

## SINTERED METALS AND ALLOYS

### CONDUCTIVE FILM MATERIALS BASED ON THERMALLY STABLE FLUORINE-CONTAINING POLYAMIDE AND NICKEL BORIDE

A. V. Paustovskii,<sup>1</sup> B. M. Rud',<sup>1</sup> V. E. Shelud'ko,<sup>1,5</sup> E. Ya. Tel'nikov,<sup>1</sup>  
N. I. Siman,<sup>1</sup> P. S. Smertenko,<sup>2</sup> V. V. Kremenitskii,<sup>3</sup>  
and Yu. I. Bogomolov<sup>4</sup>

UDC 541.64:542.954:539.216.

*The development of resistor materials science and, namely, the feasibility of developing a composite film material based on the thermally stable polyamide and nickel boride as current-conducting filler, is considered. A process for producing films is developed: the films are obtained by coating the glass substrate with polymer solution with a pre-dispersed filler, followed by forming at 80 °C with subsequent drying at 150 °C until constant weight. The microstructure and topography of the film surface is studied by SEM and AFM. The formation of two-layer composite with the formation of conducting cluster (when the content of the conducting phase is >30 wt.%) from the substrate side is shown. Volt-amps diagrams are studied and analyzed by the differential method. The R(T) dependence is obtained and the temperature resistance coefficient is determined; the latter is positive and its value is  $1.67 \cdot 10^{-3} \text{ }^{\circ}\text{C}^{-1}$ .*

**Keywords:** polyamide matrix, filler, nickel boride, conductivity, volt-ampere characteristics, temperature resistance coefficient.

#### INTRODUCTION

Conducting polymer materials are complex heterogeneous systems where fine conducting phase (CP) is distributed in the polymer matrix [1–4]. Due to low price and chemical inertness [5], the most common coal-graphite fillers are carbon black and graphite. Recently, the electrical and physical properties of polymers filled with ultrafine particles, such as carbon nanofibers and nanotubes, are intensively studied [6–8].

Since low operating temperature is the major deficiency of conductive polymer systems, thermally stable polymers (such as polyimides, aromatic polyamides, polyester maleimides, etc.) are the most commonly used as polymeric matrix [9–11].

<sup>1</sup>Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Kiev, Ukraine. <sup>2</sup>Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine. <sup>3</sup>The Technical Center, National Academy of Sciences of Ukraine, Kiev, Ukraine. <sup>4</sup>The Institute of Bioorganic Chemistry and Petrochemistry of the National Academy of Sciences of Ukraine, Kiev, Ukraine.

<sup>5</sup>To whom correspondence should be addressed; e-mail: dep65@ipms.kiev.ua.

It should be noted that the technology for producing the above composites is complicated by the stages of long-lasting pre-dispersing of components followed by hot cure and pressing. For example, polypropylene matrix-based composites [6–8] are produced by the melting technology: at first, the components are mixed in a twin-screw mixer at 200°C for 5 min and, then, the fibers are formed through the heated microholes. Polyimide- and carbon black-based composites [9] also undergo the stage of mixing of the filler with polyamide acid followed by high temperature dehydration at 300°C for 1 h. The thermal treatment of pressed samples is foreseen during the formation of epoxy composites with graphite and kaolin ( $T = 250\text{--}270^\circ\text{C}$ ,  $t = 8\text{--}12$  h) and, also, with carbon nanofibers in the presence of hardener at 50°C for 12 h [7, 9]. Similarly, hot pressing and sintering are the necessary stages for producing filled composites based on aromatic polyamides or polytetrafluoroethylene [10, 12]. A film resistive heating element based on the maleimide ether binder has been developed [11]. Different types of carbon black and graphite were used as CP. The heating element is formed at  $T = 200^\circ\text{C}$  for 20 min in a conveyor furnace, then the obtained conductive layer is protected with silicone lacquer.

The above examples show that the production of filled composites generally requires long-time dispersion, hot-pressing, and thermal treatment. Less time-consuming is the production of conductive cellulose-ether materials by coating the substrate with graphite suspension in cellulose acetate solution [13].

