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REFRACTORY AND CERAMIC MATERIALS

MOISTURE-SENSITIVE CERAMIC ELEMENTS BASED ON ALUMOMAGNESIUM SPINEL

1. EFFECT OF PROCESS PARAMETERS IN THE TREATMENT OF MIXTURES OF OXIDES MgO AND Al_2O_3 ON THE SERVICE CHARACTERISTICS OF THE MOISTURE-SENSITIVE ELEMENTS

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Most of the attention of researchers who have been developing materials for ionic ceramic humidity sensors has been focused on selection of the chemical composition and porosity of the sensors after the formation and sintering of the compacts. The chemical composition determines the affinity of the material to water, but the pore structure is the main factor that determines the service characteristics of the transducer. Those characteristics are related to the capillary condensation of moisture in pores of different sizes [1-3]. In accordance with the theory of the physical properties of porous composites, the parameters of the microstructure and macrostructure are significantly affected by the initial disperse structure, the proportions of the components and their mutual positions, and the methods used for mixing, crushing, forming, and sintering [4].

The effect of chemical composition and the pore structure on the electrical characteristics of ceramic moisture transducers based on alumomagnesium spinel has been examined sufficiently in the literature [1, 5-8]. Less attention has been given the effect of mixing, crushing, forming, and sintering of powders of magnesium and aluminum oxides on the service characteristics of such spinels when used in ceramic moisture sensors. This is the topic that will be investigated here.

Powders (analytically pure) of oxides of magnesium and aluminum with a specific surface of 17.1 and 1.4 m^2/g, respectively, were mixed and crushed in a planetary ball mill in the presence of acetone (220 ml for 1 kg of the mixture). We then used mixtures of 50% (at.) MgO and 50% (at.) Al_2O_3 to press semifinished products 15 mm in diameter and 1 mm thick, using an aqueous solution of polyvinyl alcohol. The pressing operation was performed in steel molds at a pressure of 200-500 MPa. The resulting compacts were sintered in air at temperatures of 1200-1400°C. Specific surface was determined on the basis of the thermal desorption of nitrogen in accordance with GOST 23401—78.

Since the initial powders differed greatly in specific surface, before fabricating the moisture sensors we needed to optimize the mixing time in order to achieve complete mixing of the components. The components were then to be crushed in order to lower the temperature at which the spinels form. These processes were monitored on the basis of data on the specific surface of mixtures of 50% (at.) MgO and 50% (at.) Al_2O_3: after crushing for 1, 2, 4, and 6 h, the values of specific surface were 4.5, 8.9, 16.7, and 13.8 m^2/g, respectively.

If we compare this data and the results obtained from simple addition of the specific surfaces of MgO and Al_2O_3 with allowance for their proportions, it can be concluded that after 24 h the powders mix well without further crushing. Specific surface doubles after crushing over 2 days and increases roughly fourfold after crushing over 4 days. However, the mixture begins to agglomerate when crushed for more than 4 days, leading to a decrease in its specific surface. Thus, the optimum duration of the crushing operation is 4 days. Crushing for 4 days produces a fine mixture of oxides of magnesium and aluminum that initially differed in specific surface by more than an order of magnitude.

Let us examine the effect of the initial specific surface on the specific surface of sintered compacts obtained under identical conditions. It is evident from Table 1 that almost regardless of the temperature at which the powder mixtures are

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TABLE 1. Specific Surface of Ceramic Humidity Sensors Based on Alumomagnesium Spinel (m^2/g)

Sintering temperature, °C	Pressing pressure, MPa	Time of crushing of the powder mixture, days			
		1	2	4	6
1200	200	3,4	3,4	3,2	2,6
	300	2,7	3,96	3,94	3,46
	400	3,0	2,86	3,56	2,9
	500	2,9	2,75	2,85	2,8
1300	200	1,9	1,95	2,2	2,17
	300	1,8	1,55	3,0	2,2
	400	1,8	1,85	2,15	2,14
	500	1,7	1,8	1,14	2,16
1400	200	0,075	0,08	0,096	0,14
	300	0,15	0,16	0,26	0,18
	400	0,07	0,08	0,162	0,33
	500	0,08	0,097	0,2	0,074

