NUCET NUCLEAR ENERGY AND TECHNOLOGY

Nuclear Energy and Technology 11(2): 97–103
DOI 10.3897/nucet.11.160012

Research Article

Boron-containing radiator coatings of ionization chambers of neutron flux detection sensors*

Petr B. Baskov[1], Boris S. Salamakha[1], Yakov V. Glazyuk[1], Artur A. Namakshinas[1], Sergey A. Bondarenko[1], Ilya M. Mushin[1], Alexander S. Khudin[1]

1 *NIKIET JSC, 1 Acad. Dollezhal Sq., bldg. 3, 107140 Moscow, Russia*

Corresponding author: Petr B. Baskov (baskov_pb@nikiet.ru)

Academic editor: Yury Korovin ♦ **Received** 21 February 2025 ♦ **Accepted** 23 May 2025 ♦ **Published** 19 June 2025

Citation: Baskov PB, Salamakha BS, Glazyuk YaV, Namakshinas AA, Bondarenko SA, Mushin IM, Khudin AS (2025) boron-containing radiator coatings of ionization chambers of neutron flux detection sensors. Nuclear Energy and Technology 11(2): 97–103. https://doi.org/10.3897/nucet.11.160012

Abstract

The proposed solution for the production of new boron-containing radiator materials – composite coatings with neutron conversion material (^{10}B isotope) – for ionization chambers electrodes is based on the technology of chemical and structural modification of the surface using heat-resistant oxide materials (silicon and boron oxides). The paper presents the results of the development of a neutron-sensitive radiator material based on an oxide micro-dimensional composite coating consisting of an intermediate adhesive layer of silicon dioxide (SiO_2) and a neutron-sensitive functional layer of boric anhydride (B_2O_3). The technological basis consists of the sequential processes of thermal destruction of polyorganosiloxane of the PES-5 brand and pyrolytic decomposition of boric acid (H_3BO_3). Studies using infrared and fiber-optic interferometric spectroscopy have shown that during the formation of a silicon dioxide layer, an amorphous silicate of a linear chain structure with a developed surface is formed, which contributes to the subsequent formation of a functional boric anhydride layer. The specific neutron sensitivity of boron-containing radiator coatings was measured by alpha spectrometry. It was found that at a surface density of boric anhydride of 2.5 mg/cm^2, the specific neutron sensitivity is of the order of $3 \cdot 10^{-18}$Coulomb/neutron. It is shown that the boron-containing radiator coating retains its integrity and nuclear physical properties during thermocyclic tests (4 cycles at 600 °C). The boron-containing radiator coating is characterized by high adhesion properties to the metallic surface of the electrodes (grade 321 steel) of the ionization chamber. The composite coating is resistant to vibration when exposed to high-frequency (200 Hz) and low-frequency (6–35 Hz) vibration loads.

Keywords

neutron-sensitive materials, ionization chamber, boron radiator coatings, thermal destruction

Introduction

Modern control and protection of systems for neutron diagnostics used in effective reactors include ionization chambers (IC) with radiator coatings based on amorphous boron. The maximum operating temperature of such ICs is 400 °C (Malyshev et al. 1991). The IC working gas is normally argon. Currently, nuclear plants under design have cores the operating temperature in which reaches about 600 °C, while vibration loads reach 200 Hz (Baskov et al. 2022). A topical issue nowadays is development of new heat-resistant bo-

* Russian text published: Izvestiya vuzov. Yadernaya Energetika (ISSN 0204-3327), 2025, n. 1, pp. 51–64.

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ron-containing IC radiator materials that meet modern operating requirements.

The proposed solution for obtaining new boron-containing IC radiator materials is based on a technology for chemically modifying the surface structure (Baskov et al. 2018; Sakharov et al. 2021a, 2021b) using heat-resistant oxide materials (silicon and boron oxides). A radiator material is a composite oxide coating consisting of two layers: an adhesive layer of silicon dioxide and a functional neutron-sensitive layer of boron anhydride. The amount of boron anhydride to be applied is determined based on the path length of products from the $^{10}B(n, \alpha)^{7}Li$ nuclear reaction which proceeds with a probability of 93% for thermal neutrons (Potapov 1961).

The geometrical parameters of the radiator coating were estimated based on the Bragg-Wulf formula (Bolozdynya 2017):

$$\frac{R_1}{R_0} = \frac{\rho_0\sqrt{A_1}}{\rho_1\sqrt{A_0}} \quad (1)$$

where R_0 is the alpha particle/lithium path length in air; R_1 is the alpha particle/lithium path length in the medium; ρ_0 is the air density; ρ_1 is the medium density; A_0 is the molar mass of air; and A_1 is the molar mass of the medium.