It is equally important to select CP components combining optimal electrical and physical characteristics with availability and relatively low price, compared to precious metals used in resistor production. Such fillers include borides of refractory metals, which are used as CP in conductive and resistive pastes [14]. Thick-film heaters, resistors, and other passive components of hybrid integrated circuits are manufactured on their basis using the screen-printing technique of the pastes [15]. The necessary stage of the thick-film technology is a high-temperature firing of the paste (consisting of CP and glass binder) deposited on the dielectric substrate (alumina ceramics, glass ceramics or enameling steel) [15]. For example, the temperature of firing  $\text{Ni}_3\text{B}$ - or  $\text{LaB}_6$ -based pastes is  $\sim 800^\circ\text{C}$  [16, 17].

The studies [18, 19] have investigated some properties of nickel boride  $\text{Ni}_3\text{B}$ , which is used as CP for producing thick-film heating elements, due to the metallic behavior of its conductivity [20]. The study [21] has described how to obtain  $\sim 36$  wt.%  $\text{Ni}_3\text{B}$ - and phenol formaldehyde-based pastes as a low-temperature treated dielectric matrix ( $157^\circ\text{C}$ ). A quadratic temperature dependence of electrical resistivity  $R(T)$  in the 213–333 K temperature range was established; the temperature resistance coefficient (TRC) being  $(4\text{--}7) \cdot 10^{-3} \text{ K}^{-1}$ .

The purpose of this study is to assess the feasibility of forming the films based on thermally stable polymer matrix (fluoroplastics) and  $\text{Ni}_3\text{B}$  powder, as CP, and to examine the electrical and physical properties of the composite films produced.

## MATERIALS AND EXPERIMENTAL PROCEDURE

The polymer matrix was fluorine-containing aromatic polyamide (AP): poly-1-tetrafluoroethoxy-2.4-phenyl-eneisophthalamide [22], which is Phenylone™ modified by the tetrafluoroethoxy group. Figure 1 shows its chemical structure. The following physical and chemical properties are typical for fluorine-containing AP [22]:

Point of destruction, °C. . . . .	390
Density, g/cm <sup>3</sup> . . . . .	1.484
Tensile strength, MPa. . . . .	117–127
Volume resistivity, $\Omega \cdot \text{cm}$ . . . . .	$2.7 \cdot 10^{14}$
Dielectric dissipation factor, $\times 10^3$ Hz. . . . .	0.0086
Dielectric strength, kV/mm. . . . .	200
Freezing resistance, °C. . . . .	–196

Typical for polyfluorinated radicals, the hydrophobic effect contributes to the reduction of moisture absorption and the increase in dielectric characteristics of polyamide. Composite films were obtained through preliminary mechanical (SilentCrusher S disperser, Heidolph Instruments GmbH & Co. KG, Germany; number of revolutions  $n = 75000 \text{ min}^{-1}$ ,  $t = 1.5$  min) or ultrasound (UZDN-2T, NPP Akadempribor, Ukraine; operating frequency  $\nu = 22$  kHz) dispersing of the  $\text{Ni}_3\text{B}$  powder (TU 06664-86, specific surface area  $S_{\text{sp}} = 0.15\text{--}0.25 \text{ m}^2/\text{g}$ )

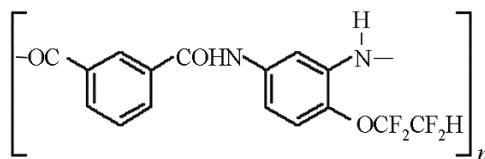


Fig. 1. Polyamide chemical structure

in 5% polyamide solution (DMFA solvent: dimethylformamide) and forming the film at 80°C (on a glass former) for 3 h with subsequent drying at 150°C till the mass is constant. The amount of filler was 30, 40, and 80 wt.% of the polymer charge, which was constant in all cases, which allowed forming up to 100 μm thick films (averaging 75–80 μm).

Thermal and mechanical research was conducted under a load of 2 MPa and a heating rate of 6 deg/min. The structure of conductive layers was studied using a JEOL JSM-6490 LV scanning electron microscope (JEOL Ltd., Japan), while the surface morphology of composite films was examined using a NT-206 atomic force microscope (ODO Mikrotestmashyny, Belarus) in static mode.