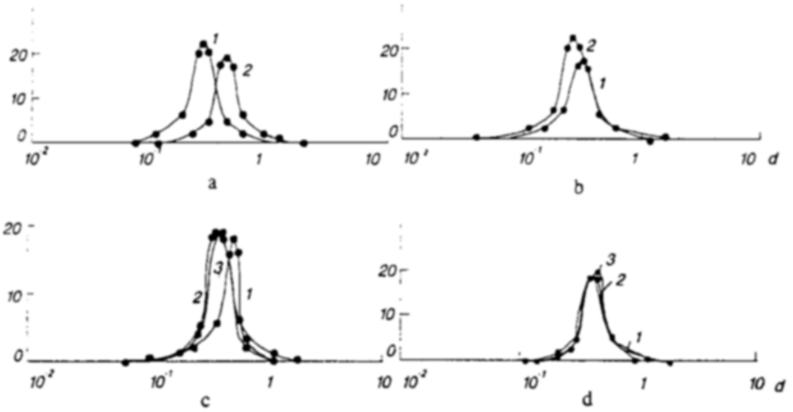

Fig. 1. Pore-size distribution in moisture-sensitive ceramic elements obtained by sintering an $MgO-Al_2O_3$ mixture: a) crushing of the mixture for 4 days, sintering at 1200 (1) and 1300°C (2); b) sintering at 1200°C, crushing for 2 (1) and 4 days (2); c) sintering at 1300°C, crushing for 2 (1), 4 (2), and 6 days (3); d) sintering at 1300°C, pressing at 200 (1), 300 (2), and 500 MPa (3).

sintered, a fine structure is obtained in the ceramic with the use of finer initial mixtures. An increase in sintering temperature always leads to a decrease in the specific surface of the sintered semifinished products.

An increase in pressure during the pressing operation to 500 MPa is accompanied by a slight decrease in the specific surface of the sintered compacts. Specific surface is affected the most by sintering temperature and the duration of the crushing operation. Regardless of sintering temperature or pressing pressure, the most dispersed structure is obtained by sintering compacts obtained from a mixture that has been crushed for 4 days (as noted above). The highest value of specific surface is achieved at a sintering temperature of 1200°C, while the lowest value is obtained at 1400°C. The optimum pressure is 300-400 MPa.

Figure 1 illustrates the change in the pore structure of the semifinished products in relation to the time taken to crush the powder mixture, the pressure at which the mixture is pressed, and the temperature at which the compact is sintered. An increase in sintering temperature shifts the pore-size distribution curve to the region of larger diameters (Fig. 1a). Porosity disappears after sintering at 1400°C and water is absorbed only by the outside surface of the transducer. Conversely, an increase in crushing time shifts the pore-size distribution curve in the direction of smaller diameters (Fig. 1b and c); mean pore size decreases in this case. Other conditions being equal, pressing pressure has almost no effect on mean pore size. The narrowest pore-size distribution is seen for pellets pressed at 300 MPa (Fig. 1d).

Let us see how all of the above factors (the specific surface of the initial mixture (represented through crushing time), pressing pressure, and sintering temperature) affect the service characteristics of the finished transducers. The service

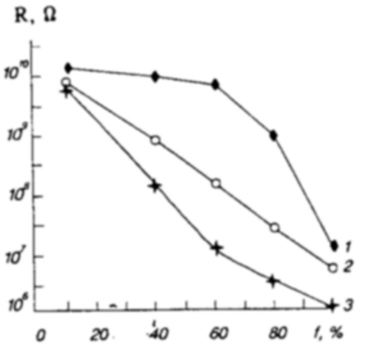

Fig. 2

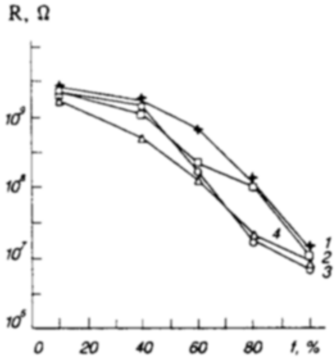

Fig. 3

Fig. 2. Change in the electrical resistivity of moisture-sensitive ceramic elements as a function of relative moisture content. The elements were made by pressing and sintering (1200°C, 2 h) mixtures of powders after crushing for 2 (1), 4 (2), and 6 days (3).

Fig. 3. Change in the electrical resistivity of ceramic elements as a function of relative moisture content. The elements were obtained with a pressing pressure of 500 (1), 300 (2), 200 (3), and 400 MPa (4) after sintering at 1300°C for 2 h.

characteristics were evaluated on the basis of the change in the electrical resistivity that occurred when the surface of the ceramic elements absorbed moisture from an artificially created medium at different test temperatures. After sintering, we applied a layer of ruthenium paste to the surface of ceramic semifinished products in the form of thin (thickness on the order of 1 mm) circular moisture-sensitive elements, attached electrodes to the specimen, and measured resistivity. Aqueous solutions of glycerin and silica gel were used as the source of moisture.

