PROBLEMS AND PROSPECTS OF FIRE PREVENTION AND EXTINGUISHING

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COMPOSITE MATERIALS BASED ON POLYMER/GRAPHENE IN ROBOTIC FIRE EXTINGUISHING SYSTEMS

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Abstract. It is shown that numerous devices contain their own electrical power sources that use a significant number of bipolar transistors and thyristors of medium and high power, which require additional cooling in the form of external radiators to remove excess heat. For their manufacture, in addition to traditional alloys based on aluminum, materials such as polymers with fillers of high thermal conductivity are promising. A composite surface saturation technology is proposed that uses boron nitride nanocrystals to reduce thermal resistance at the interface. It has been established that the heat-conducting properties both along and across the polymer fibers, as the content of the nanocrystalline form of boron nitride increases to 25 %, they increase and reach a value of 21,3 W/(m K). This value is more than twice the possible maximum thermal conductivity coefficient in the absence of a graphene layer: 9,8 W/(m K) with a boron nitride mass content of up to 50 %. Due to its characteristics, polymer/graphene composite material has promise as a material for cooling devices with high energy density.

Keywords: robotic fire extinguishing installation, processor cooling, composite material, boron nitride, graphene oxide

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Introduction

If it is necessary to provide fire protection for large autonomous and low-maintenance industrial facilities, both from the external influence of a natural fire, and to localize and suppress fires of technological equipment, buildings and structures, it is advisable to use stationary robotic fire extinguishing installations (RUP), which represent a complex of automatic system for detecting a possible source combustion and control systems for the supply of fire extinguishing agent directly to the fire.

The implementation of the principle of localizing and suppressing a fire without the direct presence of operational personnel in the working area of the fire control unit is ensured on the basis of computer tracking by various operating modes of an autonomous fire extinguishing system with real-time feedback on the size of the fire and the direction of supply of the fire extinguishing agent.

The fire control system is a complex that includes fire carriages (devices that make it possible to supply and control a fire extinguishing jet) placed at a facility at a certain interval with a fire detection and intelligent control system attached to them (Fig. 1) [1, 2].