The alpha particle and lithium that form as a result of the $^{10}B(n, \alpha)^{7}Li$ reaction have a boric anhydride path length of respectively 10.0 and 0.8 μm. As shown by calculations, a layer of boric anhydride with a surface density of not less than 1.5 mg/cm^2 requires to be formed to achieve high neutron sensitivity of the radiator.

The transition to high-temperature compositions of a composite radiator coating based on silicon and boron oxides is defined not only by heat resistance, but also by the structure amorphism factor, since amorphous and heterogeneous materials are more resistant to ionizing radiation due to annihilation of radiation-induced defects (Shurygina et al. 2012; Sakharov et al. 2016a).

Investigation of the intermediate silicon dioxide adhesive layer formation

The process of the intermediate silicon dioxide layer formation is based on thermal destruction of the PES-5 polyorganosiloxane. The thermal destruction processes were investigated by a non-contact non-destructive online method for determining the optical thickness of layers using a dedicated test bench for fiber-optic spectrophotometry (Sakharov et al. 2016b). Plates (grade 321 steel) were used as the coating substrates, the plate surfaces having been polished mechanically (the parameters Ra = 0.45 μm and Rz = 3.23 μm). The PES-5 polymer structure is a thermally resistant silica-oxygen linear chain $(Si\text{-}O\text{-}Si)_n$ bonded to organic ethyl radicals (Sobolevsky et al. 1975). The linear chain siloxane structure is inherited during heating in the course of thermal treatment. As a result, a coating is formed with high adhesive properties. The dynamics of the change in the optical thickness of the PES-5 layer in the process of thermal destruction with the formation of SiO_2 (Fig. 1) was investigated based on the change of interference patterns in a spectral region of 400 to 1000 nm (Fig. 2).

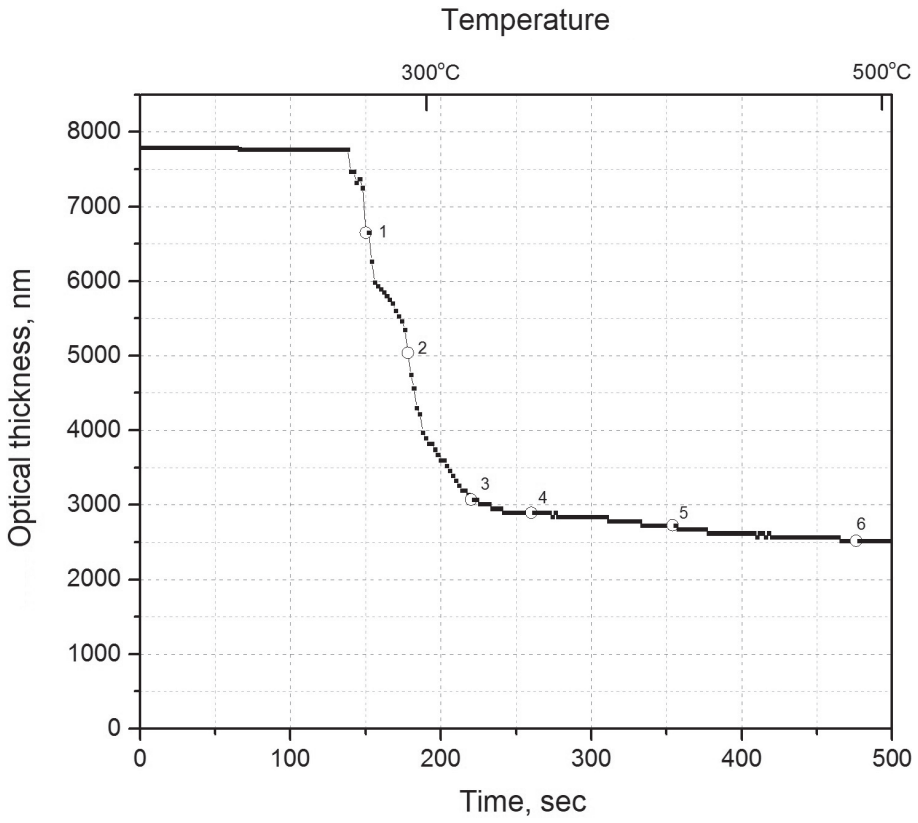

Figure 1. Dynamics of the optical thickness change in the course of thermal destruction synthesis of the silicon dioxide coating.

