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EFFECTS OF TECHNOLOGICAL PARAMETERS DURING IMPREGNATION ON THE PROPERTIES OF MODIFIED QUARTZ CERAMICS

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The main methods of moisture protection of products made of quartz ceramics are described. The advantage of quartz ceramics modified by bulk impregnation with MFSS-8 solution is shown. Experimental data on the properties of modified quartz ceramics obtained with different types of impregnation are presented.

Keywords: quartz ceramics, paint coatings (PC), moisture protection, impregnation, MFSS-8 compound.

Inorganic materials, particularly the quartz ceramic NIASIT, which possesses good dielectric, thermophysical, and technological characteristics, are used to fabricate radio-transparent items subjected to thermal stresses [1]. NIASIT has been widely applied among radio-technology items, e.g., for housings of aircraft radio systems, because of the combination of physical and technical properties. The radio-technical properties of items depend directly on their dielectric constant. The quartz ceramic NIASIT has an open porosity up to 7 – 12% and readily absorbs water.

Moisture protection is extremely important to preserve the dielectric properties of items made of quartz ceramics. Therefore, most items made of NIASIT have special coatings. As a rule, paint coatings (PCs) are applied to the outer side of items while the inner side is most often impregnated with an organosilicon binder followed by polymerization. Various solutions and methods can be used for the impregnation depending on the required final properties of the items. It is very important to combine the optimal structure and suitable side groups in the polymer because the heat resistance of polymers depends on the macromolecular structure; the resistance to thermal oxidation and non-combustibility, on the organic side groups of the chain.

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A combination of methyl and phenyl side groups gives the greatest effect [2]. A composition based on a solution of *tetrakis*(methylphenylsiloxanehydroxy)titanium (TMPT) with added phenol-formaldehyde resin SF-340 and a solution of methylphenylspirosiloxane (MFSS-8) can be singled out among impregnating compositions that are used most often. The products polymerize during heat treatment to form a heat resistant moisture-impermeable polymer. Figures 1 and 2 show the structural formulas of TMPT and MFSS-8.

Organosilicon polymers containing phenyl groups possess freeze–thaw resistance. This is important for items subjected to thermal cycling between negative and positive temperatures and for items operating at high temperatures. Impregnation by TMPT and MFSS-8 solutions followed by polymerization leads to formation on the item surface of a heat-resistant film that makes the item hermetic and fully protects it from moisture intrusion.

The thermal destruction temperature at which the mass loss is 1% can be used to evaluate the heat resistance of a polymer. For example, this temperature for the polymer based on TMPT is ~300°C; for the polymer based on MFSS-8, ≥350°C. Thus, the NIASIT ceramic with a filler of the polymer obtained from MFSS-8 is more heat resistant.

The heat resistance of the composition increases after filling with a polymer of higher heat resistance. Composites resistant to water with an insignificant loss of heat resistance are obtained upon modification of quartz ceramics by poly-

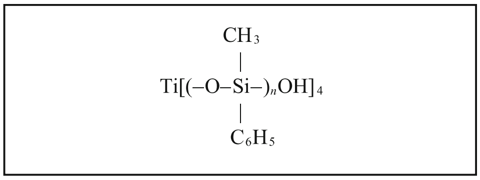

Fig. 1. Structural formula of TMPT.

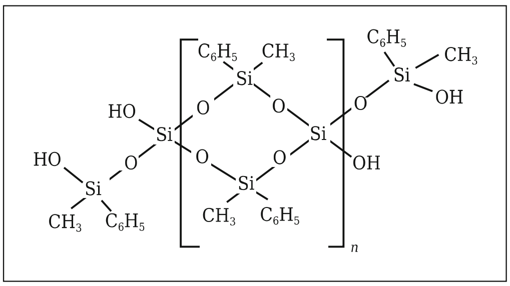

Fig. 2. Structural formula of MFSS-8.

mers. Also, the MFSS-8 polymer is destroyed to form SiO_2, which has practically no effect on the dielectric characteristics of the material. However, thermal destruction of the TMPT polymer leads to the formation of titanium oxides that, conversely, significantly affect the dielectric constant.