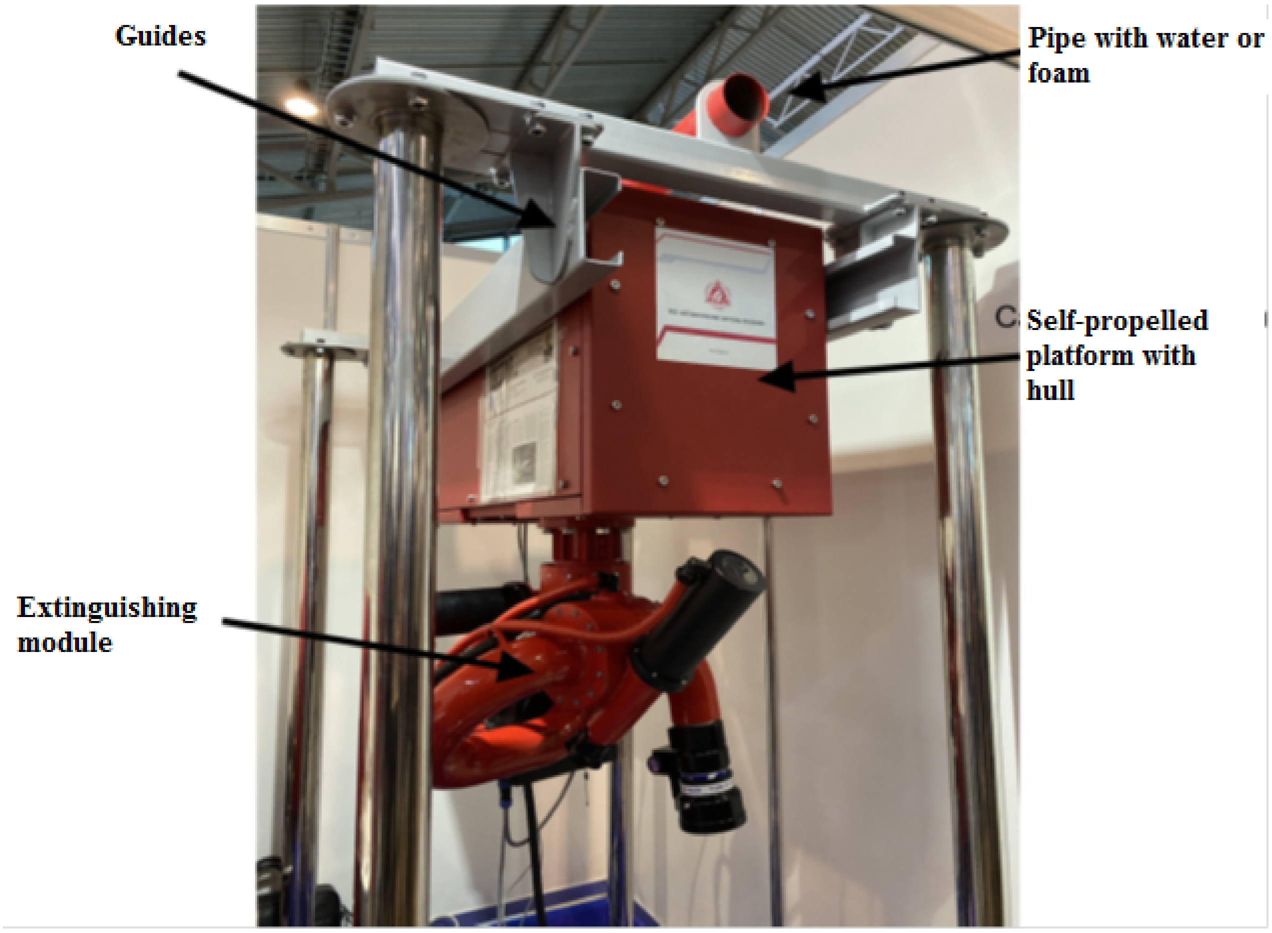

Fig. 1. **Self-propelled manual fire extinguishing installation**

The operating principle of the complex is as follows. In everyday life, RUP are located in parking areas. When a signal is received from a stationary fire alarm, the fire control units travel along the guides to the source of the fire. Using a built-in fire detector, the system determines the exact location of the fire. Next, the RUP is docked to the nearest stationary node connected to the pipeline, through which the extinguishing liquid (water or foam) is supplied. Then the fire extinguishing liquid is directed to the source using a controlled carriage. All these actions are performed automatically, without the participation of personnel. The programmable fire extinguishing complex is equipped with a video camera, with the help of which the operator can monitor the actions of the fire control unit and the source of the fire. Thus, RUP contain numerous devices (self-propelled platforms, software-controlled monitors, including drive systems, control units and electric shutters, video cameras, radio control units, etc.) that have their own electrical power sources. These devices use a significant number of bipolar transistors and thyristors of medium and high power, which require additional cooling in the form of external radiators to remove excess heat. Contact between the housings of electronic devices and metal radiators is ensured by special thermal pastes. In addition, modern high-performance processors also require forced cooling.

For the manufacture of heat sinks. except traditional alloys based on aluminum, materials such as polymers seem promising with fillers of high thermal conductivity (metals, carbon, ceramic materials). Such composites have low density and are quite easy to process [3].

In recent decades, RUP designers have proposed boron nitride as a filler for such composite materials due to its good thermal conductivity properties and high electrical insulation, which are essential for use instead of thermal pastes when cooling electronic devices [4].

To obtain polymer composite films with high thermal conductivity based on boron nitride, it was proposed in [5, 6] to use innovative technologies such as vacuum filtration and electrospinning. It was also found there that the inevitable scattering of phonons at the interfaces between fillers and the matrix leads to relatively low thermal conductivity properties ($\lambda<10$ W/(m K) in a plane perpendicular to the polymer matrix due to the observed scattering of phonons at the interfaces between fillers and matrix. To improve interfacial interactions between metal or ceramic fillers and polymer matrices, saturating the outer surface of the composite with a layer of organic molecules is considered an effective measure [7].

However, boron nitride is chemically inert and is very difficult to chemically or physically saturate with organic coupling molecules due to its high binding energy. In [8], it is assumed that the chemical activity of functional groups is formed mainly on the edges or defective areas of boron nitride surfaces and can cause weakening of its internal bonds. Theoretically, to achieve good contact, interfacial modifiers should have a chemical structure similar with fillers and matrices, and thus have similar phonon spectral characteristics based on the well-known structure-property relationship between bond types and phonon spectra [9].

