DOI: 10.31319/2519-8106.1(50)2024.305577
UDC 621.74

Sereda Borys, Doctor of Technical Sciences, Professor, Head Department of Automobiles and Automotive Industry
Середа Б.П., доктор технічних наук, професор, завідувач кафедри автомобілів та автомобільне господарство
ORCID: 0000-0002-9518-381X
e-mail: seredabp@ukr.net

Udod Andrey, Postgraduate student of the Department of automobiles and transport and logistics systems
Удод А.Н., здобувач третього (доктора філософії) рівня вищої освіти кафедри автомобілів та транспортно-логістичних систем

Dniprovsky State Technical University, Kamianske
Дніпровський державний технічний університет, Кам'янське

THERMODYNAMIC MODELING OF THE GAS PHASE DURING THE PRODUCTION OF CHROME COATINGS ON PRESS EQUIPMENT FOR THE PRODUCTION OF ELASTOMERIC MATERIALS UNDER SHS CONDITIONS

ТЕРМОДИНАМІЧНЕ МОДЕЛЮВАННЯ ГАЗОВОЇ ФАЗИ ПРИ ОТРИМАННІ ХРОМОВИХ ПОКРИТТІВ НА ПРЕСОВОМУ ОБЛАДНАННІ ДЛЯ ВИРОБНИЦТВА ЕЛАСТОМЕРНИХ МАТЕРІАЛІВ В УМОВАХ СВС

This article investigates the thermodynamic modeling of the gas phase composition during the production of protective coatings on chrome-plated steels using the self-propagating high-temperature synthesis (SHS) method. This method is an effective way to create diffusion coatings with high wear resistance and heat resistance, which makes it particularly attractive for the production of tooling used in the pressing of new elastomeric materials. The article discusses the peculiarities of the composition of the gas phase formed in the process of obtaining coatings by the SHS method. The structure and characteristics of the resulting coatings based on gas-phase and diffusion processes are described. The conditions and parameters that determine the efficiency and quality of the coatings obtained in the diffusion process are analyzed. When forming coatings on a press tooling used in the manufacture of new elastomeric materials, specialized equipment is used, including reaction equipment, systems for monitoring and regulating process parameters, and a gas utilization system. The research carried out as part of this work makes it possible to determine the rational composition of the reaction SHS charges, methods of preparation of the treated surfaces and processing modes to obtain high-quality protective coatings with specified characteristics. The results obtained can be used in the production of elastomeric materials for pressing equipment with increased wear and corrosion requirements. The developed approach to obtaining coatings by the SHS method opens up new opportunities for creating strong and durable materials used in modern industry.

***Keywords**: synthesis, chromium, coatings, silicon, aluminum, elastomeric materials, thermodynamics, gibbs phase rule.*

У статті досліджується термодинамічне моделювання складу газової фази при отриманні захисних покриттів хромованих на сталях за допомогою методу саморозповсюджувального високотемпературного синтезу (СВС). Цей метод є ефективним способом створення дифузійних покриттів з високою стійкістю до зношування та термостійкістю, що робить його особливо привабливим для виробництва оснастки, яка використовується при пресуванні нових еластомерних матеріалів. У статті розглядаються особливості складу газової фази, що формується в процесі отримання покриттів методом СВС. Описується будова та *характеристики отриманих покриттів, засновані на газофазних та дифузійних процесах. Аналізуються умови та параметри, що визначають ефективність та якість отриманих при дифузійному процесі покриттів. При формуванні покриттів на пресовому оснащені при виготовленні нових еластомерних матеріалів, використовується спеціалізоване обладнання, що включає реакційне обладнання, системи контролю та регулювання технологічних параметрів, а також систему утилізації газів. Дослідження, проведені в рамках цієї роботи, дозволяють визначити раціональний склад реакційних СВС-шихт, методи підготовки оброблюваних поверхонь та режими обробки для отримання високоякісних захисних покриттів з заданими характеристиками. Отримані результати можуть бути використані в виробництві еластомерних матеріалів на пресовому оснащені з підвищеними вимогами до зношування та корозії. Розроблений підхід до отримання покриттів методом СВС відкриває нові можливості для створення міцних та довговічних матеріалів, які використовуються в сучасній промисловості.*

