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Evolution of Porous Structure in Technologically Modified $MgO-Al_2O_3$ ceramics

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Evolution of porous structure in technologically modified spinel $MgO-Al_2O_3$ ceramics sintered at different temperature are studies. It is shown that increasing of sintering temperature from 1200 to 1400 °C result in transformation of pore size distribution in ceramics from tri- to bi-modal. It is established that increasing of humidity sensitivity in ceramics sintered at 1300 °C are related to achievement near to optimum pore size distribution and their quantity in the higher indicated region. Prolonged degradation transformation at higher temperature and relative humidity result in lose sensitivity up to 40 %.

Keywords: Spinel, Ceramics, Porous Structure, Humidity Sensitivity.

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1. INTRODUCTION

Nanostructured spinel $MgO-Al_2O_3$ ceramics are one of the most interesting materials in view of their application as active elements for environment humidity sensors [1]. It is established that sensing functionality of these materials is determined first by microstructure of ceramics grains, intergranual boundaries and pores [2], these elements being dependent mainly on ceramics sintering route. With this in mind, the correlation between sintering temperature of the above ceramics, their porous structure and exploitation properties should be studied carefully.

2. EXPERIMENTAL

The studied ceramics were prepared from Al_2O_3 with specific surface area of 67 m^2/g and $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ with specific surface area of 12.8 m^2/g. The obtained powder is mixed with an organic binder to prepare green body billets. Then, these pellets are sintered in a special technological regime with maximal temperatures T_s of 1200, 1300 and 1400 °C for 2 h within conventional ceramics technology route [3]. Results obtained with XRD method testify that ceramics sintered T_s = 1200-1400 °C contain two phases: the main spinel-type $MgAl_2O_4$ phase and some additives of additional MgO [4].

Pore size distributions in $MgO-Al_2O_3$ ceramics were studied using Hg-porosimetry (POROSIMETR 4000, CARLO ERBA STRUMENTAZIONE, Germany) in the region from 1 to 100 nm.

The humidity sensitivity of ceramics is determined by dependence of electrical resistance R on relative humidity (RH) of environment. The electrical resistance of the studied $MgO-Al_2O_3$ ceramics was measured in the heat and humidity chamber PR-3E "TABAI" at temperatures 20 °C on the region of RH = 20-98 %. The electrodes were given on the connecting cables of M-ohmmeter at the fixed frequency of current of 500 Hz (with the aim of avoidance of polarization of adsorbed molecules of water).

3. RESULTS AND DISCUSSIONS

The pore size distributions of technologically modified $MgO-Al_2O_3$ ceramics within tri- and bi-modal form are shown in Fig. 1.

The obtained results were indicated to the effects that the sintering temperature essentially influences on the porous structure of ceramics. Ceramics sintered at 1200 °C exhibit the tri-modal pore size distribution with maximums r_1, r_2 and r_3 near 0.0023, 0.035 and 0.16 μm respectively (Fig. 1a). It is established that large open pores near 0.1-0.15 μm corresponds to surface pores in ceramics. They provide absorption-desorption process of water from environment. Pores centered near 0.035 μm are so-called transporting pores providing the effective passing of water into ceramic body. According to Kelvin equation [1, 5], for the processes of capillary condensation of humidity in ceramic samples at 20 °C in investigated range of RH (20-98 %) were responsible for cylindrical nanopores with a radius smaller 2 nm.

Such pore size distribution provides the humidity-sensitivity of $MgO-Al_2O_3$ ceramics on a wide range of RH from 30 to 98 %. Degradation transformations at 40°C and RH = 95 % during 240 h result in decreasing of humidity-sensitivity of materials at lower RH up to 40 %. Such changes testify to satiations of some nanopores by water and insufficient amount of transporting pores which do not destroy all water from ceramics.

With increasing of T_s to 1300 and 1400 °C tri-modal pore size distribution was transformed to bi-modal with r_1 and r_3 maximums. At changes of T_s pore size distribution is fully transformed. It is represented in different intensities of peaks and their position. So, the r_1 practically was not dependence on T_s according to the position. But intensity increases from 48 to 91 mm^3/g. The maximum r_3 was moved toward the higher radiuses, but appreciably increased its intensity (Table 1). Changes caused by pore size distribution were reflected in humidity-sensitivity of $MgO-Al_2O_3$ ceramics. In spite of a small amount of transporting pores, ceramics