Volt-amps characteristics (VAC) were determined during bench test using a 14TKS-100 automated tester (JSC Test Technical Center NPO PM, Russia). The voltage was increased step by step at 150 msec intervals for each step and the measuring time of 90 msec. The subsequent data processing was carried out using the differential method [23].

Temperature dependences of electrical resistivity were measured using a computer-assisted installation by the amperemeter-voltmeter method. An UT70D multimeter (UNI-T, China) with RS-232 interface was used as a measuring and interface instrument. To reduce errors in determining  $R$  caused by the nonohmicity of contacts, the survey current passed through the sample in two directions. The accuracy of measurement of the electric potential drop between measuring probes amounted to 1 μV. During measuring, the temperature of the sample was supported using a RIF-101 precision software heat regulator. The residual gas pressure in the working chamber of the installation was ~2.67–4.00 Pa.

## RESULTS AND DISCUSSION

Figure 2 show the thermal–mechanical curves of the composite films. Adding 80 wt.% Ni<sub>3</sub>B (compared to 40 wt.%) increases the temperature when the composite begins to deform. Thus, even with so much filler, the strain strength of the composite remains high enough and, therefore, this very sample has been selected for further research.

The determination of surface resistivity has revealed that the top layer of the film is dielectric and the conductive layer is that on the substrate side. Figure 3a shows a secondary-electron microscope image of the microstructure of the conductive layer. Conductive layer is a composite with Ni<sub>3</sub>B grains (0.1–5.0 μm) evenly distributed in the polymer matrix (Fig. 3b).

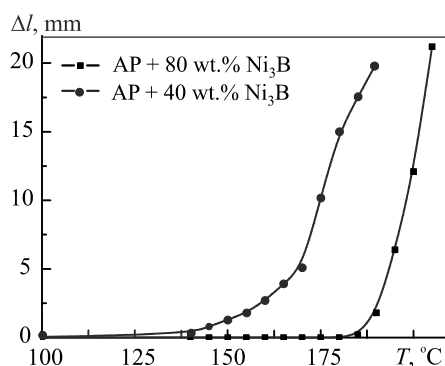


Fig. 2. Variation of the film relative elongation  $\Delta l$  with temperature under 2 MPa

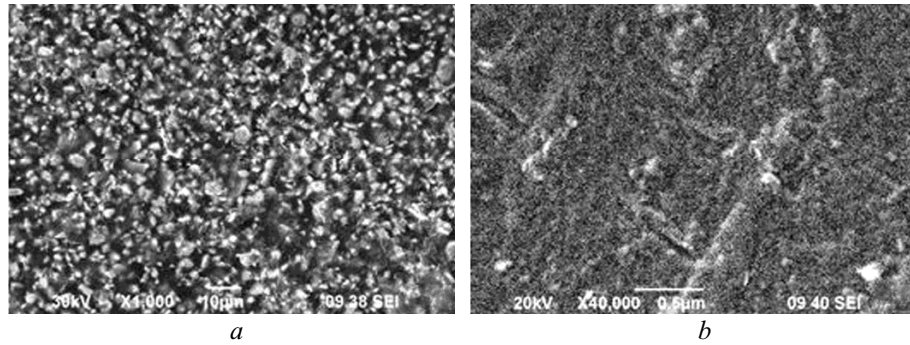


Fig. 3. Microstructure of conductive layer (a) and polymer matrix (b) in 80 wt.% Ni<sub>3</sub>B composite

Figure 4 shows 2D topography, cross-section 1–2 of the upper surface of the composite, and 3D image obtained using the atomic force microscope. This surface roughness was  $R_a = 3.0$  nm, and the width of individual pimples varied from 14 up to 16.7 nm.

The topography (2D, 3D) of the surface on the substrate side indicates the sedimentation of Ni<sub>3</sub>B on the substrate during forming that leads to greater film surface roughness ( $R_a = 100$  nm) on the substrate side (Fig. 5). Pimples up to 800 nm in height and 9.7–18.5 µm wide dimples are observed on such surface.