***Ключові слова**: синтез, хром, покриття, кремній, алюміній, еластомерні матеріали, термодинаміка, правило фаз Гіббса.*

Problem's Formulation

Increasing the reliability and durability of machine and plant parts in the vulcanization of rubber products is becoming an extremely urgent task in the context of rapid technological progress in Ukraine. The use of surface hardening methods, in particular the SHS method, is becoming an effective tool for strengthening and ensuring the stability of parts in high temperatures and aggressive environments. The use of the self-propagating high-temperature synthesis method to create protective coatings is one of the promising areas in this field. The study of the influence of the composition of the SHS charge in the production of coatings in the thermodynamic modeling of the resulting coatings opens up wide opportunities to improve the reliability and durability of press tooling in the case of degeneration of elastomeric materials. Taking into account the high requirements for the stability of materials in production conditions, the development of a rational gas phase for the production of protective coatings based on the SHS method is an urgent and promising task.

Analysis of recent research and publications

Analysis of the recent research and publications is a key stage in determining the relevance and direction of research in the field of obtaining protective coatings by the SHS method on steels [1—2]. Previous studies in this area demonstrate a wide range of possibilities of this method in the formation of high-quality protective layers with excellent mechanical and protective characteristics [3—4]. Some works focus on optimizing the composition of powder mixtures to achieve optimal coating properties, while others study the effect of SHS modes on the structure and microhardness of the formed coatings [5—8]. Such an analysis allows us to identify the most promising areas for further research and improvement of technologies for obtaining protective coatings in industrial production. An important aspect of the analysis is also taking into account current trends in the use of the SHS method for obtaining protective coatings. The application of the SHS technology has made it possible to link the structure of materials formed during combustion to the kinetics of rapid exothermic reactions. Studies have shown that a solid flame in its pure form is a rare phenomenon that can occur only in systems with a highly developed contact surface of the reactants. Gaseous SHS coatings have shown better characteristics than their analogues because they have the properties of the applied material and high adhesive strength. According to research, the amount of gaseous reaction products increases with increasing temperature, and condensed products can occur in areas of ultra-high temperatures.

Obtaining innovative chromium coatings on structural materials used in the production of new elastomeric materials [9—11] has become an urgent task in the context of the rapid development of technology in Ukraine. The development of new materials, the introduction of innovative technologies and approaches to surface treatment, and the improvement of coating quality control methods create ample opportunities to improve the efficiency and reliability of protective coatings.

Formulation of the study purpose

Formation of the research objective within the framework of this work involves an in-depth investigation of the processes of self-propagating high-temperature synthesis and their impact on the formation of protective coatings on steels used for the manufacture of press tooling. The objective is to investigate the combustion processes of powder mixtures using gas transport agents, the composition of the gas phase, and to determine the rational composition of reactive SHS-charges to be produced to improve their protective characteristics and service life in aggressive environments. The development of new technological approaches to the production of coatings based on the SHS method is intended to ensure high quality coatings and reduce their consumption, which is an urgent task for industrial enterprises.

Presenting main material

The coatings applied in SHS-processes, when accompanying gas-transport reactions occur, are very peculiar. They consist of a film of the applied product, as in gas-phase deposition, and a wide transition diffusion (gradient) zone, as in diffusion saturation. As a consequence, gas-phase SHS coatings have the best features of their analogs — they have the properties of the applied material (i.e. they can be much more wear-resistant or heat-resistant than the base) and high adhesion strength of powders, in which the particles of one substance are covered by a layer of another, which provides a sufficiently large specific contact surface of the reactants, if, of course, the particles are small enough. Micron sizes are satisfactory under such conditions. If the particles are not fused, the interaction between the reactants occurs in a solid-phase way in the regime of reaction diffusion. Low values of mass transfer constants in the solid phase can be compensated by a large contact surface. High temperature is an important intensifying factor. The pure solid flame regime can be realized in the case when all substances (not only initial and final, but also intermediate ones) are in solid state.