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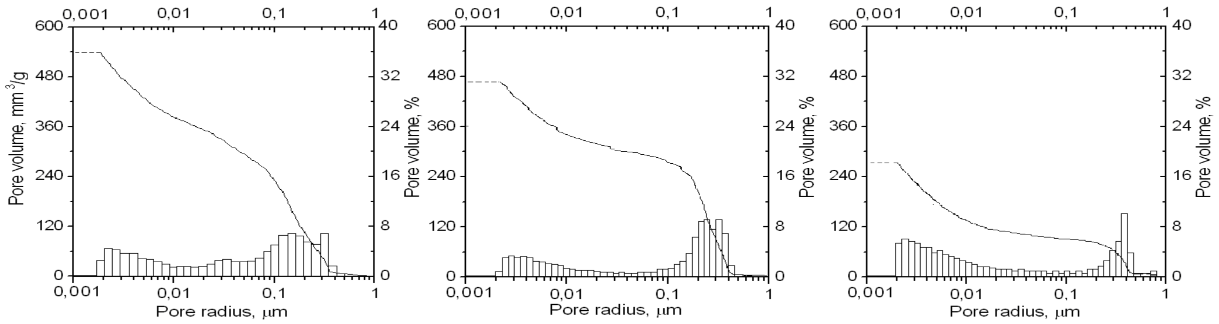
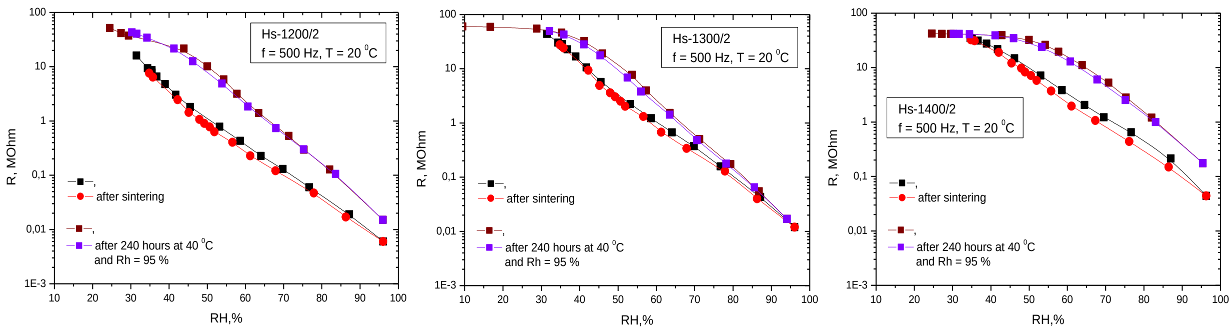


a b c

Fig. 1 – Pore size distributions of $MgO-Al_2O_3$ ceramics sintered at 1200 °C (a), 1300 C (b) and 1400 °C (c)

Table 1 – Pore size of $MgO-Al_2O_3$ ceramics sintered at 1200-1400 °C within bi-modal distributions

T_s	r_1, µm	I_1, mm³/g	r_2, µm	I_2, mm³/g	r_3, µm	I_3, mm³/g
1200	0.0023	68	0.035	51	0.16	103
1300	0.0029	48	-	-	0.27	137
1400	0.0025	91	-	-	0.38	154



a b c

Fig. 2 – Exploitation properties of $MgO-Al_2O_3$ ceramics sintered at 1200 °C (a), 1300°C (b) and 1400°C (c)

sintered at 1300 °C are characterized by linear dependence of electrical resistance R vs. RH in all studied region without hysteresis in absorption-desorption cycles. But after degradation tests they loses sensitivity up to 35 % just as in ceramics sintered at 1200 °C. However position of characteristics before and after degradations does not change practically.

Humidity-sensitivity of ceramics sintered at 1400°C are characterized linearity but with appreciable hysteresis. After 240 h at 40 °C and $RH = 95$ % form of dependences is changes and replaces to right part. It is correspond to specific pore size distributions of this ceramics with deficient amount of large pores with radius of 0.5 µm and pores centred near 0.15 µm.

4. CONCLUSION

The increase of humidity sensitivity in ceramics sintered at $T_s = 1300$ °C, it seems, was related to achievement near to optimum pore size distribution and their quantity in the higher indicated region. It is shown that in all sintered samples there are pores with radius higher 2 nm, which though do not participate in the processes of capillary condensation, but their presence is needed for support operate short time in humidity sensitive elements on the change of relative humidity. The sintered temperatures allow to refine the most significant changes in porous structure of ceramic materials. Evolution of pore size distribution in nanoporous humidity-sensitive spinel $MgO-Al_2O_3$ ceramics leads to corresponding changes in their water sorption processes.

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REFERENCES

1. E. Traversa, *Sensors and Actuators,* B **23**, 135 (1995).
2. G. Gusmano, G. Montesperelli, E. Traversa, *J. Am. Ceram. Soc.*, **76**, 743 (1993).
3. H. Klym, A. Ingram, O. Shpotyuk, J. Filipecki, I. Hadzaman, *Phys. Stat. Sol. C*, **4**, No 3, 715 (2007).
4. H. Klym, A. Ingram, I. Hadzaman, O. Shpotyuk, A. Popov, Yu. Kostiv, *Journal of Physics: Conf. ser.* (2013), in press.
5. T. Seiyama, N. Yamazoe, H. Arai H., *Sensors and Actuators*, **4** 85 (1983).