Hollow axially symmetric items are impregnated by bathing their cavities in special rotators for a certain time (surface impregnation) or holding a solution within the item in an impregnating device for a certain time to a definite height (variable depth impregnation) or by holding the item in a solution until it is impregnated over the whole thickness (bulk impregnation). Bulk impregnation can produce a composite that is resistant to moist medium without using a PC, which expands the possible applications of the items. PCs are known to be susceptible to the formation of various defects (scratches, blistering, exfoliation) during operation that leads to a loss of their protective properties. Also, the technological manufacturing process of items made of bulk-impregnated ceramics is shorter because a PC can be damaged usually after testing of the items during manufacturing control (Fig. 3).

A solution of MFSS-8, which is more heat resistant than TMPT, is used for bulk impregnation because higher temperatures affect the outside than the inside and the polymer on the surface should be resistant to these temperatures. The polymer distributed in the pores improves the operating properties of the ceramic and can be used for items made of radio-technical quartz ceramics [3]. NIASIT ceramic modified in this manner can be used without applying PCs on the outer surface of the items.

Materials can be impregnated by natural penetration of a solution into the matrix and with preliminary evacuation. Two processes occur during natural impregnation, i.e., penetration of the solution into the ceramic open-pore system and expulsion of air contained in the ceramic. The process is significantly accelerated in the latter version because displacement of a gas situated in pores by a solution is partially or fully impossible. A unilateral frontal spreading of a solution and spreading of a solution from all sides can occur with complete immersion of an item in a solution. Obviously, complete immersion of thick-walled items in a solution not only leads to over consumption of the solution but also hinders removal of gas from the pores. The whole bulk material is often not fully impregnated. In this instance, evacuation and frontal spreading of the solution are preferred. The completeness of the impregnation can be monitored visually because the light transmission of an impregnated ceramic is considerably greater than that of an unimpregnated ceramic. Complete immersion is allowed for bulk impregnation of small samples (10 – 15 mm on a side as a minimum) because they are completely impregnated after short times.

The properties of bulk-impregnated ceramics can be affected by various technological factors such as the time spent

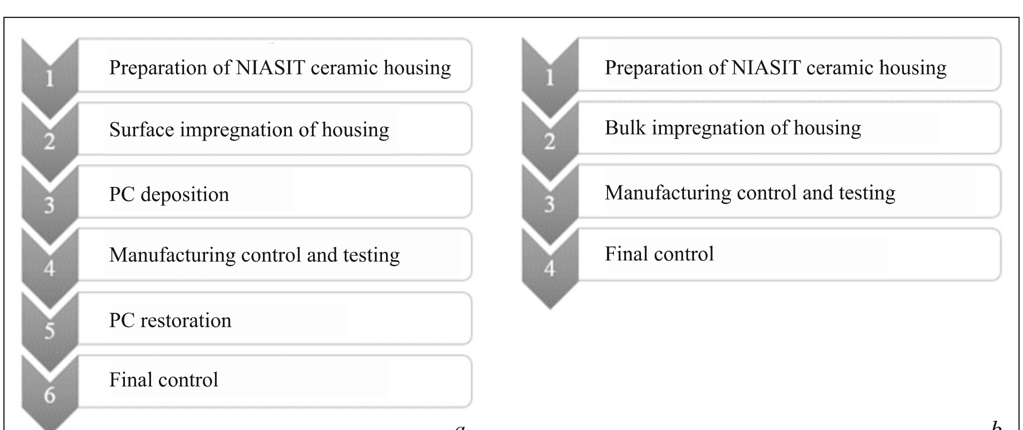

Fig. 3. Technological scheme for preparation of items from quartz ceramic with surface (*a*) and bulk impregnation (*b*).

in the solution, matrix and solution temperature during impregnation, density of the impregnating solution, and the action of physical factors (pressure, vacuum, ultrasound oscillations, etc.). Several technological factors affecting the impregnation of porous ceramic items by a polymer solution were discussed before [4]. The mathematical dependences of the material properties on the impregnation time and other characteristics were given.

