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INFLUENCE OF HEAT TREATMENT MODES ON THE PERFORMANCE CHARACTERISTICS OF RESISTIVE CERMET COATINGS

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Abstract. Dielectric and resistive coatings based on glass ceramics with nickel boride additives have been synthesized. It was found that the microstructure of the resistive coating consists of a large number of phases. X-ray fluorescence analysis revealed the presence of Ni and Cr borides in the structure of the resistive layer. It was found that the change in the structure and specific surface resistance of resistive pastes practically does not affect the temperature coefficient of resistance of the synthesized resistive tracks.

Keywords: film heating element, cermet, microstructure, glass-ceramic, coating.

Introduction

In the context of an increasing shortage of natural energy carriers, the use of electric current as a source of thermal energy is becoming increasingly important. One of the problems is the development of an environmentally friendly, low-inertia electric heater for heating premises, mobile railway and urban electric transport. Now the technology for the production of flat heating elements is expensive, low-performance, energy-intensive and is based on the method of multiple screen printing followed by complex thermal treatment of functional layers. The dielectric and resistive pastes used in this process are made on the basis of precious metals. The article analyzes alternative technologies for the manufacture of flat heating elements using surface engineering methods [1].

Given the high chemical and thermal stability, the material for the resistive coating is used brand PRN paste (Paste-Resistive-Nickel). PRN pastes are made by adding nickel borides (NiB) to the glass-ceramic composition of the $BaO\text{-}SiO_2\text{-}ZnO$ system. The resistive coating was applied to a glass-ceramic surface obtained from steel. Steel in the annealed state does not have structural and phase changes during cyclic heating and cooling in the temperature range of 25–450 °C, and is also resistant to corrosion under atmospheric conditions. The thermal expansion coefficient of 430 steel is $10.4 \cdot 10^{-7}\ K^{-1}$, and glass-crystalline materials based on the $BaO\text{-}SiO_2\text{-}ZnO$ system ($10 \cdot 10^{-7}\ K^{-1}$) are close in value to the thermal expansion coefficient, which eliminates the possibility of delamination coating from the substrate [2].

Problem Statement

Development of a ceramic resistive material based on nickel and chromium borides. Establishing the possibility of regulating the operational characteristics of film heating elements (power, resistance) by changing the modes of thermal operation.

Experimental Approach

For the deposition of resistive coatings, we used special paste-like suspensions on a ceramic basis (BaO-SiO_2-ZnO) with the addition of fine powders of nickel and chromium borides. A resistive coating was applied to a glass-ceramic surface obtained on steel grade 12X17. Steel in the annealed state has no phase changes during cyclic heating-cooling in the temperature range of 25–450 °C, and is corrosion-resistant under atmospheric conditions. The TCLE of 12X17 steel is $10.4 \cdot 10^{-7}\ K^{-1}$ and is close in value to the TCLE of glass-crystalline materials based on the BaO-SiO_2-ZnO system ($10 \cdot 10^{-7}\ K^{-1}$), which eliminates the possibility of delamination of the coating from the substrate [3]–[5].

For glass-crystalline systems BaO-SiO_2-ZnO, a standard heat treatment is used, which consists in holding at the temperatures of the onset of crystallization. To reduce the exposure time, the heat treatment temperature is increased. Such a mode of heat treatment ensures obtaining a high-quality homogeneous coating, the surface of which does not require finishing machining [6].

For thermal treatment of glass-ceramic coatings, preliminarily applied by screen printing, industrial tunnel furnaces of the PEK-8 type with an OVEN TRM 148 control unit were used. The 5-meter-long PEK-8 tunnel furnace allows annealing of samples in eight different temperature zones (Fig. 1). To achieve the appropriate structure, the optimal modes of thermal treatment of coatings were experimentally established, which consist in annealing at different temperatures depending on the furnace zone: (T_1 = 485 °C, T_2 = 600 °C, T_3 = 696 °C, T_4 = 773 °C, T_5 = 780 °C, T_6 = 780 °C, T_7 = 685 °C, T_8 = 568 °C). The holding time of the insulating coatings during heat treatment was 1 hour. For resistive coatings, similar temperature conditions of heat treatment were used, and the exposure was 1 and 1.5 hours.