The SHS method produces refractory compounds of various chemical and phase compositions (carbides, nitrides, silicides, chalcogenides, intermetallics, hydrides), as well as reduced metals. In addition, the SHS method can produce inorganic materials with various physical properties (powdered, sintered, solid and porous, cast), as well as products of certain shapes and sizes. It is also possible to grow single crystals from molten combustion products.

Since SHS reactions are accompanied by intense light emission, high temperatures, and proceed in the same fast regimes as the propagation of combustion waves, they are classified as a type of combustion and studied within the framework of combustion theory, and combustion products are studied using material science methods. Thus, the field of chemical engineering, like many others, is at the intersection of chemical physics and materials science.

Modern expanded understanding of SHS is a combustion process of any chemical nature, which leads to the formation of valuable in practical terms solid-phase materials.

The regularities of combustion wave front propagation in SHS processes are numerous and can be controlled by various parameters, for example, by changing the ratio of reagents, varying the degree of dilution of the charge with inert products, heating the charge, etc. The influence of these parameters, the ultrafast front propagation, is mainly due to changes in the combustion temperature. A method of lowering the combustion temperature in SHS processes is to dilute the initial substances with combustion products, and a method of increasing it is to preheat the charge.

Technologies based on the SHS phenomenon differ in many respects, including: types of chemical reactions and processes, external influences, types of feedstock, charge structure, product morphology and methods of processing or refining, and the purpose of the final product. Determination of reaction products allows us to model the process of formation of protective layers in the conditions of the SHS, and based on the calculation of adiabatic combustion temperatures of SHS systems, we can solve the equation of heat balance of the systems under consideration. By analyzing the reaction products, it is possible to create a model of the process of forming protective coatings under SHS conditions. Based on the calculations of the adiabatic combustion temperatures of the SHS systems, we can solve the heat balance equation for the systems under consideration.

To obtain SHS coatings, samples from steels 20, 45, U8, 40X, 40X16M were used. Mixtures of powders with a dispersion of 60—250 μm were used as reaction agents. In determining the required dispersion of the reagents, we were guided by studies that found that the maximum completeness of the transformation is observed when using a reaction mixture with a fraction of 100—120 microns. The protective coatings on the samples under the conditions of the SHS were obtained using the developed pilot plant DDTU12, consisting of the following main functional systems: reaction equipment; system for monitoring and controlling technological parameters; gas utilization system. The processed press tooling is shown in Fig. 1.

Fig. 1. General view of the complete press tooling

Today, composite materials (rubbers, rubber) based on natural and artificial rubber have become an integral part of the metallurgical, textile and chemical industries. The use of rubbers makes it possible to produce structural and tribotechnical products characterized by enhanced damping properties, high elasticity and corrosion resistance. In addition, the use of rubbers instead of metals reduces the material consumption of structures and machines, shortens the production time of parts (even those with complex configurations), and increases corrosion resistance. The pressing was carried out on a hydraulic vulcanization press 100—400 2E. with plate sizes 400×400 of new elastomeric materials based on a copolymer of vinyl dell fluoride and hexopropylene, ethylene-propylene rubber, containing as a filler, carbonized polyacrylonitrile fiber, stone (granite) flour, aluminosilicate microspheres. Rubber is a mixture of substances, the main component of which is natural or artificial rubber. It is known that pure rubber is characterized by low mechanical, thermal, chemical and electrical properties. Effective fillers for natural and artificial rubbers are clay, carbon black, modified montmorillonite octadecylamine, silica, aluminosilicate hollow microspheres, carbon black.