Also, CP sedimentation has been established, when examining the microstructures of the cross-section of composites, as evidenced by the occurrence of conductivity of the thick film on the substrate side at different CP contents. A good example is the microstructure of the cross-section of 80 wt.% CP composite (Fig. 6), confirming the formation of conductive layer on the substrate side resulting from the Ni<sub>3</sub>B sedimentation.

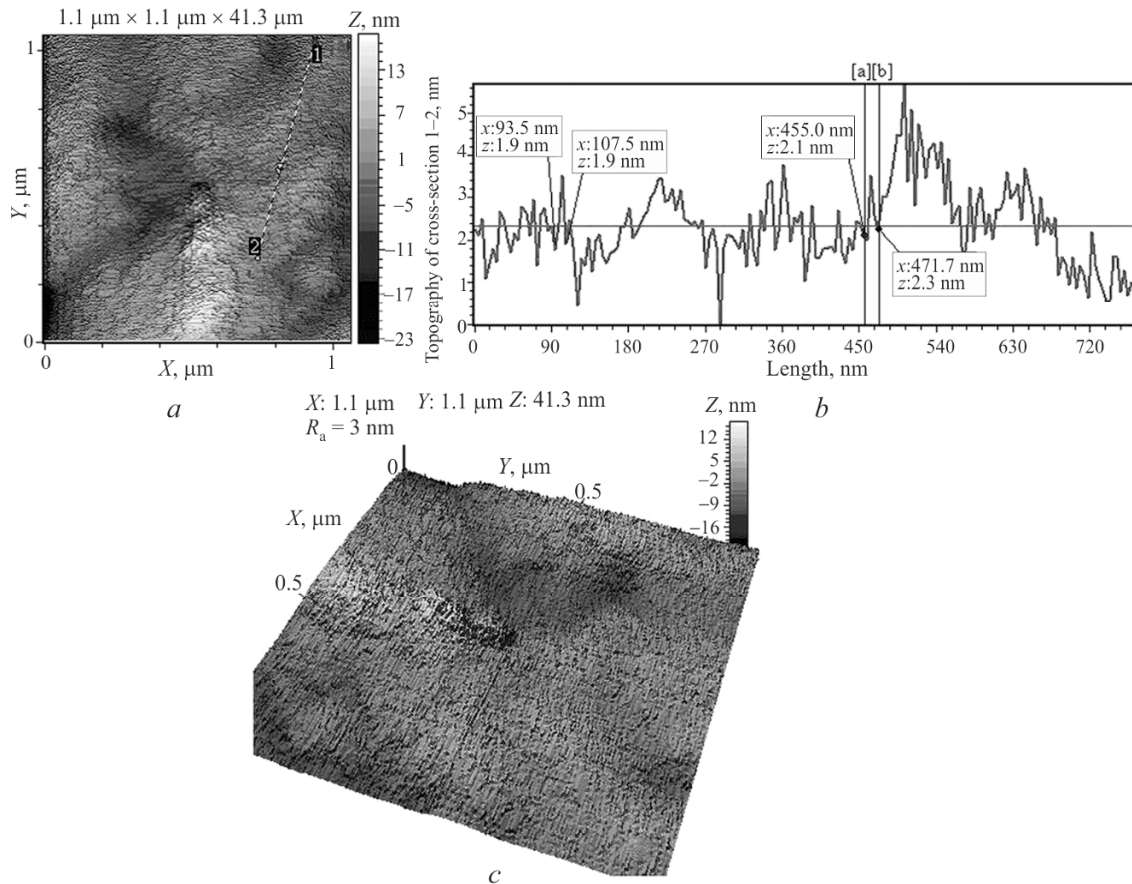


Fig. 4. Topography (a), cross-section 1–2 (b) and 3D-image (c) of 40 wt.% Ni<sub>3</sub>B composite