To solve this problem [10] proposes an innovative technology for saturating the surface of a composite material, called «self-modifying nanointerface», which uses boron nitride nanocrystals to reduce the thermal resistance at the interface between boron nitride and the polymer matrix. On the one hand, the material used has the same lattice structure as and boron nitride itself, providing similar spectral characteristics of phonons. On the other hand, boron nitride nanocrystals contain a significant amount of hydroxyl and amino groups to interact with the polymer matrix of the composite material, which significantly improves the process of interfacial heat transfer.

The resulting flexible polymer composite based on boron nitride with a content of 25 % by weight can provide a material thermal conductivity coefficient of 21,3 W/(m K) in the perpendicular direction relative to the polymer matrix, which is more than twice the stated maximum. At the same time, high thermal conductivity in the direction in the plane of the polymer matrix of 20,3 W/(m K) is maintained. Molecular dynamics simulations show that the perfect matching of the phonon spectrum between boron nitride nanocrystals and conventional fillers and the strong interaction between self-modified fillers and the polymer matrix are the two main factors contributing to the reduction of the interfacial thermal resistance of the composite material.

Research methods

Boron nitride nanocrystals were synthesized by a simple hydrothermal method: 0,1 g of boric acid powder was dissolved in distilled water (10 ml) followed by the addition of 0,035 g of melamine. The mixture was stirred at 90 °C until completely dissolved and hydrothermally heated in a stainless steel autoclave with Teflon coating at a temperature of 200 °C for 16 hours. After the reaction, the solution was dialyzed for two days and frozen to obtain boron nitride nanocrystal powder.

Hexagonal boron nitride powder was dispersed in 100 ml of ultra-pure isopropyl alcohol with 0,02 g of boron nitride nanocrystal powder and stirred for more than a day at room temperature, followed by centrifugation at 12 000 rpm for 10 min. Spherical boron nitride powder was collected and dried by freeze drying. The required amount of sodium alginate and polyvinyl alcohol was dissolved in water with vigorous stirring at a temperature of 90 °C for 30 min, followed by stirring with 0,05 % by weight citric acid at room temperature for 24 hours. Upon completion of the process at room temperature for 24 hours, a certain amount of spherical boron nitride powder was stirred for another 30 min until a gel was obtained.

The mixed suspension may also contain air bubbles formed while stirring, the gel was therefore dripped onto a flat support where visible air bubbles were carefully removed. Flat surface of monolithic ice containing ions Ca_2+ (3 wt. % $CaCl_2$) was pressed tightly onto the gel to form a flat film. Through after 10 min, the solid ice was removed, and the frozen gel film formed on the ice substrate was immersed in ethanol for half an hour, followed by replacing the solvent with acetone. The composite film was obtained after drying at a temperature of 60 °C and low humidity (below 15 %) [8].

In general, the process of obtaining samples of composite material based on boron nitride is shown in Fig. 2.