The aim of the present work was to study the effects of several technological factors during preparation of NIASIT quartz ceramic modified by MFSS-8 on its performance. The effects of heating the starting material, ultrasonic waves, holding at low temperature before polymerization, and the duration of the temperature rise to the polymerization temperature were investigated. The effects of these factors were evaluated from the density, porosity, water absorption, strength, and dielectric characteristics of the samples; hermeticity, from He permeation; and a test for light transmission. Light transmission was evaluated from the color of white light (strength ~100 lm) passing from the source through a sample of thickness 14 mm.

EXPERIMENTAL

The temperature is known to affect the impregnation rate of a material because the temperature governs the mass-transfer kinetics. Also, the air concentration in pores is less in a heated ceramic, i.e., the gas will be expelled faster. It can be assumed that impregnation of a heated ceramic will be faster, provided a thermally stable impregnating solution is available. MFSS-8 can increase its molecular mass upon prolonged storage even at room temperature. Polymerization is activated upon heating it. Therefore, a study of the properties of the obtained ceramic with impregnation of the heated matrix held practical interest. A low temperature (55°C) less than the boiling point of Me_2CO (56°C) was selected because an Me_2CO solution was used.

The structure of the quartz ceramic did not have geometrically regular perforating capillaries of a certain size and was characterized by a complex network of irregularly shaped voids. The voids could be shaped as channels and capillaries with necks positioned at various angles and had dead-end branchings. The surfaces of the channels and capillaries could be uneven. Figure 4 shows a diagram of a projection of the pore network. Several investigations summarized in a book [5] indicated that the solution distribution rate and air expulsion rate from the pores were different in separate local sections of the ceramic. Gaseous products from polymerization could be trapped within the ceramic because of the complex pore structure. Presumably, this manifested in items of the quartz ceramic with polymer introduced into the pores as a local change of light transmission, which complicated visual and optical control for the presence of cracks.

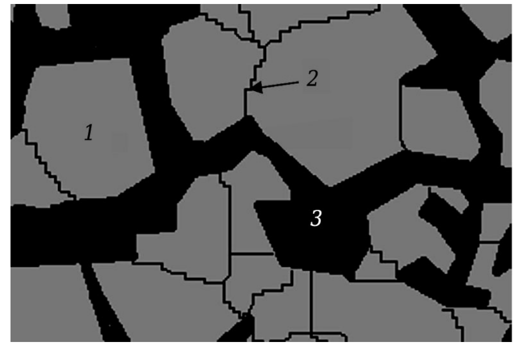

Fig. 4. Diagram of positioning of pore space between sintered ceramic particles: ceramic particles (*1*), boundary of ceramic grains sintered to each other (*2*), pores (*3*).

Experiments in which the impregnated ceramic was additionally held at low temperatures and the temperature rise during polymerization was also slow were performed for better removal of gaseous and low-boiling compounds and were interesting from this point of view.

Ultrasound vibrations are known to be an effective means for degassing materials and liquids. This was also tested during the research. Samples of NIASIT ceramic for which the initial properties of density, porosity, water absorption, flexural strength, dielectric constant, and dielectric loss tangent (at 10^{10} Hz) were determined were prepared for the work. The samples were impregnated along the whole depth by complete immersion of them in an Me_2CO solution of MFSS-8. The samples were dried at 150°C for 3 h before impregnation to remove moisture. The MFSS-8 solution at room temperature (21 – 22°C) was diluted with Me_2CO to density 974 – 975 kg/m^3. Samples were immersed in the solution for 18 – 20 h for complete impregnation. The completeness of impregnation was evaluated visually. The samples changed from white opaque to semi-transparent after complete impregnation. Impregnated samples were withdrawn from the solution and stored in air for 3 h before heat treatment. Impregnated and air-dried samples were heated in a drying cabinet with a stepwise temperature rise to 275°C and held there for 5 h.