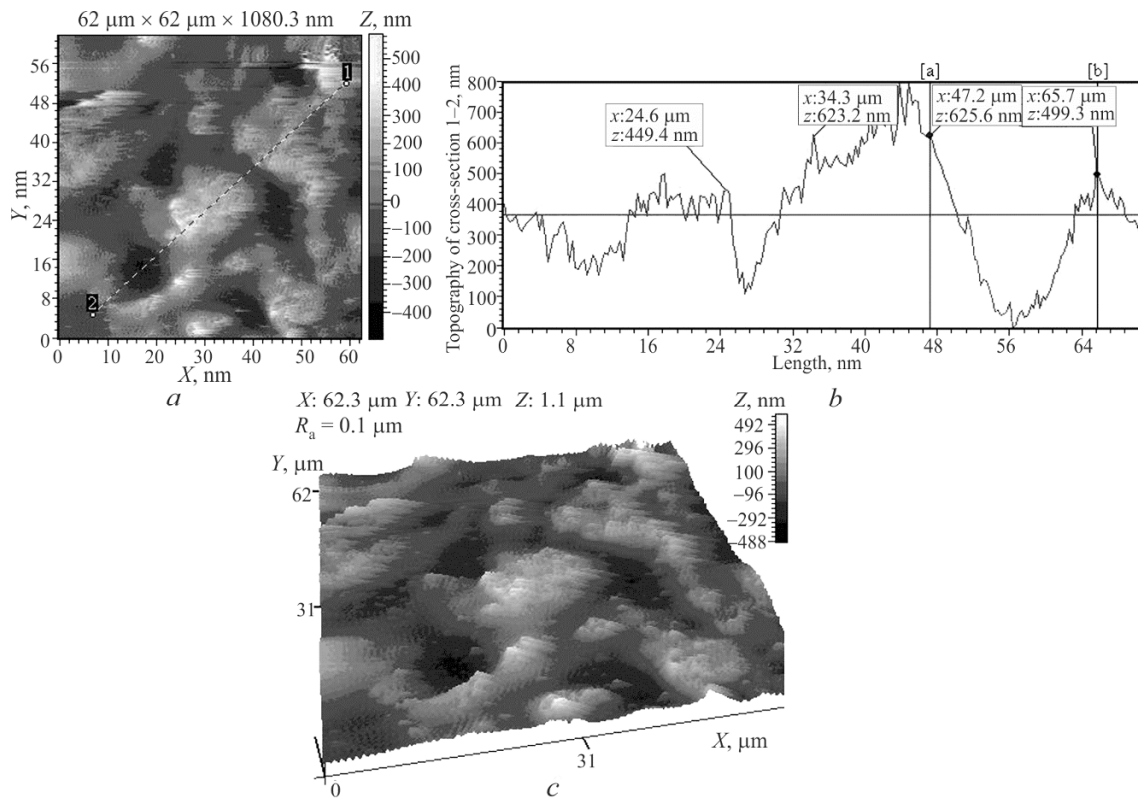


Fig. 5. Topography (a), cross-section 1–2 (b) and 3D-image (c) of 40 wt.% Ni<sub>3</sub>B composite (on the substrate side)

Study on the variation of content with the resistivity of film surface  $\rho_{fs}$  on the substrate side has shown that a conductive cluster (Fig. 7) is formed, when the Ni<sub>3</sub>B content is >30 wt.%. CP sedimentation and changes in the phase composition across film thickness, when studying ruthenium-containing resistors, are described in [24, 25].

Surface resistivity of the layer on the substrate side was 280, 75, and 10  $\Omega \cdot \text{mm}^2/\text{m}$ , which corresponds to the 30, 40, and 80 wt.% content of the filler in the polymer charge. Such composite can be used as resistive film with a dielectric layer of the same polymer. Since Ni<sub>3</sub>B-based thick films are used as heating elements, bonding pad for multiple-level boards, thermistors, the study of these composites with 30–80 wt.% content of CP (where higher conductivity is seen) was of particular interest.

Figure 8 shows 40 and 80 wt.% Ni<sub>3</sub>B composite film VAC measured in the slit geometry. Conductive layer side VAC are ohmic.