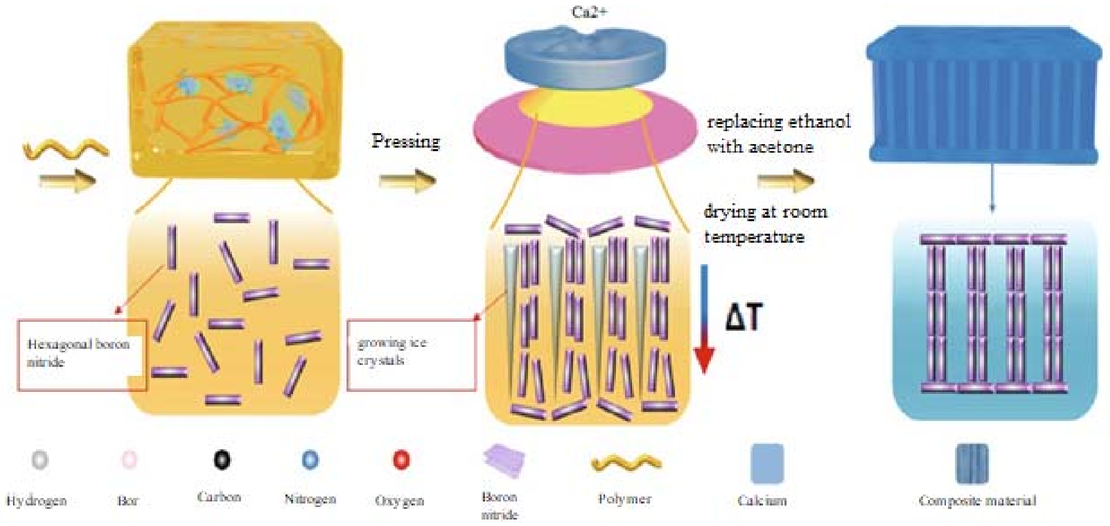

Fig. 2. **Manufacturing process of boron nitride composite material**

Theoretical analysis

In [11], it was proposed to use a large-scale atomic-molecular mass-parallel simulator in the nonequilibrium molecular dynamics mode to estimate the value of the interfacial thermal resistance of the composite material under study. Interatomic interactions in the polymer material were described by a matched force field, while the bonds within the graphene layer and the layer of boron nitride nanocrystals were described by the parameterized Tersoff potential for hybrid nanostructures [12]. The mode of nonequilibrium molecular dynamics of the thermal field and the heat removal process at the layer boundary were ensured by the stationarity of the heat flow at all points of the composite material sample under study. There is a temperature difference at the interfaces between layers of composite material, and the interfacial thermal resistance R_1 across the layer can be calculated using the equation:

$$R_1 = \frac{\Delta T}{Q/A},$$

there ΔT is the temperature difference at the interface between the layers; Q – heat flow; A – area of the interface between samples, with dimensions 17×17×107 mm.

The simulation results are presented in Fig. 3.

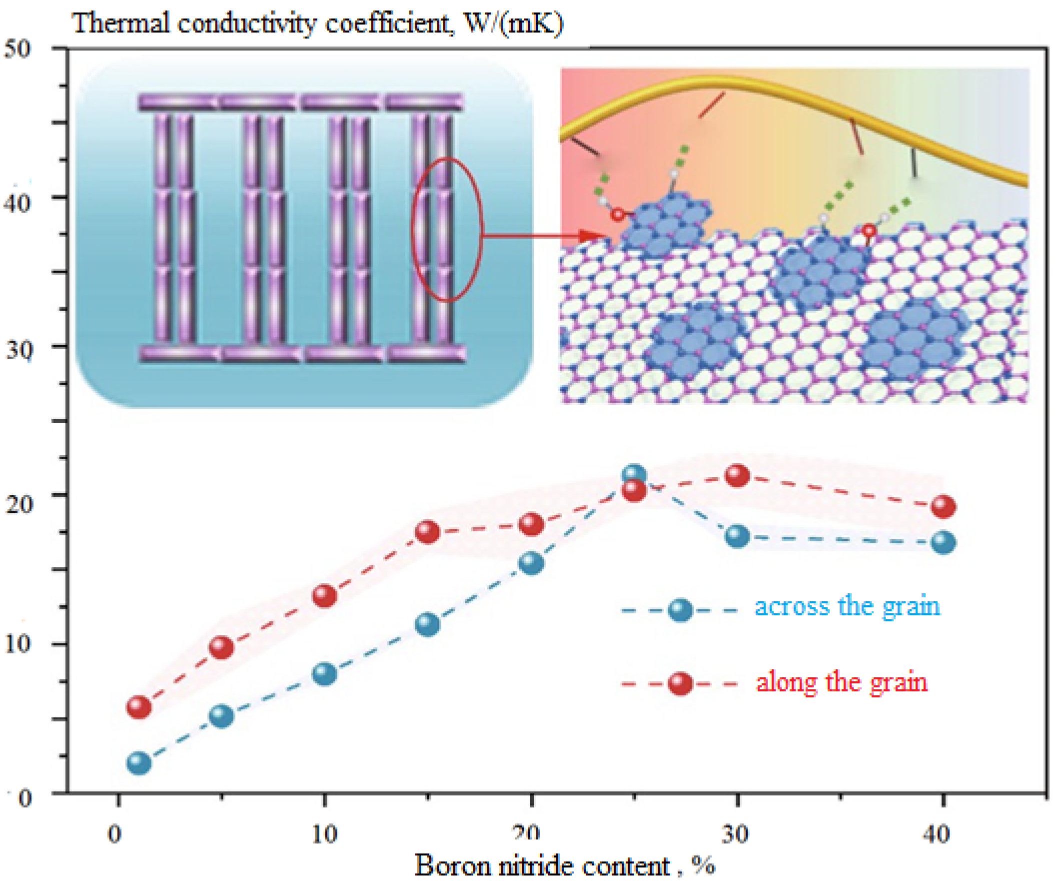

Fig. 3. **Results of modeling heat transfer in a composite material in different directions relative to the fibers**

During the simulation, the total thermal resistance of samples of composite material modified with boron nitride nanocrystals is $R_1 = 5{,}18\cdot10^{-8}$ $m^2\cdot K/W$, which is quite consistent with the results of the full-scale experiment described in [13].