Figure 2 shows how the service characteristics are affected by mixing time — the time of crushing of the initial powders. An x-ray phase analysis (DRON-0.5 diffractometer, FeK_α-radiation, selective filter) performed after mixing revealed the presence of the spinel $MgAl_2O_4$ and residues of oxides of aluminum (up to 3%). The content of aluminum oxides depended on the fineness of the initial powder mixtures (and, thus, on crushing time) and sintering temperature. No oxides of magnesium were observed.

Since the best transducers are those that have the lowest resistivity and simultaneously exhibit the largest change in resistivity with a change in moisture content, it follows from the data in Fig. 2 that the most stable characteristics (high sensitivity within a broad range of moisture contents — from 10 to 98%) are exhibited by ceramic moisture-sensitive elements obtained by sintering mixtures that have been crushed for 4 h, providing that the elements are made from the most dispersed mixture and are shown by x-ray phase analysis to contain aluminum-magnesium spinel. Transducers fabricated from powders that have been crushed for 2 days have a high sensitivity at high (80-98%) and low (10%) relative moisture contents but lose their service characteristics at moderate values of moisture content. The sensitivity of the transducer decreases in the low-moisture-content range when the powders are crushed for 6 days. Up to 3% aluminum oxides remain in the semifinished products after short crushing (2 days). These oxides can result in the formation of inflections on the curves in the region of moderate moisture contents (Fig. 2), where their sensitivity decreases. An increase in mixing and crushing times leads to an increase in the content of spinel $MgAl_2O_4$ and a decrease in the number of unreacted particles of MgO and Al_2O_3. The particles agglomerate with an increase in crushing time to 6 days, as indicated by the reduction in their specific surface. This is also accompanied by a deterioration in the parameters characterizing the pore structure and in the service characteristics of the transducer.

Figure 3 shows the effect of the pressure at which the ceramic elements are pressed on the sensitivity of the transducers to a change in moisture content. The best characteristics were exhibited by specimens pressed at a pressure of 300-400 MPa. This result is evidently related to the formation of the initial pore structure (Fig. 1d). That structure contains large-diameter pores when the powders are pressed at low pressure (200 MPa). The large pores remain in the material after sintering at low temperatures, leading to a decrease in the sensitivity of the transducer in the range of low relative moisture contents. The small pores are closed at high pressures (500 MPa). The best proportion between the numbers of pores of different

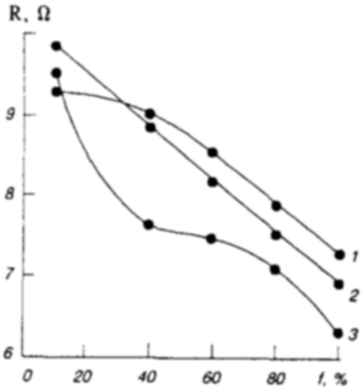

Fig. 4. Change in the electrical resistivity of moisture-sensitive ceramic elements as a function of relative moisture content. The elements were sintered at 1400 (1), 1300 (2), and 1200°C (3). Time of crushing of the initial mixture was 4 days, pressing pressure was 300 MPa.

sizes after sintering is obtained at moderate pressures, which also ensures that the transducer will be highly sensitive to moisture content throughout the investigated range.

An increase in sintering temperature is accompanied by a decrease in the sensitivity of the transducer (Fig. 4) and the specific surface of the sintered semifinished product (Table 1). This result is related to the occurrence of recrystallization, the growth of individual pores due to spheroidization of the particles, and the dissolution of small isolated particles in coarser particles. The change in the pore structure which occurs with an increase in sintering temperature leads to a change in the process of capillary condensation and ultimately affects the service characteristics of the transducer.

Thus, the following conclusions can be made from the study results. The time spent crushing the oxides of magnesium and aluminum affects the specific surface of the mixture and moisture-sensitive ceramic elements sintered from those oxides and ultimately affects the sensitivity of the transducer. An increase in crushing time to 4 days increases the specific surface of the powder mixture and the dispersity of the structure and improves the service characteristics of the transducer.

The specific surface and service characteristics depend to a large extent on the sintering temperature, decreasing with a decrease in the latter to 1400°C. Pressing pressure has less of an effect. The optimum regime is pressing at 300-400 MPa and sintering at 1200-1300°C over 2 h.

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