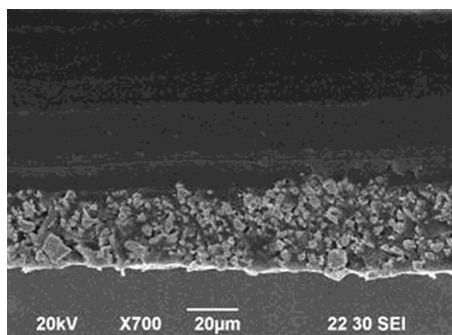


Fig. 6. Microstructure of the cross-section of 80 wt.% Ni<sub>3</sub>B film

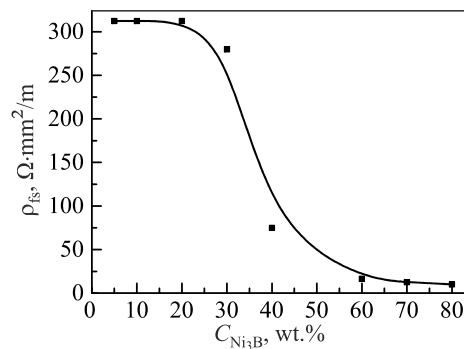


Fig. 7. Variation of film resistivity with Ni<sub>3</sub>B content

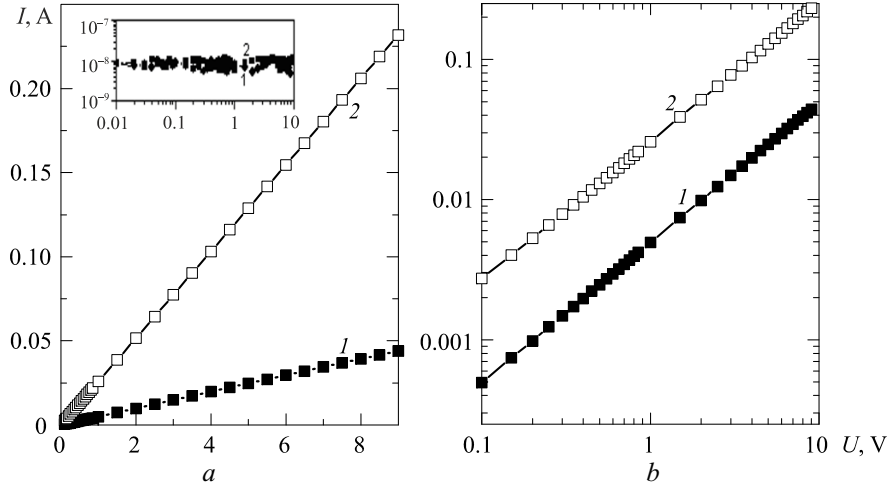


Fig. 8. VAC of 40 (1) and 80 wt.% Ni<sub>3</sub>B (2) composite films in linear (a) and logarithmic (b) coordinates on the conductive layer side; picture insert (Fig. 8a) shows VAC of composite 1 in slit geometry on the dielectric side at both electrical polarities

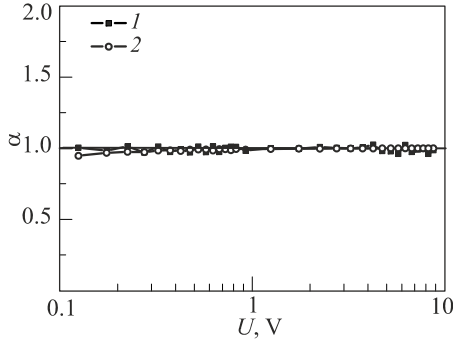


Fig. 9. Variation of value  $\alpha$  with voltage for 40 (1) and 80 wt.% (2) Ni<sub>3</sub>B films

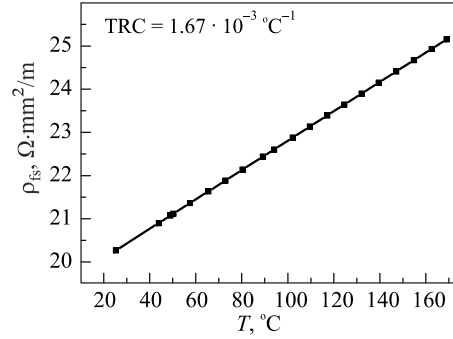


Fig. 10. Variation of resistivity with temperature of 80 wt.% Ni<sub>3</sub>B composite

The analysis of experimental VAC was conducted using the differential method [23], where dimensionless value  $\alpha(U)$  was determined:

$$\alpha(U) = \frac{d(\lg I)}{d(\lg U)} = \frac{UdI}{IdU}, \quad (1)$$

where  $U$  is the voltage (V),  $I$  is the current (A). This allowed determining the areas with a constant value of  $\alpha(U)$ .