Fig. 1. Heat treatment process of insulating coatings in a furnace PEK-8 [7]

To study the structure of the formed surface layers, metallographic analysis was carried out according to the standard technique on a MICROTECH® MMT-14Ts microscope using the TopView software.

The determination of the elemental composition by X-ray fluorescence analysis was carried out on an X-ray spectrometer SER-01 “ElvaX Light”. ElvaX Light SER-01 is a modification of the ElvaX spectrometer with an extended range towards light elements.

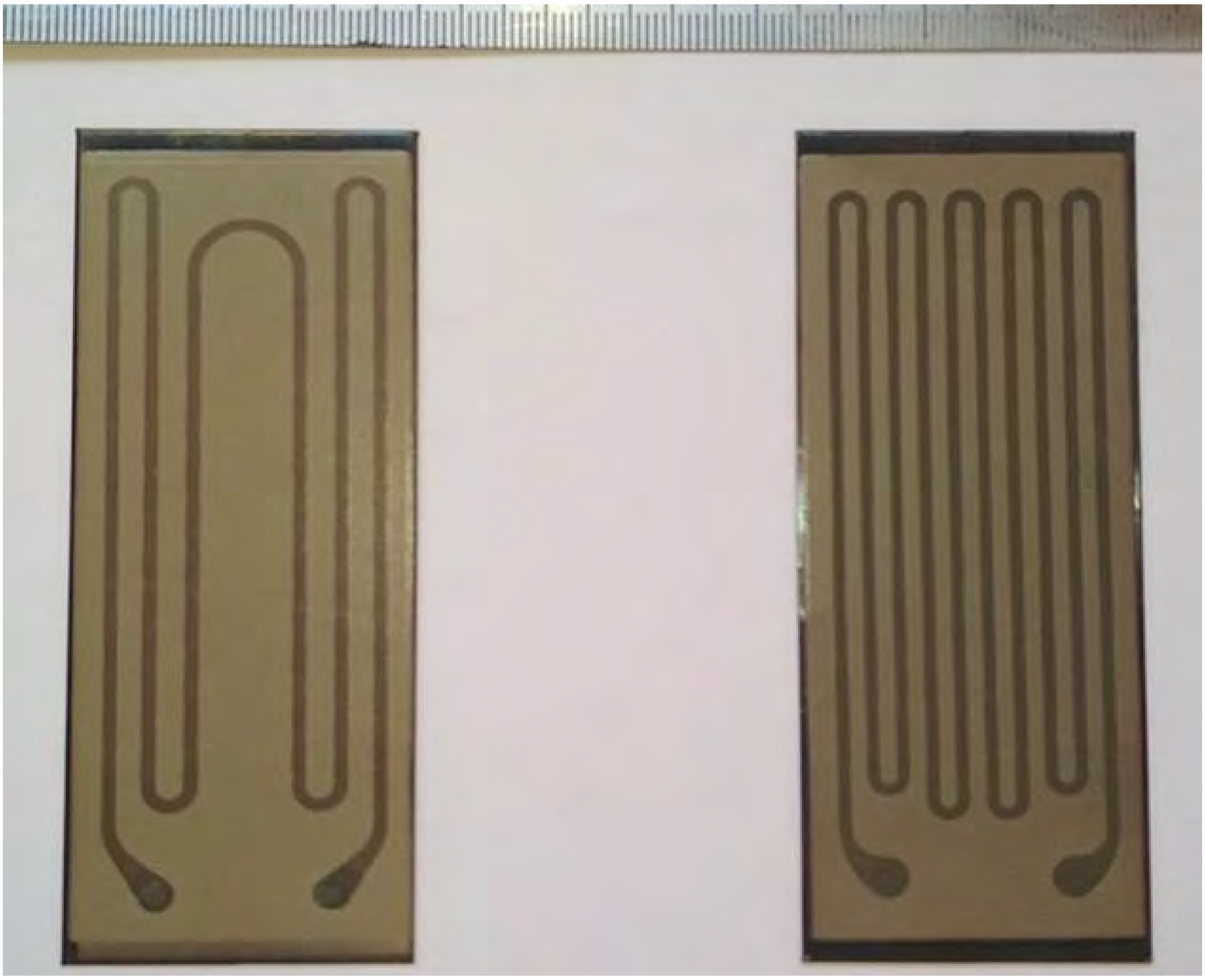
Investigations of the microhardness of coatings after annealing on NOVOTEST TC-MKV1 Microhardness testers. The principle of operation of this device is identical to the principle of operation of the Vickers hardness tester.

