at an Fe^{3+} concentration of 0.2–0.3%. A similar tendency is especially sharply expressed in the shrinkage of specimens with Ni^{2+}. This fact apparently means that there exists a sharply expressed optimum impurity concentration, accelerating sintering, which for the given type of magnesium oxide lies within 0.2–0.4 at.%. A similar phenomenon, but less sharply expressed, has already been observed in the surface activation of magnesium oxide ([5]).

In conclusion it must be noted that so sharp a dependence of the course of sintering of magnesium oxide on additions in amounts of 0.1 at.% and less can hardly be explained from the standpoint of the theory of sintering by macroscopic flow ([6]). It is known that impurities increase the yield point of magnesium oxide ([7]) and its strength. At high temperatures this strengthening by impurities cannot be significant, but nevertheless one would expect that the introduction of impurities into magnesium oxide would slow sintering rather than sharply accelerate it, as is observed in reality.

The present work has established that impurities of Zr^{4+}, Fe^{3+}, Sc^{3+}, and Ni^{2+}, already at a concentration of 0.1 at.%, exert a decisive influence on the course of sintering of spectrally pure magnesium oxide, considerably accelerating it. When chemically pure magnesium oxide is used, this effect is not observed. Spectrally pure magnesium oxide begins to sinter at a temperature of about 1300°, whereas the sintering of chemically pure magnesium oxide at this temperature is already completed ([4]). At 1600°, specimens of spectrally pure magnesium oxide have a bulk density higher than that achieved with less pure materials. The sharp influence on the course of sintering of spectrally pure magnesium oxide of comparatively small amounts of additions, and the readily detectable difference in the character of their action, illustrate a sufficiently clear connection between the crystallochemical characteristics of the additive cations and their relative effectiveness.

The obtained dependence of the influence of additions on the sintering of magnesium oxide on their concentration permits the conclusion that active magnesium oxide can be considered truly pure only if the total content in it of cation impurities with charge and polarizability greater than those of Mg^{2+} does not exceed 0.05–0.01%. Theoretical conclusions made on the basis of results obtained with less pure materials apparently cannot be regarded as having general validity.

With the introduction of 0.2–0.5 at.% Zr^{4+}, the sintering of sufficiently pure magnesium oxide can be brought almost to theoretical density already at 1320°.

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