Also, this dependence allows identifying the area where values  $\alpha$  are almost equal to 1, indicating VAC linearity and, therefore, an optimal working of the composite film. This interval covers the voltage range from 0.1 to 10 V (Fig. 9).

Figure 10 shows the variation of temperature with resistivity of 80 wt.% Ni<sub>3</sub>B composite. Temperature resistance coefficient was calculated based on the famous formula [26]:

$$\text{TRC} = \frac{R_T - R_0}{R_0(T - T_0)}, \quad (2)$$

where  $R_T$  and  $R_0$  are the resistivity of the thick film at the temperatures  $T$  and  $T_0$ , respectively.

## CONCLUSIONS

The feasibility of producing current-conducting thick films based on the thermally stable fluorine-containing aromatic polyamide and trinickel boride as conductive phase has been considered. The thermal treatment of the composite produced by coating with the Ni<sub>3</sub>B suspension in polyamide solution, has been carried out at 80–150°C, which requires no high-temperature firing.

An intensifying effect of the filler appearing in the increase of the strain strength has been observed when 80 wt.% CP, compared to 40 wt.% CP.

It has been established a CP sedimentation with the formation of two-layer composite, contributing to a unilateral conduction on the substrate side.

The variation of the electrical resistivity of the composite with CP content has been studied. It has been established the formation of the conductive cluster, when >30 wt.% CP content. The outer layer of the composite is a dielectric. The films possess linear VAC: they have a constant value  $\alpha = 1$  in the voltage range of 0.1–10 V, which corresponds to the optimal performance.

The temperature resistance coefficient determined based on the  $R(T)$  dependence is positive and its value is  $1.67 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$ . Such composites can be used as elements for heat-variable resistors.

## REFERENCES

1. *Conductive Polymers: Industrial Study with Forecasts to 2010 & 2015*. Study No. 2071. The Freedomia Group, Cleveland, USA (2006), p. 224.
2. M. Ates, T. Karazehir, and A. Sezai Sarac, “Conducting polymers and their applications,” *Cur. Phys. Chem.*, **2**, No. 3, 224–240 (2012).
3. A. G. Grozdov, E. A. Kosareva, O. A. Shtyleva, et al., “Conductive polymers,” *Khim. Prom. Segod.*, No. 5, 44–49 (2007).
4. Yu. A. Mikhailin, “Conductive polymers and their application,” *Polimer. Mater.*, **28**, No. 9, 2–4 (2001).
5. Yu. A. Mikhailin, *Structural Polymer Composite Materials* [in Russian], Konstruk. Polimer. Kompoz. Mater., 2-nd Edition, Izdat. NOT, Moscow (2008), p. 822.
6. O. A. Moskalyuk, A. N. Alyoshin, E. S. Tsobkhallo, et al., “Electrical conductivity of polypropylene fibers with dispersed carbon fillers,” *Fiz. Tverd. Tela*, **54**, No. 10, 1993–1998 (2012).
7. A. G. Bannov and G. G. Kuvshinov, “Study of electrical conductivity and permittivity of epoxy composites with addition of carbon nanofibers,” *Materialoved.*, No. 10, 47–51 (2011).
8. A. S. Stepashkina, A. N. Alyoshin, and P. P. Rymkevich, “Effect of temperature on volt-amps characteristics of composite materials based on polypropylene matrix and carbon fillers,” *Fiz. Tverd. Tela*, **57**, No. 4, 814–818 (2015).
9. V. E. Gul’, V. F. Blinov, M. G. Golubeva, et al., “Electrical properties of carbon blacked polypyromeltitimide films at high temperatures,” *Plast. Massy*, No. 9, 45–46 (1976).
10. U. Abdurakhmanov, F. T. Boymuratov, and G. I. Mukhamedov, “Electrical conductivity of composite materials based on phenylon and nickel particles,” *Radiotekh. Elektronika*, **55**, No. 2, 237–240 (2010).
11. T. I. Kolesnikova, L. I. Dukhovnyi, I. Yu. Shelekhov, et al., *Resistive Heating Element Based on Maleimide Ether Polymer*, in: *Application of Conventional and New Films: Proceedings*. Frantsevich Institute for Problems of Materials Science, NAS of Ukraine, Kiev (1994), pp. 108–111.
12. G. A. Syrenko, V. P. Sviderskii, V. D. Gerasimov, et al., *Antifriction Thermally Stable Polymers* [in Russian], Tekhnika, Kiev (1978), p. 247.
13. E. N. Ratnikov, Yu. L. Pogosov, and G. A. Mel’nikova, “Conductive cellulose ether polymers,” *Plast. Massy*, No. 1, 34–35 (1973).
14. V. G. Grebenkina, V. P. Yusov, and V. N. Sorokin, *Bulk Resistors* [in Russian], Nauk. Dumka, Kiev (1976), p. 210.
15. S. Kasap and P. Capper (Eds.), *Springer Handbook of Electronic and Photonic Materials*, Springer Science, Business Media Inc., New York (2006), p. 1406.