The resistance of resistive coatings was measured in the temperature range of 20–300 °C using a high-precision Schneider Electric Thorsman category 3 multimeter.

Main Material Presentation

Glass-ceramic insulating coatings were synthesized on the surface of 12X17 steel. The thickness of the coatings was 130–150 µm.

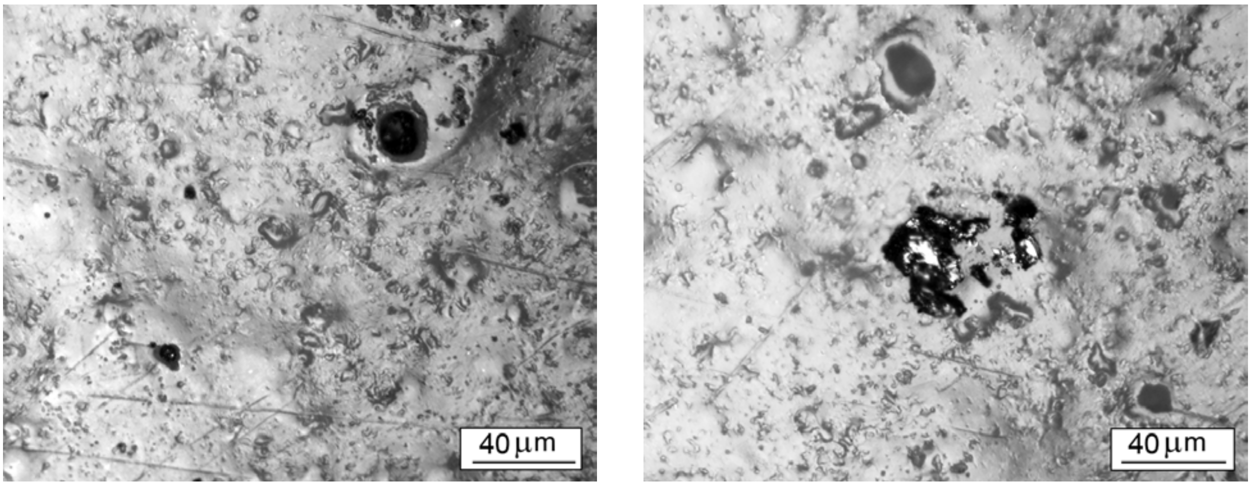
Resistive tracks on a ceramic base (BaO-SiO_2-ZnO) were synthesized on the surface of a glass-ceramic coating with the addition of fine powders of nickel and chromium borides [8]. The surface of the resistive track is smooth, dark gray. No visible macrostructural defects were found after the synthesis of the tracks. For the rubber tracks shown in Fig. 1 applied a different exposure during the processing time: 1 hour (Fig. 2, *a*) and 1.5 hour (Fig. 2, *b*).



a *b*

Fig. 2. Film heating elements with different nominal resistance at room temperature:
a – 80 Ohm at 20 °C; b – 280 Ohm at 20 °C

The microstructure of the obtained coatings was investigated using an optical microscope after polishing the samples. It was found that the volume of the dielectric coating contains a large number of pores of various sizes, unevenly distributed on the surface of the samples (Fig. 3, *a*). The formation of pores can be explained by the completed process of sublimation of organic solvents (terpeniol), which contain coatings before heat treatment at temperatures of 700–800 °C. As a result of the heat treatment, a crystal-amorphous structure is obtained. The amorphous structure due to its high brittleness will be wicked during polishing, as shown in Fig. 3, *b*.

