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Thermophysical Properties of Glass-Ceramic Coatings of PbO–ZnO–B_2O_3 System Doped with Al_2O_3, SiO_2, and BaO Oxides

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The study of heat and electrophysical properties in the system 'stainless steel–glass-ceramic coating' is carried out. Insulating coatings based on the glass-ceramic material of the PbO–ZnO–B_2O_3 system are synthesized on stainless steel substrates. The temperature dependences of the dielectric loss tangent and dielectric constant of the obtained functional coatings are investigated. The heat capacity, thermal diffusivity and thermal conductivity of the coatings are investigated using a laser flash analysis. These properties are then compared to ones of the substrates. By the method of differential thermal analysis, the optimal modes of heat treatment of glass-ceramic coatings are established. An optimal material with the best electrophysical properties is revealed. Possibilities of using dielectric coatings as functional layers for film heating elements are analysed.

Key words: glass-ceramic material, insulating coatings, thermophysical properties, film heating element.

Проведено дослідження тепло- та електрофізичних властивостей в систе-

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мі «корозійнотривка сталь–склокерамічне покриття». На підкладках із корозійнотривкої сталі синтезовано ізоляційні покриття на основі склокерамічного матеріалу системи $PbO–ZnO–B_2O_3$. Досліджено температурні залежності тангенсу діелектричних втрат та діелектричної проникності одержаних функціональних покриттів. Методом лазерного спалаху досліджено теплоємність, температуропровідність та теплопровідність одержаних покриттів порівняно із аналогічними властивостями підкладок. Методом диференційного термічного аналізу встановлено оптимальні режими термічної обробки склокерамічних покриттів. Визначено оптимальний матеріал з найкращими електрофізичними властивостями Проаналізовано можливості використання діелектричних покриттів як функціональних шарів для плівкових нагрівних елементів.

Ключові слова: склокерамічний матеріал, ізоляційні покриття, теплофізичні властивості, плівковий нагрівний елемент.

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1. INTRODUCTION

Coatings and materials that contain metal oxides are widely used in various fields of science and technology [1–3], foundry [4–6], tools [7, 8], and medicine [9–11]. Metal oxides [12–14] and nanooxides [15] are introduced into their composition to improve the performance properties of functional coatings. Oxides are also introduced into the composition of electrode materials for surfacing coatings [16, 17]. Layered coatings with oxide layers allow to rationally combining the properties of these layers and the base, and are characterized by high wear resistance and corrosion resistance [18–20]. Such coatings are used in light filter designs [21], as well as for simultaneous protection of steel from wear and corrosion [22–24].

Works [22–24] studied the stress-strain state of layered oxide coatings under different load orientations, as well as with defects [25]. Researchers [26–28] studied heat transfer and heat transporting in layered materials and coatings for their rational design. The theoretical approaches proposed in [29–31] can also be applied to modelling and development of oxide systems.

Requirements for protective functional dielectric coatings depend on their operating conditions. Therefore, the coating should be chosen depending on the type of operating environment, the quality of a stainless steel surface, and the properties of the substrate material.

When forming an insulating layer, it is important to ensure that it is securely bonded to the substrate, as a failure of the continuity will reduce its operational reliability. This applies to dielectric coatings for film heating elements (FHEs) made using the technology of thick films, which operate continuously at elevated temperatures (150–

350°C). Such coatings shall not exfoliate from the substrate upon multiple heating from room to operating temperature. That is why the parameters of the thermophysical properties of functional coatings should be as close as possible to the properties of the substrate. During long-term operation, no phase transformations should occur in their structure, which would cause a change in the dielectric properties. Such coatings should be highly resistant to corrosive environments, and the structural and geometrical parameters of the surface microgeometry should be such as to provide a high-quality application of the resistive layer [32, 33].

Therefore, the study of heat and electrophysical properties in the system 'stainless steel–glass-ceramic coating' has been carried out. Temperature dependences of the dielectric loss tangent, dielectric permittivity and specific resistance of dielectric coatings based on the $PbO–ZnO–B_2O_3$ glass-ceramic system doped with Al_2O_3, SiO_2, and BaO oxides applied to AISI 420 stainless steel substrates are investigated.