Rubber-based composites may prove to be competitive and eventually replace traditional materials in a number of applications, as there are many advantages to using these materials. For example, rubber-based composites often have a lower density than traditional materials such as metals. This leads to a reduction in the weight of products, which is important in a variety of industries where lightness is a key characteristic. Rubber composites are characterized by shock absorption, flexibility, and elasticity, which makes them capable of handling dynamic loads and adapting to various forms of deformation without losing structural properties. Compared to metals, rubber composites can be less susceptible to corrosion, making them more durable and less costly to maintain in some operating conditions. The ability of rubber to insulate thermally makes them attractive for applications in construction and other industries where thermal insulation is important.

Formation of multicomponent siliconized coatings occurs under conditions of thermal self-ignition or combustion of powder media containing gas-transport additives. The time-varying temperature at first due to external heating and then due to ignition leads to the fact that neither thermal nor chemical equilibrium is possible until the process is completed and the products cool down. The rates of chemical processes are determined by kinetic laws depending on both temperature and diffusion factors. However, assuming, at least at the stage of heating, that the inhibition of diffusion processes of the gas phase is small, and the rate of temperature change is small compared to the rate of gas-phase chemical reactions, it can be assumed that each temperature value corresponds to the equilibrium composition of products.

Then, having calculated the equilibrium composition of reaction products for a number of specific temperatures from the range of its change, it is possible to follow the chemical picture of the process development.

Calculation of the equilibrium composition of products was carried out for the initial mixture consisting of M substances containing l chemical elements. At fixed values of volume (V) and temperature (T) from these elements as a result of chemical reactions can be formed m_k — substances present in k = 0, 1...q different phases. The set of substances includes l atomic and (m - l) molecular components, reactions of formation of which are represented in the form of dissociation equations:

$$M_{jk} \leftrightarrow \sum_{j}^{k} a_i k_j \cdot A_j \,, \qquad (1)$$

where $i_k = 0, 1, \ldots, m_k$ — number of the product belonging to the k-th phase; $j = 0, 1, \ldots, l$ — chemical number; $a_i k_j$ — number of atoms of j-th grade in i-th substance.

Strengthening in thermal autoignition occurs under non-stationary temperature conditions. The time-varying temperature leads to the fact that neither thermal nor chemical equilibrium is possible until the process is complete. It is possible to follow the chemical picture of the process by calculating the equilibrium composition of the reaction products for a number of specific temperatures from a range of temperature changes.

This is legitimate, since the rates of chemical processes are determined by kinetic laws that depend on both temperature and diffusion factors. Assuming that the inhibition of diffusion processes in the gas phase is small, and the rate of temperature change is small compared to the rate of gas-phase chemical reactions, it can be assumed that each temperature value corresponds to the equilibrium composition of products.

Calculation of the equilibrium composition of products was carried out for the initial exothermic mixture consisting of M substances containing l chemical elements. At fixed values of volume (V) and temperature, from these elements as a result of chemical reactions can be formed mk substances present in $k = 0,1....$ different phases. The set of substances includes l atomic and (m - l) molecular components, reactions of formation of which are represented in the form of dissociation equation

$$M_{ik} \leftrightarrow \sum_{j} a_{ikj} \mathrm{A}_{\mathrm{j}} \,, \qquad (2)$$

where $i_k = 0,1...$, m_k — number of the product belonging to the k-th phase; $j = 0,1..$, l — chemical number; A_j — number of atoms of j-th grade in i-th substance.