After additional modification of the interfaces between the layers of the composite material with graphene oxide, the total thermal resistance of the samples is $R_1 = 1{,}4\cdot10^{-8}$ $m^2\cdot K/W$.

Simulation results and their analysis

The graphs presented in Fig. 3 allow one to study the heat-conducting properties of a composite material modified with nitride nanocrystals depending on the direction of heat movement. From these graphs it follows that the thermal conductive properties both along and across the polymer fibers, as the content of the nanocrystalline form of boron nitride increases to 25 % of its mass content, increases and reaches a value of 21,3 W/(m K). This value is more than twice the possible maximum thermal conductivity coefficient in the absence of a graphene layer: 9,8 W/(m K) with a boron nitride mass content of up to 50 % [14].

The different inflection points in the graphs of the thermal conductivity coefficients of a composite material modified with boron nitride along and across the fibers of the polymer material in [15] are explained by differences in the shrinkage process caused by drying the material after replacing ethanol with acetone, which obviously affects the formation of heat-conducting heat distribution paths.

Since the nanocrystalline fraction of boron nitride acts as a thermal binder between both boron nitride and the polymer, the thermal conductivity of composites with different mass ratios of the nanocrystalline fraction in boron nitride was studied (Fig. 4).

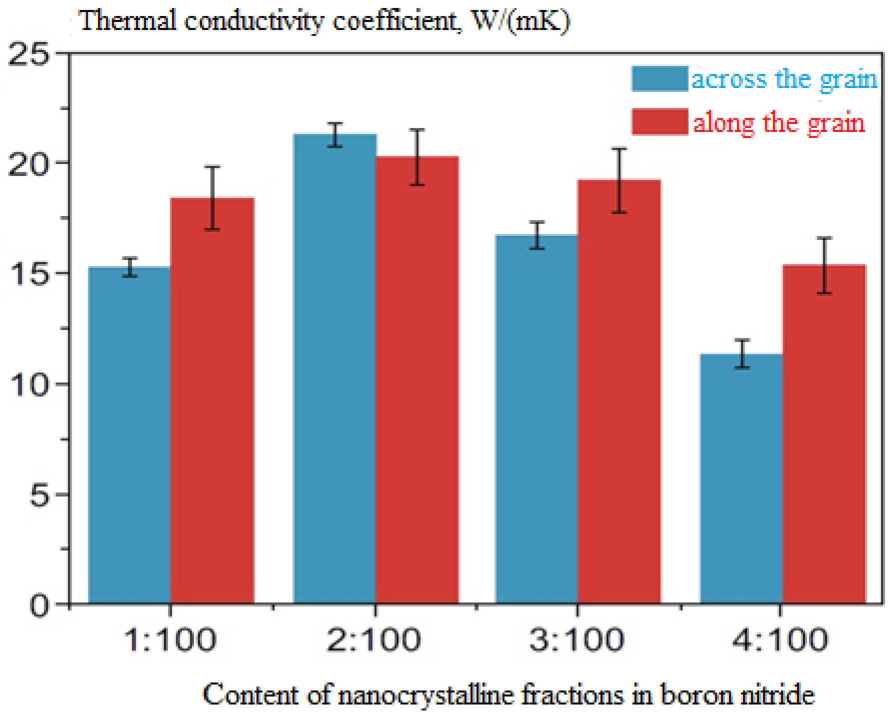

Fig. 4. **Dependence of the thermal conductivity coefficient of a composite material from the direction of heat propagation**

As shown in Fig. 4, a small concentration of nanocrystalline boron nitride fraction (1:100) does not provide effective internal contact between boron nitride and the polymer, while an excessive amount of nanocrystalline boron nitride particles (4:100) impairs the heat transfer between boron nitride and the polymer.