2. MATERIALS AND RESEARCH METHODS

To prepare coatings based on the $PbO–ZnO–B_2O_3$ glass-ceramic system, mixtures of powders, the compositions of which are shown in Table 1, are used. Each mixture is poured into an allundial crucible and melted at 1180°C. After holding at this temperature for 60 min, the melt is rapidly cooled to form an amorphous structure and prevent crystallization. The dried granules are ground and sieved to obtain powder fractions with a granule size of not more than 56 μm.

A dielectric paste is prepared by adding 25–35% butyl acetate and 2–3% nitrocellulose lacquer to the powder mixture. The slurry is stirred for 2–3 hours in a vertical mill to form the appropriate molecular bonds between the particles. The resulting mixture is applied to a prepared sample surface of AISI 420 steel and dried at 70°C. For all specimens, the standard heat treatment [34] is performed with a two-step annealing at 380 and 440°C, with exposure at these temperatures for 45 min. The thermal treatment of the coatings is performed without a protective atmosphere to activate the formation of oxides.

TABLE 1. Chemical compositions of powders for the synthesis of the $PbO–ZnO–B_2O_3$ glass-ceramic system based coatings.

Marking	Chemical composition, % wt.					
	PbO	ZnO	B_2O_3	SiO_2	Al_2O_3	BaO
SC 100-1	75.5	12.0	8.4	2.1	2.0	–
SC 90-1	75.3	11.6	8.5	2.1	0.8	1.7
SC 88	75.1	11.2	9.4	1.9	–	1.9

The specific heat capacity, thermal conductivity and thermal diffusivity studies of the functional coatings with respect to the substrates are performed by the method of laser flash analysis in the temperature range from 0 to 500°C using Netzsch LFA-427 apparatus [33]. To improve the homogeneity of the crystal structure of the coating, the heat treatment modes are optimized using differential thermal analysis (DTA) of the initial powder mixtures.

The electrophysical properties of the formed insulating layers are evaluated by measuring the temperature dependences of the resistivity and dielectric characteristics in the 'heating-cooling' mode of the samples in a furnace at a rate of 4 ± 1°C/min in the temperature range of 20–300°C.

3. RESULTS AND DISCUSSION

For the synthesis of functional insulating coatings, the glass-ceramic materials of the PbO–ZnO–B_2O_3 system are doped with BaO, Al_2O_3, and SiO_2 compounds. These materials have high insulating properties when choosing the right technological process of application to the substrate [35–37]. The dielectric strength of such coatings is $(8–23)\cdot 10^6$ V/m, which satisfies the technological requirements for the production of dielectric layers of an FHE.

As substrates for insulating coatings, materials with minimal thermal expansion (AISI 420 steel, *etc.*) or high heat transfer rates, which will have no phase transformations in the operating temperature range of the heating element, are selected.

Functional coatings based on the PbO–ZnO–B_2O_3 glass-ceramic system are applied to the AISI 420 steel surface using a thick film technology. As this oxide system relates to fusible glass-ceramic cements, there are doubts about its use as an insulating coating for an FHE, which is operated at elevated temperatures. Glass-ceramic cements are devoid of the disadvantages of conventional amorphous glass materials. After spreading on the surface and crystallization, they form a solid crystalline structure typical of the sital.

As a result, their resistance to high temperatures increases sharply, because the viscosity of the original glass material is no longer responsible for this property, but the liquidus temperature of the crystalline material is responsible for it. The dilatometric softening temperature of SC 90-1 sealant in the amorphous state is 330°C, and in the crystalline state it is 480–500°C [34].

Doping the PbO–ZnO–B_2O_3 glass-ceramic system with Al_2O_3 and SiO_2 oxides reduces the ability to crystallize but at the same time increases the moisture resistance of the coatings. BaO oxide is introduced to improve the adhesive properties of the substrate with the coating [37].