16. D. E. Dyshel', E. Ya. Tel'nikov, and L. A. Babanina, *Ni<sub>3</sub>B-Based Conductive Pastes on Metallic–Dielectric Substrates for Multiple Boards*, in: *New Materials for Thick Film Technology in Microelectronics: Proceedings*. Frantsevich Institute for Problems of Materials Science, NAS of Ukraine, Kiev (1991), pp. 48–52.
17. E. Ya. Tel'nikov, *Electrical–Physical Properties of Resistive Thick Films Based on Barium and Lanthanum Hexaborides* [in Russian], Summary of the PhD Thesis, 01.04.07, Kiev (1990) p. 19.
18. Yu. K. Kul'ba, V. P. Linnik, V. I. Loginov, et al., *X-ray and Thermal Study of Powder Conductive Layers Based on Borium Trinickel*, in: *New Materials in Microelectronics: Proceedings*. Frantsevich Institute for Problems of Materials Science, NAS of Ukraine, Kiev (1988), pp. 131–136.
19. D. E. Dyshel', B. M. Rud', and E. Ya. Tel'nikov, *Developing Pastes for Manufacturing Thick Film Heaters*, in: *Application of Conventional and Development of New Film Materials: Proceedings*. Frantsevich Institute for Problems of Materials Science, NAS of Ukraine, Kiev (1994), pp. 104–107.
20. G. V. Samsonov, T. I. Serebryakova, and V. A. Neronov, *Borides* [in Russian], Atomizdat, Moscow (1975), p. 376.
21. A. S. Veksler, L. I. Dukhovnyi, and A. L. Petrov, "Nickel boride thick films," *Neotgan. Mater.*, **33**, No. 9, 1070–1071 (1997).
22. B. F. Malichenko and O. N. Tsypina, "Polyamides based on fluorinealkylphenylenediamine and aromatic diacids," *Vysokomolek. Soed.*, **B11**, No. 5, 361–364 (1979).
23. P. Smertenko, L. Fenenko, L. Brehmer, and S. Schrader, "Differential approach to the study of integral characteristics in polymer films," *Advan. Coll. Inter. Sci.*, **116**, Nos. 1–3, 255–261 (2005).
24. A. Cattaneo and M. Prudenziati, "Effects of refiring processes on electrical and structural properties of thick-film resistors," *Electrocomp. Sci. Technol.*, **6**, Nos. 3–4, 165–171 (1980).
25. G. Samoggia, M. Scagliotti, and M. Prudenziati, "Reflectivity of thick film (cermet) resistors," *Thin Sol. Films*, **103**, Nos. 1–3, 323–331 (1983).
26. D. E. Dyshel', *Electrical–Physical Properties of Resistive Thick Films Based on Doped Tin Dioxide* [in Russian], Summary of the PhD Thesis, 01.04.07, Frantsevich Institute for Problems of Materials Science, NAS of UkrSSR, Kiev (1990) p. 22.