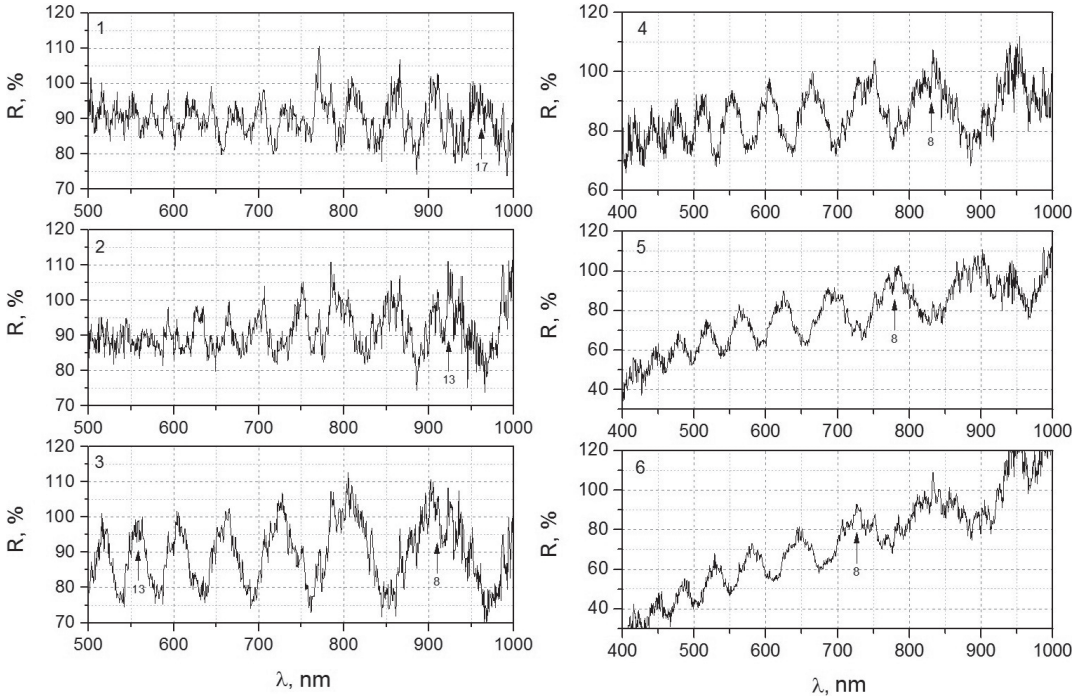

Figure 2. Change in interference patterns at different stages of the PES-5 thermal destruction process.

No changes occur in the initial heating step with the PES-5 polymer, and the optical thickness remains constant (7785 nm). As the temperature of about 217 °C is reached, the thermal destruction stage begins, which is characterized by an abrupt drop in the optical thickness value. When the temperature reaches 300 °C, much of the organic component is removed, and a solid coating is formed. A further temperature increase to 500 °C leads to a change in the optical thickness value to 2235 nm, according to a hyperbolic dependence, due to the consolidation of the silicon-oxygen frame.

The optical thickness of the coating as of the end of the process is still far from reaching the theoretical value for glassy amorphous silica (1425 nm) and even more so for crystalline quartz (1240 nm). This is probably explained by the presence of vacant "free volume regions" that thread throughout the oxide composition structure. Gravimetric measurements showed that the layer mass formed was equivalent to the silicon dioxide mass the PES-5 contains.

The thermally destroyed coating formed in the course of "rapid" heating is characterized by a low density (1.74 g/cm^3) compared to the density value (1.76 g/cm^3) of silicalite, a silica modification, the structure of which is threaded with "free volume nanofields" (Iler 1982). The density was determined based on gravity measurement and fiber-optic interferometry data.

As shown by infrared spectroscopy data (Table 1), the coating obtained by thermal destruction of the PES-5 polyorganosiloxane structurally represents linear siloxane chains (the absorption band in the region of 1020 cm^{-1}) bound by rectifiable Si-O-Si bridges with a bond angle of 180° (the absorption band in the vicinity of 1200 cm^{-1}), so the structure is preserved that is close to that of the original PES-5 polysiloxane precursor (Fig. 3). There are no impurities of organic components. Sorbed moisture is present (absorption bands of OH groups in the region of 3400 cm^{-1}), which is indicative of a developed surface of silica synthesized by thermal destruction method.

The so obtained silicon dioxide coating retains a stable amorphous structure (Fig. 4).

Fig. 5 shows a schematic image of the coating structure formation in the process of consolidating the siloxane structural motifs inherited from the PES-5 polymer.

Based on the investigation data, a model is proposed for consolidating a model of nanodispersed SiO_2, which includes structuring of nanoscale (2.5 to 19 nm) polysiloxane fragments $(Si\text{-}O\text{-}Si)_n$ remaining in the polyorganosiloxane molecule thermal destruction process. The polymer backbone, which does not practically contain hydrocarbon (C_2H_5) substituents, are found to contain OH groups which, even in a limited quantity, contribute to linear structures being cross-linked into siloxane blocks, the basis of the composite radiator coating intermediate layer.