As a result of the differential thermal analysis (DTA), the temperature dependences of the heat flux of the initial powders for the synthesis of glass-ceramic coatings SC 90-1, SC 100-1, SC 88, and SC 90 are obtained. It is found that the process of glass formation is accompanied by a small and short-term endothermic effect. Due to the crystallization of the glass material, a significant release of thermal energy is observed on the heat flux diagrams. The heat treatment temperatures are determined depending on the slope angle of the thermal effect curve (Fig. 1), which indicated the phase transformations in the coatings due to the release or absorption of thermal energy (ΔH).

The heat treatment process started with heating from room temperature. For each of the grades of sealant powders, the temperature of the beginning of the glass softening process and the temperature of the onset of crystal growth (crystallization) are determined, which are shown in Table 2. To make the coating structure homogeneous, the

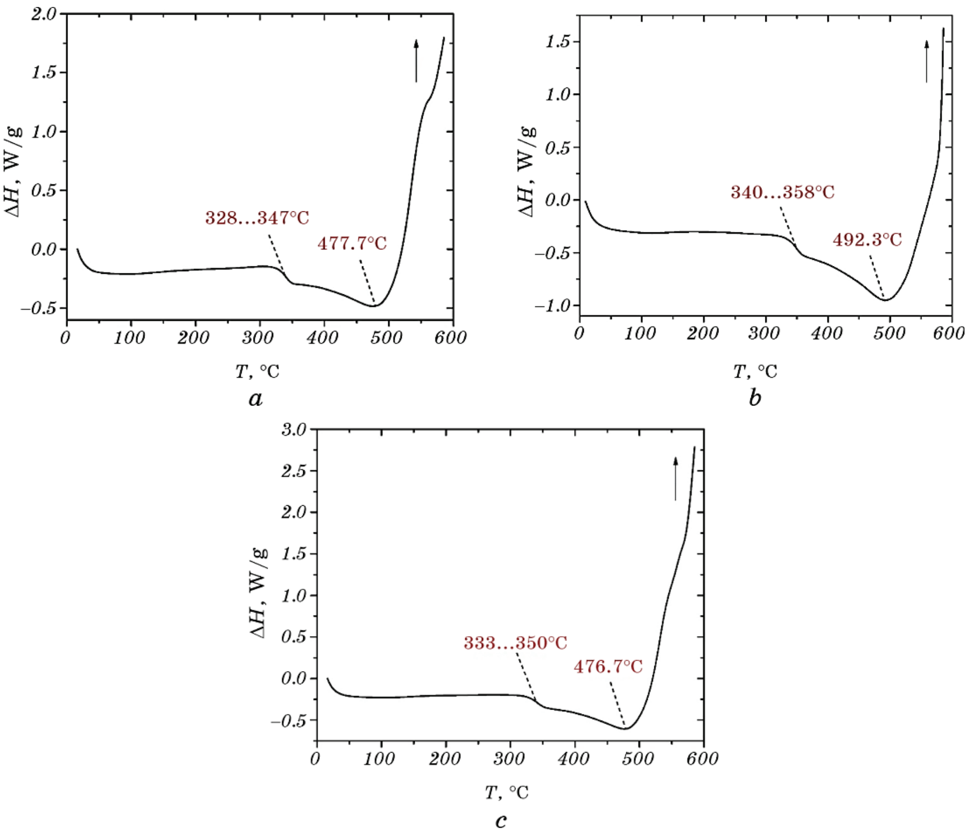

Fig. 1. Diagrams of changing the heat flux in coatings based on glass-ceramic materials of grades SC 90-1 (*a*), SC 100-1 (*b*), and SC 88 (*c*).

TABLE 2. Heat treatment modes for the coatings based on the $PbO–ZnO–B_2O_3$ glass-ceramic system.

Marking	Heat treatment mode			
	The temperature of glass formation t_1, °C	Holding at the temperature of glass formation $\tau_2 - \tau_1$, min	The crystallization temperature t_2, °C	Holding at the crystallization temperature $\tau_2 - \tau_1$, min
SC 100-1	378	45	492.3	60
SC 90-1	367	45	477.7	60
SC 88	370	20	476.7	45

glass formation temperature is raised by 15–20°C. The duration of isothermal holding and the rates of heating and cooling are set experimentally.