1st impregnation version of the quartz ceramic samples. Samples at room temperature were placed in a beaker with impregnating solution that was hermetically sealed to avoid evaporation of Me_2CO. *2nd impregnation version*. Samples were heated beforehand to 55°C, placed into a beaker with impregnating solution, and hermetically sealed. *3rd impregnation version*. Samples heated to 55°C were placed into a heated solution and were held at 50 ± 15°C for 24 h after impregnation. *4th impregnation version*. It was analogous to the 1st but the temperature rise rate to the polymerization temperature was decreased by three times for better removal of gaseous products released during solidification of the resin. *5th impregnation version*. Impregnation was performed with ul-

TABLE 1. Properties of Samples of Quartz Ceramic NIASIT Before and After Impregnation and Polymerization

Parameter	Sample parameters					
	before impregnation	after impregnation by version				
		1	2	3	4	5
Bulk density, g/cm^3	1.98	2.04	2.03	2.05	2.04	2.01
Open porosity, %	9.47	0.03	0.02	0.04	0.04	0.04
Water absorption, %	4.76	0.01	0.01	0.02	0.02	0.02
Hermeticity Q_{He}, Pa·m^3/sec	—	2.1×10^{-5}	1.3×10^{-5}	6.5×10^{-7}	5.6×10^{-5}	1.2×10^{-3}
Dielectric constant	3.43	3.49	3.46	3.51	3.49	3.44
Dielectric loss tangent, 10^{-4}	5.0-7.0	3.0	3.0	2.0	2.0	2.0
Flexural strength, MPa:						
at 20°C	56 ± 8	63 ± 5	64 ± 5	59 ± 9	65 ± 7	72 ± 9
at 950°C	89 ± 1.3	106 ± 10	110 ± 2	118 ± 21	111 ± 2	10.7 ± 7
Color of light* passing through ceramic	W/l-y	Y/o	O/r	R/o	R/o	L-y/o

* W/l-y, from white to light-yellow; Y/o, from yellow to orange; O/r, from orange to red; R/o, from red to orange; L-y/o, from light-yellow to orange.

trasound irradiation, during which vigorous gas evolution was observed.

RESULTS AND DISCUSSION

Table 1 lists the initial properties of the ceramic and the properties obtained from the various impregnation versions with subsequent polymerization. The data indicated that impregnation of quartz ceramic NIASIT by MFSS-8 solution with subsequent polymerization reduced water absorption and porosity to null values. The dielectric constant practically did not change. The dielectric loss tangent decreased insignificantly. This confirmed the advantage of using the proposed method of moisture protection for radio-technical devices. It is noteworthy that, as a rule, impregnation strengthened the material. The results also confirmed this. It is known that a weaker initial ceramic can be strengthened more by introducing a polymer into its bulk.

The strength values at 950°C showed that the strengthening of the ceramic at high temperatures was also retained, despite chains in the polymer being destroyed at such temperatures. The density, porosity, and water absorption did not change and the strength and dielectric properties of the ceramic did not improve or worsen during the research on the various impregnation and polymerization versions. The differences in the obtained values were due to measurement error and possible structural differences of the individually selected samples.

An evaluation of the gas permeability of the samples using He permeation showed that samples prepared by the 3rd impregnation version (additionally dried at 50°C before polymerization) had the best hermeticity. This probably occurred because of redistribution of oligomers in the sample bulk and an increase of their concentration in the lower layer. This promoted the formation of a zone less permeable for He during the polymerization. The 5th impregnation version (ultrasound treatment), in which samples with the best light transmission were obtained, could also be noted. This indicated that they contained the least gaseous products. The version in which a heated matrix was impregnated turned out to be worst with respect to light transmission. The heated Me_2CO solution probably evaporated during this so that its viscosity increased and, as a result, filling of dead-end channels and capillaries by the solution was hampered.

CONCLUSION

The advantage of modification of the quartz ceramic by impregnation with a solution of MFSS-8 and subsequent polymerization for moisture protection and strengthening was confirmed.

The effects of several technological factors during impregnation and polymerization of the quartz ceramic by MFSS-8 solution on the final properties of the samples were investigated. They included impregnation of a heated matrix, preliminary drying of the impregnated ceramic before polymerization, a slow temperature rise to the maximum temperature for polymerization, and the action of ultrasound during impregnation. The results showed that the versions for modification did not substantially affect the density, porosity, water absorption, strength, and dielectric characteristics of the ceramic.

The observed changes in light transmission of the samples were interesting. Samples impregnated with ultrasonic irradiation had the best light transmission. This impregnation method could be used to prepared items with special optical characteristics.

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