Table 1. Interpretation of the spectrum absorption basebands in infrared region

Absorption band	Interpretation	Source
455 cm^{-1}	beta oscillation of Si-O bond	(Vlasov et al. 1974; Plyusnina 1977)
803 cm^{-1}	ν_s bonds of SiO	(Vlasov et al. 1974; Plyusnina 1977)
1020 cm^{-1}	ν_{as} oscillation of Si-O bond (1000–1100 cm^{-1} interval)	(Chukin 2008)
1200 cm^{-1}	Si-O-Si (rectifiable siloxane group, bond angle 180°)	(Chukin 2008)
3417 cm^{-1}	Hydroxyl groups (OH)	(Vlasov et al. 1974; Plyusnina 1977)

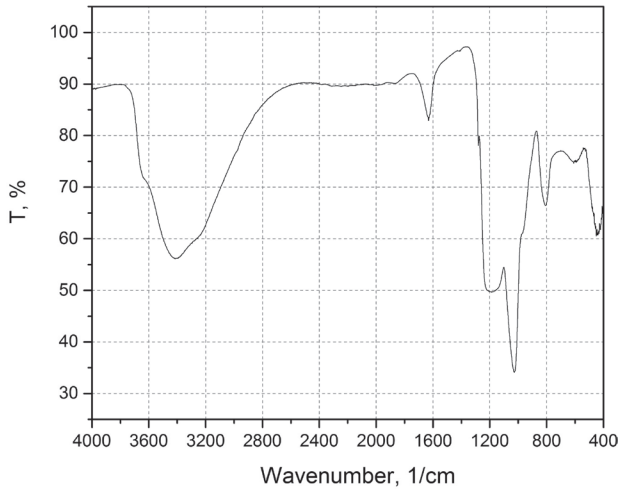

Figure 3. Infrared spectrum of the PES-5 polysiloxane thermal destruction product.

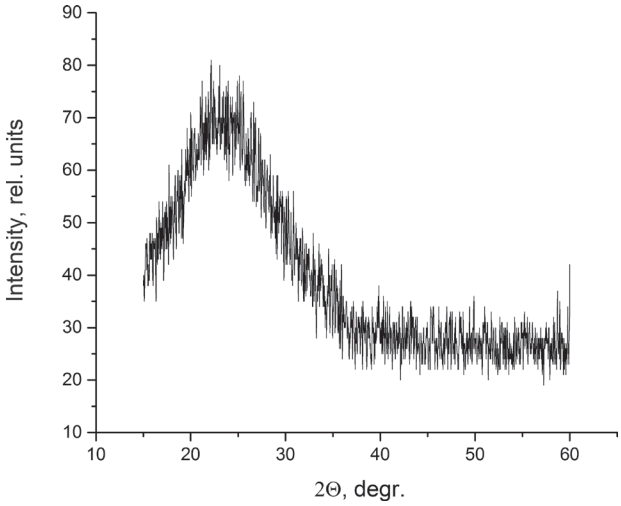

Figure 4. X-ray diffraction patterns of the PES-5 polysiloxane thermal destruction product (amorphous halo).

The presence of "free volume regions" and hydroxyl groups makes it possible to add coatings of alloying components, e.g. boron oxide, to the silica frame being formed.

Investigation of the boric anhydride functional layer formation

To explore the steps of the borosilicate coating formation, a PES-5 and boric acid solution in isopropanol was used as the precursor. An oxidizing environment was used for heating at different temperatures in the interval of 300 to 700 °C. Fig. 6 shows the evolution dynamics of the coating's infrared spectra as a function of temperature.

As shown by the spectra, the PES-5 thermal decomposition is at its early stage at 300 °C. There are intense bands in the region of 2960 cm^{-1} representative of organic radicals, which belong to PES-5, due to the sufficiently high thermally oxidative stability of the Si-C bond. The frequency maxima at 1004, 1040 and 1094 cm^{-1} belong to the silicon-oxygen frame of the PES-5 molecules. Representative of boric acid is absorption in the interval of 1355 to 1464 cm^{-1} and the presence of a hydroxyl groups band of 3200 cm^{-1}.

At a temperature of 400 °C, borosilicate bonds start to form as absorption bands of 650 and 920 cm^{-1} (Matsuda et al. 1992). A narrow and intense band with a maximum at 1391 cm^{-1} is representative of the B-O bond to the boron atom in a triple coordination (Vlasov et al. 1972). Instead of three equally intense bands with maxima at 1095, 1044 and 1004 cm^{-1}, an intense band appears, which represents a doublet with maxima at 1038 and 1158 cm^{-1}. The presence of two bands in the valence region of the Si-O-Si groups is associated with the presence of two structurally nonequivalent bonds. There is a sharp decrease observed in the intensity of the absorption bands for ethyl groups that surround the PES silicon-oxygen frame.