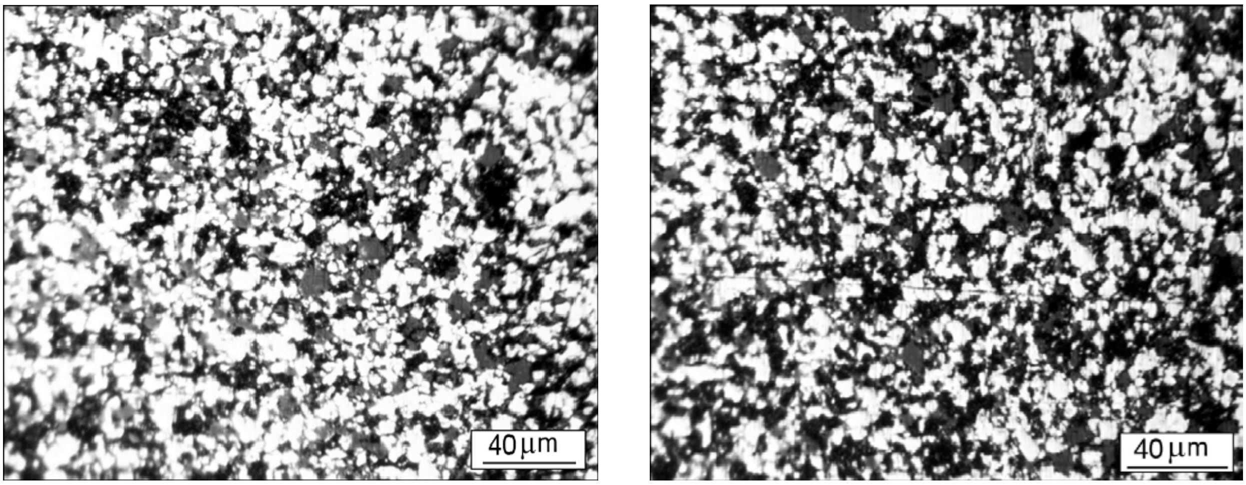


a *b*

Fig. 3. Microstructure of insulating coatings

It was found that the microstructure of the resistive coating consists of a large number of phases. Dark areas on the microstructure indicate the presence of crystal amorphous glass ceramics in the volume of the resistive layer. The light areas are the leading structure consisting of two or more phases (Fig. 4).

The Vickers microhardness of the leading phase was measured. The measurements were carried out at loads of 0.0098–0.49 N. The value of the microhardness of the resistive layer varied in the range 77–345 HV. Such a large difference in the microhardness values indicates that the resistive layer has a high-phase nature.



a *b*

Fig. 4. Microstructure of resistive coatings: a – 80 Ohm at 20 °C; b – 280 Ohm at 20 °C

To establish the elemental composition of the obtained insulating and resistive coatings, X-ray fluorescence analysis was carried out. It was found that the synthesized insulating materials created on the basis of oxides BaO, ZnO and SiO_2 (Table 1). The presence of oxides MgO, MnO_2, CuO was also found, which are added to the coating structure for better adhesion of coatings to the substrate and activation of crystallization processes during heat treatment. The very crystalline structure of the coating provides an appropriate level of electrical insulating properties at high temperatures. It was found that the resulting glass-ceramic coating belongs to Celsian ceramics.

X-ray fluorescence analysis of resistive coatings showed the presence of elements Ni and Cr in the structure (Table 2). The glass-ceramic fraction of the coating was not taken into account in the analysis.

Taking into account the fact that the spectrometer SER-01 "Elvax Light" does not make it possible to assess the presence of boron in the material, it can be assumed that Ni and Cr form borides.

Table 1

Chemical composition of the synthesized insulation coating obtained by X-ray fluorescence analysis

Atomic number of the oxide element	Chemical compound	Concentration, at. %
56	BaO	44.304 ± 0.113
14	SiO_2	9.862 ± 0.064
30	ZnO	9.148 ± 0.037
12	MgO	3.949 ± 0.110
25	MnO_2	3.295 ± 0.042
29	CuO	1.558 ± 0.013
26	Fe_2O_3	0.789 ± 0.017