Mathematically the formulation of the problem is reduced to minimization of the thermodynamic potential

$$\mathrm{F}(\mathrm{ni}_{\mathrm{k}}) = \sum_{k} \sum_{i_k} ni_k (l_n \frac{n_{ik}}{N_k} + G_{ik}) = [F(n_{ik})]_{min} \qquad (3)$$

under the constraints on the unknown n_{ik} derived from the law of conservation of matter

$$\sum_{\mathrm{k}} \sum_{ik} a_{ikj} \cdot n_{ik} = b_j \,. \qquad (4)$$

Gibbs phase rules

$$f + g \le l + 2 \qquad (5)$$

and their non-negativity requirements $n_{ik} \ge 0$, where

$$N_k = \sum_{ik} n_{ik} \,; \qquad (6)$$

$$N = \sum_{k} N_k \,; \qquad (7)$$

$$G_{ik} = \mu_{ik} / RT \,. \qquad (8)$$

Determination of reaction products allows us to model the process of formation of protective layers under SHS conditions, and on the basis of calculation of adiabatic combustion temperatures of SHS systems we will be able to solve the heat balance equation of the systems under consideration. Calculation of the equilibrium composition of reaction products in powder SHS — mixtures was performed using the application package of the program "Astra", for system XC + Si + Al + NH_4Cl + J_2.

In this work, powders in quantities based on their stoichiometric ratios were used to create the energy component. As a result of combustion of powder mixtures with gas transfer agent (GTA), it is possible to form a gas phase containing compounds I_2, CI with chemical elements included in it. Dependences of concentration of gaseous and condensed reaction products on temperature in the combustion mode are shown in fig. 2, 3. With increasing temperature, an increase in the amount of halides is observed. This confirms the possibility of transfer of alloying elements for the formation of coatings.

The chromium component and silicon interact in stoichiometric. The inert additive (Al_2O_3) was varied in the range from 50 to 70 wt%, and gas-transport agents (NN_4Cl, I_2) — from 1 to 3 wt%. As will be shown below, the choice of such a ratio between the components allows obtaining optimal process temperatures during thermal autoignition.

Variation of the equilibrium composition of reaction products from temperature is presented in figs. 1, 2. It should be noted that in the temperature region 800—1200 K the fraction of condensed phase decreases, which is associated with the decomposition of the used gas-transport agents (NH_4Cl, I_2). At the same time its decomposition occurs, which is confirmed by the appearance of decomposition products in the system and the increase of gas moles. The gaseous product interacts with the elements of the powder mixture (chromium component and silicon) and transforms them into the gas phase (HCl, J, J_2, NH_3, Si, SiCl, $SiCl_2$, $SiCl_3$, $SiCl_4$, SiJ).