Dilatometric measurements showed that the softening temperature of glass-ceramic materials based on the powders of SC 90-1, SC 100-1, SC 88, and SC 90 grades in the amorphous state is approximately 330°C, while in the crystalline one it is 470–500°C. This allows obtaining on the surface of these coatings a resistive layer for an FHE whose synthesis temperature will not exceed the liquidus temperature (550–590°C) of the crystallized coating material.

To compare the thermokinetic properties of the obtained dielectric layers and substrates, their thermal diffusivity and thermal conductivity are studied in the temperature range 0–500°C. Formed coatings based on glass-ceramic materials of grades SC 90-1, SC 100-1, and SC 88 have a high affinity of values of specific thermal conductivity and thermal diffusivity with the substrate, which will ensure the stability of heat transfer from the resistive coating to the substrate of an FHE [33].

Dielectric losses are known to cause dielectrics to heat up, which can lead to accelerated aging or thermal breakdown, especially if the dielectric losses are related to electrical conductivity [38]. Thus, when selecting a material during the design of an FHE, it is necessary to estimate the dielectric losses that may occur under these specific operating conditions. Besides, the dielectric loss is an indicator of the change in the microstructure of the dielectric.

In all materials in the studied frequency range (10^2–10^5 Hz), the tangent of the dielectric loss angle tgδ decreases according to the hyperbolic law in the range from 0.35 to 0.0001 (Fig. 2). Besides, at low frequencies in the temperature range of 20–300°C, there is a tendency for the formation of maxima and minima in values of tgδ with increasing temperature, which indicates the presence of a mechanism of relaxation polarization of the dielectric due to the change in the polarity of current carriers at the boundaries of structural defects (pores). The increase in the intensity of relaxation processes in coatings based on powder SC 88 indicates an increase in the number of charged particles at the interface between the main coating material and structural defects. This factor indirectly indicates the increase in the volume fraction of pores in the structure of the synthesized coatings. The increase in the number of defects in coatings based on powder SC 88 can be explained by the decrease in the temperature interval between the beginning of the glass formation process (t_1) and the crystallization process (t_2) due to the absence of refractory Al_2O_3 oxide in their compositions.

It is found that the coating material based on SC 90-1 powder, which is doped simultaneously with the oxides of barium (1.7%), silicon (2.1%), and aluminium (0.8%), does not create relaxation processes at low frequencies and temperatures of 25–250°C. This indicates a minimal number of structural defects (pores, dendritic liquations) in the volume of the synthesized coating. This is substantiated by quantita-