At 500 °C, the B-O bond band shifts to 1400 cm^{-1}, and a further decrease in its half-width is observed. There is a major decrease taking place in the absorption band of organic radicals, a shift is observed in the silicon-oxygen bonds into the higher frequencies region (respectively 1051 and 1178 cm^{-1}), and there is an increase in the intensity of the doublet's high-frequency component with

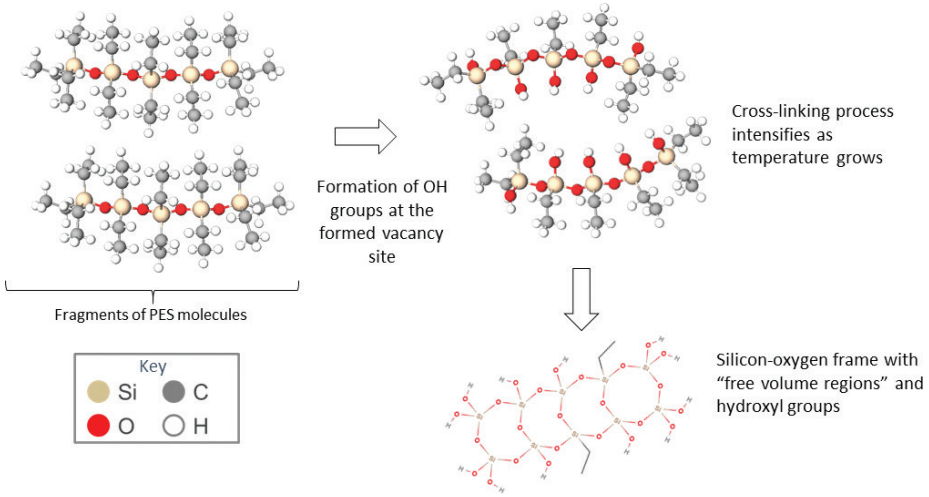

Figure 5. Diagram of the silica coating formation involving siloxane structural fragments.

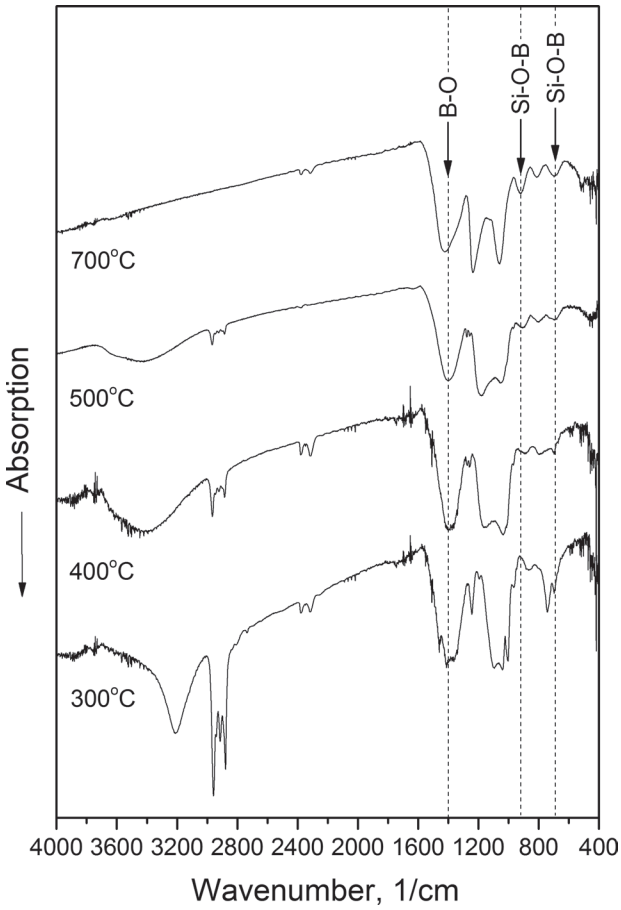

Figure 6. Infrared spectra of the thermally degraded coating at different temperatures..

respect to the low-frequency component. Absorption bands of borosilicate bonds are finally formed.

At 700 °C, there are bands present on the spectrum at 652, 920 and 1420 cm^{-1} (Si-O-B, B-O) and at 812, 1059 and 1236 cm^{-1} (Si-O, Si-O-Si), which characterize the fully formed thermally sealed borosilicate coating. There is no absorption in the region of hydroxyl groups and organic radicals.