This is explained by the lower thermal conductivity coefficient of boron nitride compared to with a polymer, although they contain a large number of structural units that improve the process of their interfacial interaction with the polymer matrix [16].

In Fig. 5 shows that without any modifications, the boron nitride-based composite exhibits a thermal conductivity coefficient across and along the polymer fibers of only 10,4 and 13,2 W/(m K) respectively.

Considering that graphene oxide has a large number of OH-chains for interaction with the polymer matrix and only a slight saturation of the lattice (less than 2 %) with boron oxide [10], it was also used to modify the composite material with graphene oxide. Such a material has a thermal conductivity coefficient depending on from the direction across or along the polymer fibers was 12,8 and 16,7 W/(m K) respectively.

Due to its characteristics including good thermal conductivity, sufficient mechanical strength, flexural ability, excellent electrical insulation, and dimensional stability, polymer/graphene composite material holds promise as a cooling material for high-power-density devices.

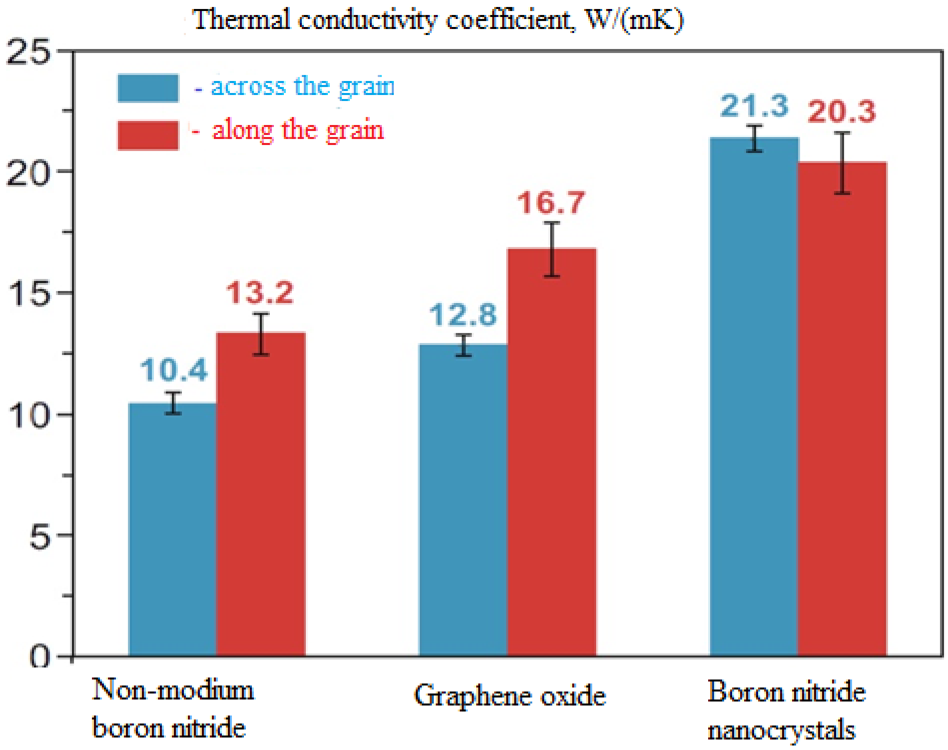

Fig. 5. **Thermal conductivity coefficient of composite material depending on boron nitride modifications**

Thus, in order to evaluate the cooling efficiency of such a material under real operating conditions of a RUP, a commercially widely used thermal paste and a sample of a polymer/graphene-based composite material with the same area of 3×3 cm^2 and a thickness of 80 μm were separately placed between a processor with a thermal power of 54 W (Fig. 6) and aluminum radiator.