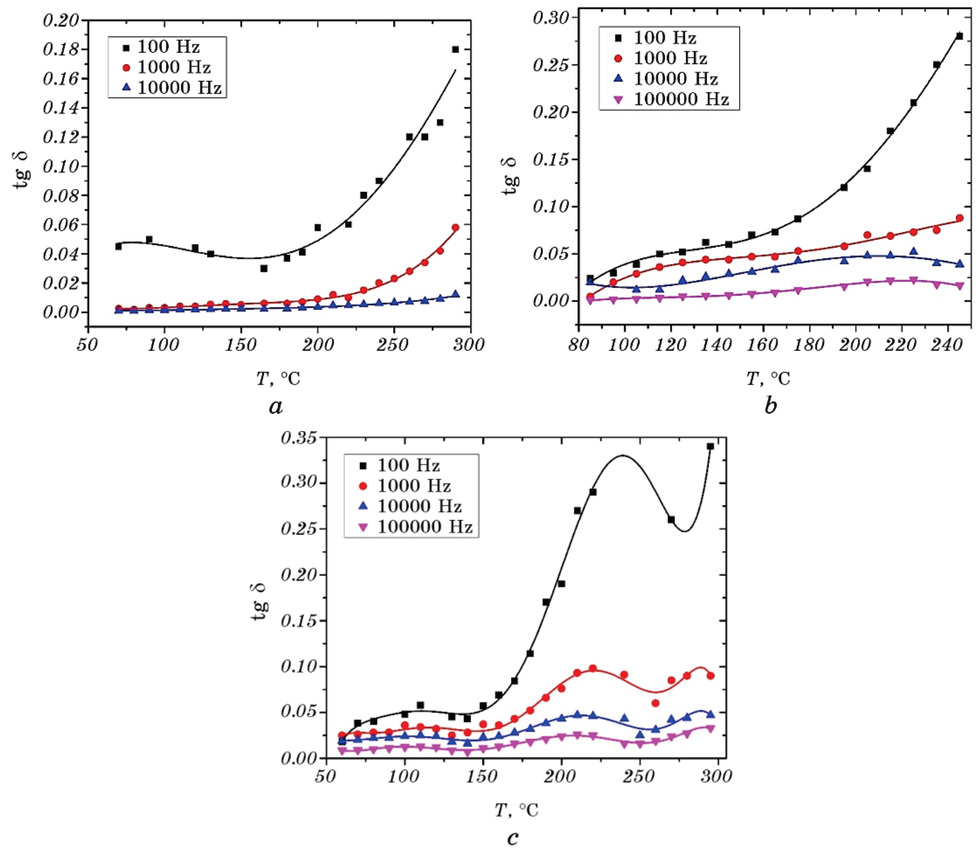

Fig. 2. Temperature dependences of the dielectric loss tangent of coatings based on glass-ceramic materials of grades SC 100-1 (*a*), SC 90-1 (*b*), and SC 88 (*c*).

tive microstructural analysis of coatings [32]. It should be noted that the values of the dielectric permittivity of the synthesized coatings decrease with increasing frequency range (10^2–10^5 Hz) (Fig. 3).

The decrease in the dielectric permittivity, in this case, is caused by electronic or ionic thermal polarization, whose dielectric contribution is usually quite small (10^{-3}–10^3). The increase of the dielectric permittivity in the temperature range of 20–300°C is caused by rapid polarization processes and practically independent of frequency. Instead, the dielectric loss tangent (tgδ) and the dielectric loss coefficient decrease with increasing frequency.

The absence of extrema on the curve of changing the dielectric permittivity of the coating based on the powder of SC 90-1 grade indicates the absence of any microstructural changes in the studied temperature range, which will ensure the stable operation of the dielectric.