Vibration resistance testing of electrodes with a boron-containing radiator coating

The boron-containing radiator coatings were tested for resistance to mechanical overloads in a horizontal and a vertical plane under the action of vibrations at the VEDS-1500 vibration test bench. For testing, a series of samples was prepared with the composite coating functional layer surface density being 1.5 mg/cm^2. The samples were successively exposed to high-frequency (200 Hz) vibrations with different acceleration amplitudes (1 to 8 g), the exposure time for each of the modes being 30 min. The surface density of the composite radiator functional coating is found to be invariable, the coating remaining therefore intact. The composite coatings were also tested in conditions of exposure to low-frequency resonant vibrations as specified in GOST 29075-91 (GOST 29075-91 2004). Test conditions: frequency range 6–8, 8–10, 10–13, 13–16, 16–20, 20–26, 26–35 Hz, acceleration amplitude 1.5 g, vibration impact time 15 min (with each frequency range). Vibration was changed from the lower frequency to the upper frequency with exposure to the uppermost frequency in each range. The vibration resistance test results show that the boron-containing radiator coating has high adhesion properties, which are confirmed by gravimetric and radiometric measurements.

Radiometric performance of boron-containing radiator coatings

Samples of electrodes with a composite boron-containing coating were tested radiometrically in conditions of exposure to a neutron flux of 10^4 neutron/(cm^2·s) from a Pu-Be source. The measured spectrum (Fig. 7) was used to determine the energy yield (ΣE) from the radiator coating surface, which was converted to the coating's specific sensitivity (η) using the formula:

$$\eta = \frac{\sum E \cdot e}{\Phi_0 \cdot S \cdot \tau \cdot \varepsilon} \quad (2)$$

where ΣE is the total energy yield from the radiator coating, eV; ε is the ionization energy in the IC (argon), 30 eV; e is the electron charge, C; Φ_0 is the neutron flux, neutron/($s \cdot cm^2$); S is the electrode area, cm^2; τ is the spectrum recording time, s; and η is the specific sensitivity of the radiator coating, C/neutron.

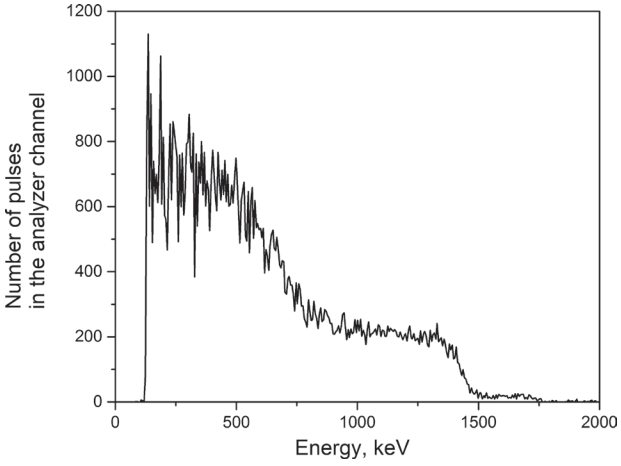

Figure 7. Spectrum of output pulses from charged particles for electrode sample with boron radiator coating (surface density 2.5 mg/cm^2).

The spectrum can be seen to include broad bands with energies of less than 0.83 MeV (due to ^{7}Li) and 1.47 MeV (due to the alpha particle). The peaks are broadly shaped due to partial energy losses in the radiator material. The energy yield of the coating when irradiated with thermal neutrons (measured within 1800 sec) was 5.7·107 keV.

Table 2. Effects of thermocyclic loads on the energy yield and specific neutron sensitivity values for radiator coating samples with different surface densities of boric anhydrite

Characteristics	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Functional layer surface density, mg/cm^2	0.5	1.0	1.5	2.5	3.0
η (pre-annealed), 10^{-18} C/neutron	2.7	3.1	3.3	3.4	3.4
η (annealing 1), 10^{-18} C/neutron	1.3	2.6	2.8	2.9	3.2
η (annealing 2), 10^{-18} C/neutron	1.1	1.9	2.6	3.1	3.0
η (annealing 3), 10^{-18} C/neutron	0.7	0.8	1.6	2.9	3.2