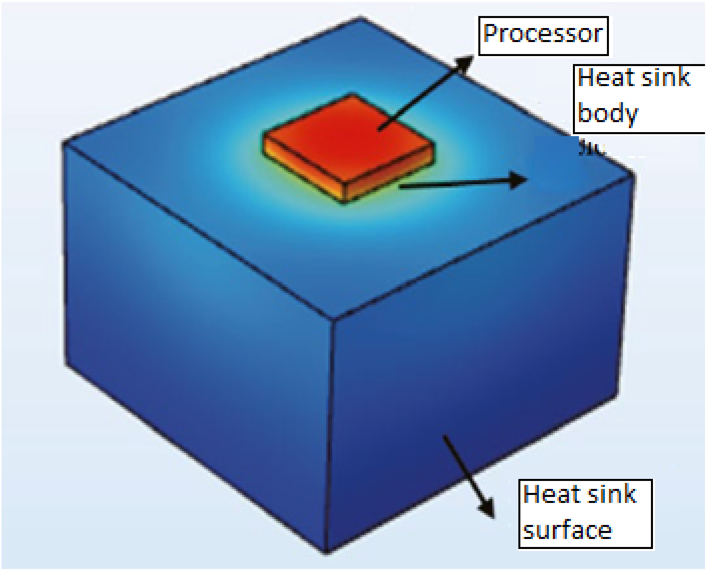

Fig. 6. **Forced CPU cooling circuit**

In Fig. 7 shows the dynamics of changes in the temperature of the central processor depending on the time of operation with contact materials (thermal paste, composite film based on polymer/graphene) and without them, operating in maximum power mode. Compared to the case of non-contact materials, the steady-state temperature of the processor using a composite film can be significantly reduced by 60 °C, which is more than when using thermal paste (30 °C), confirming the significantly more effective cooling capacity of the studied material.

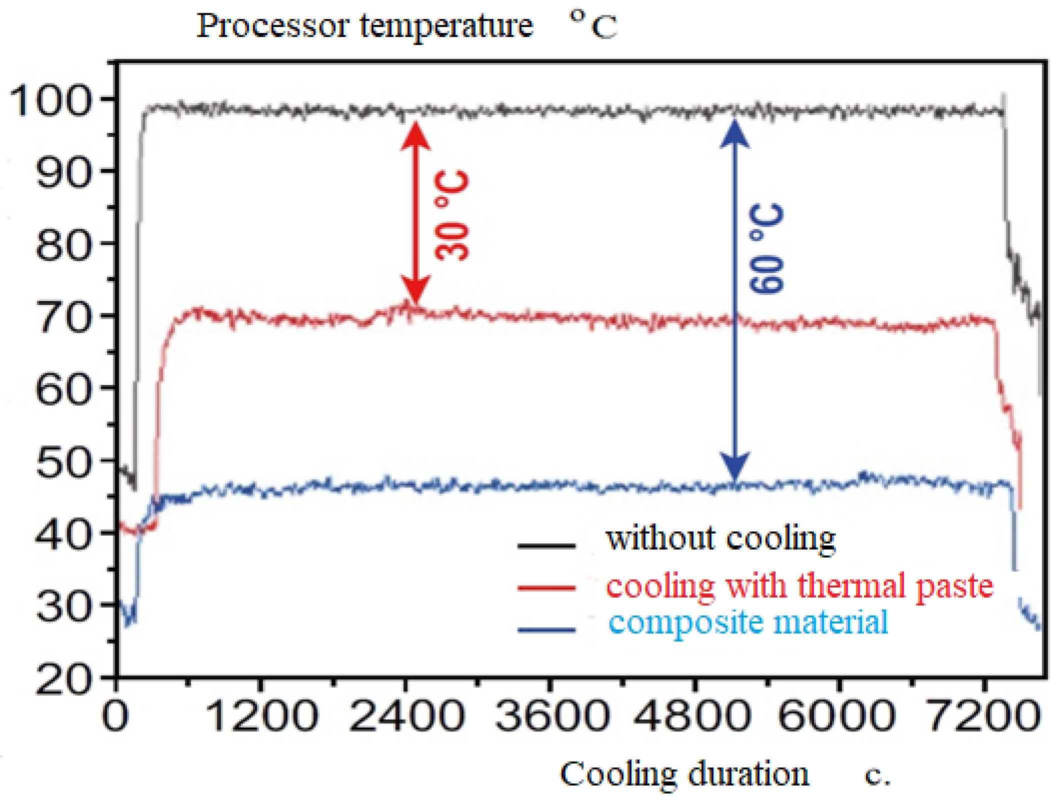

Fig. 7. **Temperature on the processor case**

Conclusion

Ultra-high thermal conductivity and excellent electronic insulation make the resulting flexible polymer/graphene composite the most promising heat dissipation solution for next-generation high-power electronic devices. This technological idea of a self-modifying nanointerface provides an innovative strategy for improving interfacial interactions and can be extended to the fabrication of other organic-inorganic hybrids and composite materials that are not easily fabricated using traditional organic molecule-based surface modification strategies.

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