To evaluate the efficiency of dielectric coatings at high tempera-

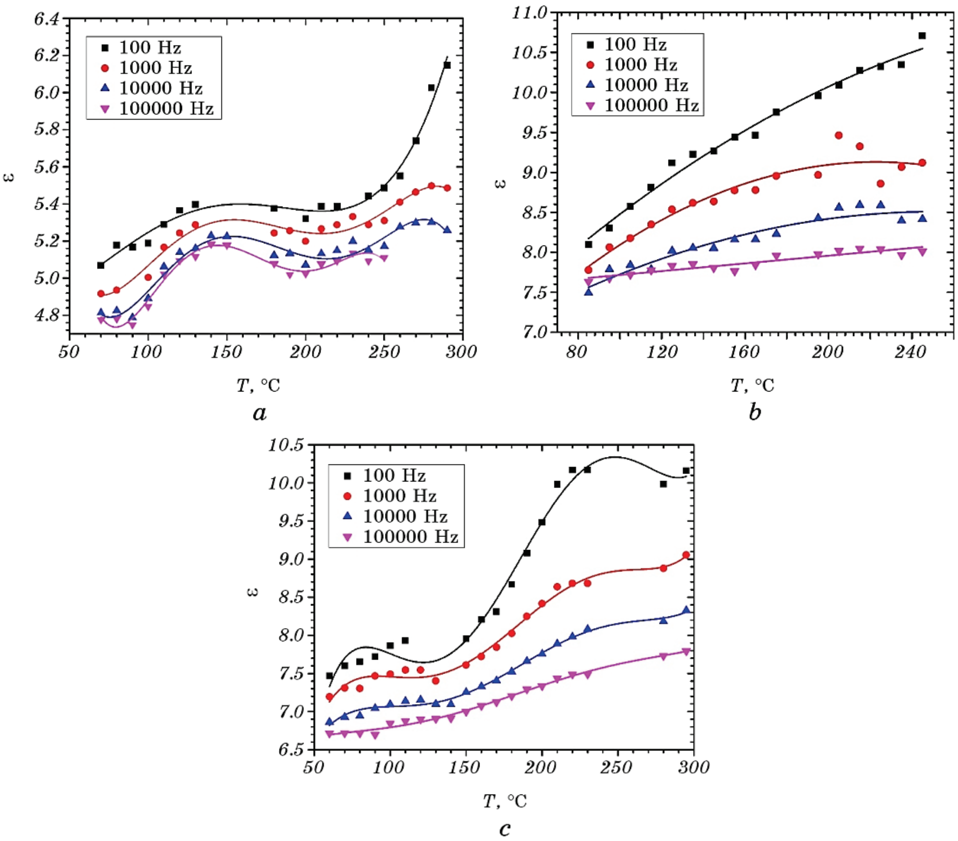

Fig. 3. Temperature dependences of the dielectric permittivity of coatings based on glass-ceramic materials of grades SC 100-1 (*a*), SC 90-1 (*b*), and SC 88 (*c*).

tures, the dielectric loss coefficient $\varepsilon'' = \varepsilon' \mathrm{tg}\delta$ is calculated. With increasing temperature, in coatings based on glass-ceramic materials of grades SC 90-1, SC 100-1 and SC 88, there is an overall tendency of increasing the dielectric loss coefficient over the whole temperature range of 20–300°C. The temperature dependences of tgδ and the dielectric loss coefficient increase exponentially with the temperature increase since the conductivity also changes according to this law. The electrical conductivity makes a significant contribution to changing the dielectric loss of synthesized coatings at high temperatures and low frequencies. Due to the absence of relaxation processes in the coatings based on SC 90-1 powder, the synthesized coatings will have a slight scattering of the dielectric loss values, which will increase the stability of the insulator during its operation.

Like electric polarization, the charge transfer in the dielectric occurs mainly under the influence of the electric field, but only a small fraction of free electric charges contribute to the conductivity characteristic of the dielectric, whereas polarization is the displacement in the electric field of all related dielectric charges. However, in an alternating electric field, these processes are almost indistinguishable.

Thus, it is found that the values of the specific resistance of coatings based on glass-ceramic materials of grades SC 90-1, SC 100-1, and SC 88 decrease with increasing temperature in the range of 20–300°C. Moreover, at room temperature the specific resistance of all coatings varies within $5\cdot10^{10}$–$5\cdot10^{11}$ Ω·m, whereas at temperatures 150–200°C it is $5\cdot10^{8}$–$1\cdot10^{10}$ Ω·m. Changing the slope angles of linear dependences of the change of the specific resistance at low and high temperatures indicates a change in the nature of the electrical conductivity [38, 39].

Given that the average operating temperature of an FHE is 160–190°C, it can be argued that insignificant dielectric losses and a decrease in the specific resistance of the synthesized dielectric coatings will not significantly affect the reliability and safety of the heating device as a whole.

4. CONCLUSIONS

The glass-ceramic coatings of the $PbO–ZnO–B_2O_3$ system on the surface of AISI 420 steel have been synthesized. The thermal and electrophysical properties of the obtained dielectric coatings after doping with Al_2O_3, SiO_2, and BaO oxides are investigated. It is shown that the $PbO–ZnO–B_2O_3$ glass-ceramic coatings doped simultaneously with the oxides of 2.1% wt. SiO_2, 0.9% wt. Al_2O_3, and 2.1% wt. BaO have an optimal complex of electrophysical properties, which will allow their use as insulating material in electronics and electrical engineering at operating temperatures up to 250°C.

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