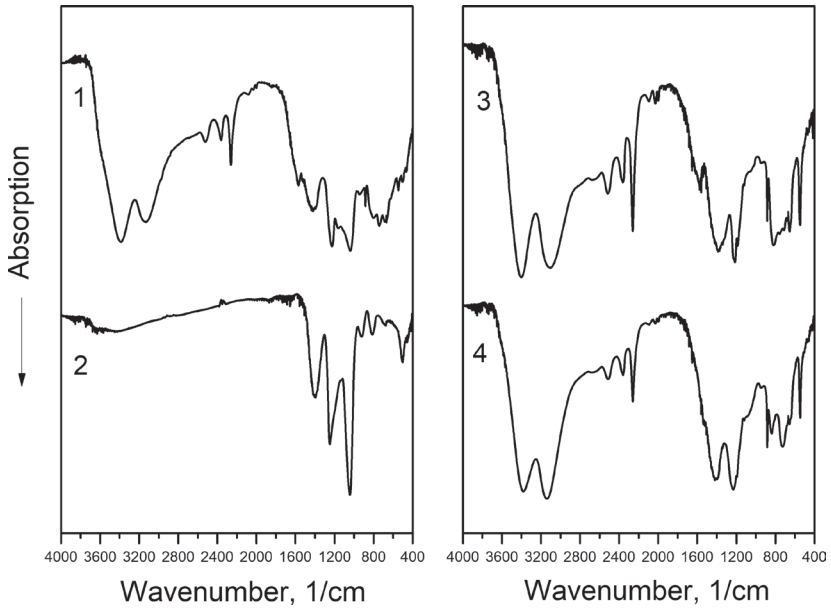

Figure 8. Infrared spectra of composite boron-containing coatings: 1 – sample 1 prior to thermocyclic tests; 2 – sample 1 following thermocyclic tests; 3 – sample 4 prior to thermocyclic tests.

The coating's specific neutron sensitivity value was $\eta = 3.4 \cdot 10^{-18}$ C/neutron. It should be noted that boron with the natural ^{10}B isotope enrichment (19.6%) was used in the process of the coating synthesis.

To determine the best possible concentration of boric anhydride based on the neutron sensitivity performance of the radiator coating, the effects of thermocyclic tests in an oxidizing environment on the energy yield were investigated for a series of samples with a composite boron-containing coating at different surface densities of the functional layer (0.5 to 3.0 g/cm^2). Annealing conditions in a single cycle: annealing temperature 600 °C, exposure time 4 h, heating rate 5°/min, inertial cooldown. The investigation results are shown in Table 2.

It was found that the best possible value of the functional layer surface density was 2.5 mg/cm^2. As the boron content increases, the specific neutron sensitivity value does not change, which fits theoretical calculations. A minor difference in readings following thermal cycles is caused by external factors, such as external gamma background and electrical interference. However, samples 1 through 3, in which the content of boric anhydride in the coating's functional layer is less than 2.5 mg/cm^2, exhibit a decrease in the specific neutron sensitivity in the course of the thermocyclic tests, which is possibly explained by the thermal emission of boric anhydride. This confirms the change in the nature of the infrared spectra prior to and after the thermocyclic tests (Fig. 8). A decrease in the intensity of the band in the region of 1400 cm^{-1} is observed against the silicon-oxygen frame bands (1200 and 1020 cm^{-1}), and there are no bands of hydroxyl groups representative of wet boric anhydride.

At the same time, the coating structure with a surface density of 2.5 mg/cm^2 (sample 4) and more remains practically invariable, which explains the stability of the neutronic properties in the course of the thermocyclic testing. The radiometric performance of the coatings remains invariable in the course of the thermocyclic tests in an argon environment (pressure 1 atm).

Conclusion

The paper presents the investigation results for a composite radiator coating consisting of two layers: an intermediate adhesive layer of silicon dioxide and a functional layer of boric anhydride. The investigation results for the formation of the intermediate adhesive layer of the composite coating by fiber-optic interferometry and infrared spectroscopy methods showed that the thermal destruction product of polyorganosiloxane (PES-5) had a linear chain silicate structure with a developed surface inherited from the PES-5 precursor. This contributes to the increase in the adhesive properties to the stainless steel surface and to the

functional boron-containing layer. A series of the radiator coating samples was obtained with the boric anhydride surface density in the functional layer being between 0.5 and 3 mg/cm^2. It was found by alpha spectrometry method in the process of the Pu-Be source irradiation (a flux of 10^4 neutron/(cm^2·s) that the content of ^{10}B atoms in the functional layer ($8 \cdot 10^{18}$ atom/cm^2 ≈ 2.5 mg/cm^2 B_2O_3) is the best possible one in terms of neutron sensitivity parameters, and the sensitivity value is $\eta = 3.4 \cdot 10^{-18}$ C/neutron. A further increase in the ^{10}B concentration does not result in an increase in this value. It has been shown that the radiator coating in the thermocyclic tests (four cycles at 600 °C) remains intact and retains its properties with the boric anhydride surface density in the functional layer of 2.5 mg/cm^2 and more. The samples with a boron-containing composite coating were found to remain intact when exposed to high-frequency (200 Hz) and low-frequency (6-35 Hz) loads.