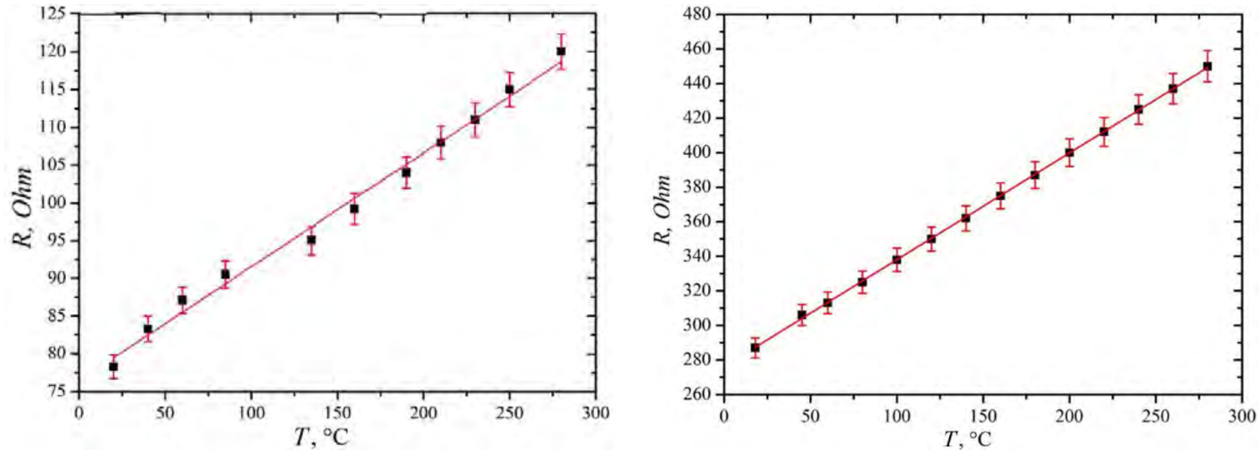
Table 2

Elemental composition of the synthesized resistive coating obtained by X-ray fluorescence analysis

Atomic number of element	Element	Concentration, at. %
28	Ni	92.4510 ± 0.0481
24	Cr	7.2391 ± 0.0485
26	Fe	0.3100 ± 0.0174
12	Mg	< 0.0001
13	Al	< 0.0001
14	Si	< 0.0001

To establish the temperature coefficient of resistance of the obtained resistive materials, the resistance of the tracks was measured in the temperature range of 25–300 °C (Fig. 5). With an increase in temperature, the resistance of the tracks synthesized on the basis of pastes increases linearly [9].

It has been established that an increase in the duration of exposure during heat treatment of coatings leads to a decrease in the resistivity of resistive coatings. The specific resistance of the coatings after exposure for 1.5 hours was 8–11 % less in comparison with exposure for 1 hour.



a *b*

Fig. 5. Influence of temperature on resistance of resistive tracks: a – 80 Ohm at 20 °C; b – 280 Ohm at 20 °C

The linear dependence of the change in resistance on temperature allows you to calculate the temperature coefficient of resistance of the resistive tracks. It was found that the change in the structure and specific surface resistance of resistive pastes has practically no effect on the temperature coefficient of resistance of the synthesized resistive tracks (0.00207–0.00210 K^{-1}). This allows the use of resistive nickel-boron pastes in a wide range of specific resistances.

Conclusions

Dielectric and resistive coatings on a glass-ceramic base with the addition of nickel borides were synthesized on the surface of 12X17 steel. The thickness of the dielectric coatings was 130–150 μm, and the thickness of the resistive track was 40–60 μm.

It was found that the microstructure of the resistive coating consists of a large number of phases. The presence of crystal amorphous glass ceramics in the volume of the resistive layer is indicated by dark areas on the microstructure. The light areas are the leading structure consisting of two or more phases.

It has been established that an increase in the duration of exposure during heat treatment of coatings leads to a decrease in the resistivity of resistive coatings. The specific resistance of the coatings after exposure for 1.5 hours was 8–11 % less in comparison with exposure for 1 hour.

To establish the temperature coefficient of resistance of the obtained resistive materials, measurements were carried out in the temperature range 25–300 °C. It has been established that changes in the structure and specific surface resistance of resistive pastes have practically no effect on the temperature coefficient of resistance of the synthesized resistive tracks. This allows the use of resistive nickel-boron pastes in a wide range of specific resistances.

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