References

- Baskov PB, Marichev GV, Sakharov VV, Stepanov VA (2021) Nuclear optical converters for detecting strong neutron fields. Nuclear Energy and Technology 8(1): 31-36. https://doi.org/10.3897/nucet.8.82558
- Baskov PB, Mosyagina IV, Sakharov VV, Ivkina OV, Khudin AS, Kirichenko GP (2018) Small thorium fission chambers for recording fast neutrons in reactor installations. Atomic Energy 125(1): 33–38. https://doi.org/10.1007/s10512-018-0438-x
- Bolozdynya AI (2017) Experimental nuclear physics. Lecture No. 2. Interaction of charged particles with matter. MEPhI Publ. https://enpl.mephi.ru/download/lectures/lect_5.pdf [accessed Nov.29, 2023] [in Russian]
- Chukin GD (2008) Surface chemistry and structure of dispersed silica. Moscow, Paladin Publ., Printa LLC, 172–172. https://www.chem.msu.su/rus/books/chukin-2008/chukin-2008.pdf [accessed Nov. 29, 2023] [in Russian]
- GOST 29075-91 (2004) Nuclear instrumentation systems for nuclear power plants (2004). Moscow, IPK Izdatelstvo Standartov Publ., 22–22. https://ohranatruda.ru/upload/iblock/6dd/4294825607.pdf [accessed Nov. 29, 2023] [in Russian]
- Iler R (1982) Chemistry of silica. Part 1. Moscow, Mir Publ., 416–416. [in Russian]
- Malyshev EK, Zasadych YuB, Stabrovsky SA (1991) Gas-discharge detectors for monitoring nuclear reactors. Moscow, Energatomizdat Publ., 160–160. [ISBN 5-283-03042-3] [in Russian]
- Matsuda A, Tohge N, Minami T (1992) Preparation of B_2O_3-P_2O_5-SiO_2 coating films by the sol-gel method. Journal of Materials Science 27: 4189–4194. https://doi.org/10.1007/BF01105125
- Plyusnina II (1977) Infrared spectra of minerals. Moscow. Moscow State University Publ., 174–174. [in Russian]
- Potapov SP (1961) On the use of stable boron isotopes. Atomnaya energiya 10(3): 244–252. https://elib.biblioatom.ru/text/atomnaya-energiya_t10-3_1961/p244/ [accessed Nov.1, 2023] [in Russian]
- Sakharov VV, Baskov PB, Berikashvili VSh, Ivkina OV, Kosov DE, Mosyagina IV, Frolov NN, Sharipova MA (2012a) Oxide nanolevel modification of the surface of inorganic materials. Rossiyskiy himicheskiy zhurnal 1–2: 36–43. https://elibrary.ru/download/elibrary_18013627_10974709.pdf [accessed Nov. 1, 2023] [in Russian]
- Sakharov VV, Baskov PB, Mosyagina IV, Frolov NN, Kurbatkin II, Muraveva TI, Torskaya EV, Ivkina OV, Sharipova MA (2012b) Chemical synthesis of neutron-detecting ultrathin optical materials. Izvestiya vuzov. Yadernaya energetika 4:1 30–142. https://doi.org/10.26583/npe.2012.4.15 [in Russian]
- Sakharov VV, Baskov PB, Ivkina OV, Mosyagina IV, Frolov NN, Khorozova OD, Khudin AS (2016b) Low-temperature consolidation in thermodecompositional nanosized amorphous layers of oxide zirconium and aluminum. Uprochnyayushchiye tekhnologii i pokrytiya 6: 43–48. https://elibrary.ru/download/elibrary_26097972_13559243.pdf [accessed Nov. 29, 2023] [in Russian]
- Sakharov VV, Mosyagina IV, Baskov PB, Stepanov VA (2016a) Physico-material science combinatorics of film-fiberglass materials for radiation-luminescent detection of neutron fluxes. Voprosy radiatsionnoy bezopasnosti 2: 55–63. https://elibrary.ru/download/elibrary_26723423_34666726.pdf [accessed Nov. 29, 2023] [in Russian]
- Shurygina NA, Glezer AM, Blinova EN (2012) The role of structural parameters of nanocrystals in the mechanical behavior of amorphous nanocrystalline alloys. Nauchnye vedomosti. Seriya: Matematika. Fizika 23: 206–214. https://elibrary.ru/download/elibrary_21196140_42910592.pdf [accessed Nov. 29, 2023] [in Russian]
- Sobolevsky MV, Muzovskaya OA, Popeleva GS (1975) Properties and applications of organosilicon products. Moscow, Khimiya Publ., 296–296. [in Russian]
- Vlasov AG, Florinskaya VA, Venediktov AA, Dutova KP, Morozov VN, Smirnova EV (1972) Infrared spectra of inorganic glasses and crystals. Leningrad, Khimiya Publ., 304–304. [in Russian]
- Vlasov AG, Florinskaya VA, Venediktov AA, Zubareva EP, Kurtsinovskaya RI, Morozov VN, Smirnova EV, Yakhkind AK (1974) Structure and physicochemical properties of inorganic glasses. Leningrad. Khimiya Publ., 360–360. [in Russian]