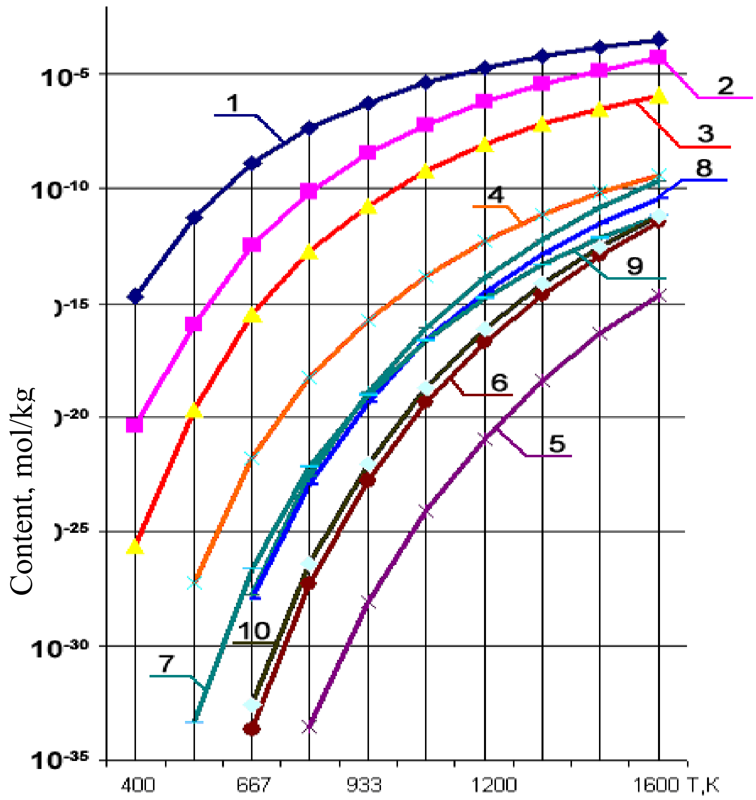

Fig. 2. Dependence of concentration of gaseous reaction products on temperature in the combustion mode for the system: XC + Si +Al + NH_4F + I_2: 1 — HCl; 2 — J; 3 — J_2; 4 — NH_3; 5 — Si; 6 — SiCl; 7 — $SiCl_2$; 8 — $SiCl_3$; 9 — $SiCl_4$; 10 — SiJ

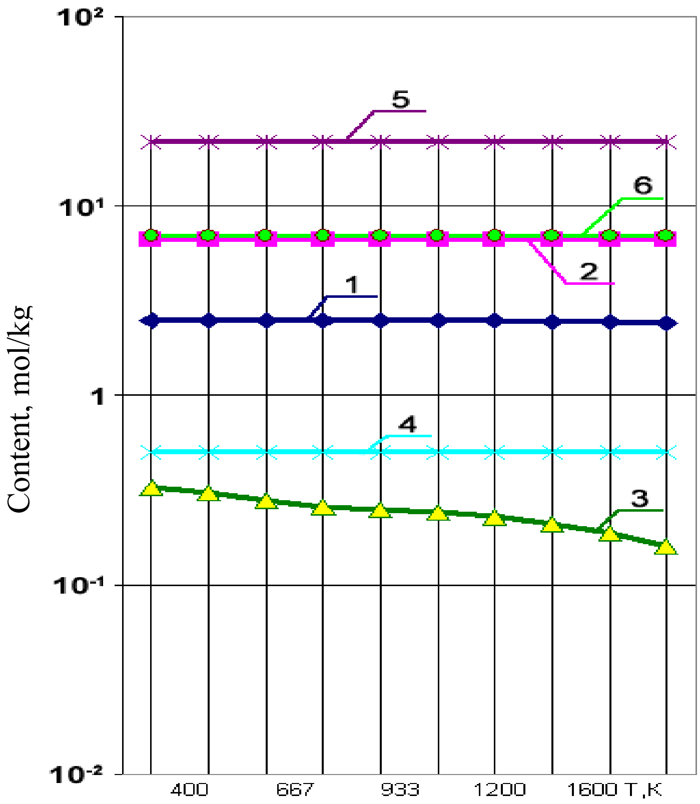

Fig. 3. Dependence of concentration of condensed reaction products on temperature in the combustion mode for the system: XC + Cr +Al + NH_4Cl + I_2: 1 — Al; 2 — Al_2O_3; 3 — Al_2Cl_3; 4 — AlN; 5 — Cr; 6 — CrSi

Conclusions

Results of the research have confirmed the effectiveness of using the method of self-propagating high-temperature synthesis as an effective way to obtain protective coatings on steels used for the manufacture of press tooling. The research data obtained show the possibility of forming coatings resistant to aggressive environments using this method. In addition, as a result of SHS, various phases are formed, such as oxides, nitrides and carbides, which improve the protective properties of the coating. Compared to other coating methods, such as vacuum sputtering or electrochemical deposition, SHS proves to be a more profitable and promising method. The research results confirm the relevance of implementing this method in industry to improve the quality and durability of protective coatings on metal products. In the temperature range of 800—1200 K, the proportion of the condensed phase decreases due to the decomposition of the gas transporting agents used (NH_4Cl, I_2). At the same time, its decomposition occurs, which is confirmed by the appearance of decomposition products in the system and an increase in gas moles. The gaseous product interacts with the elements of the powder mixture (chromium component and silicon) and converts them to the gas phase (HCl, J, J_2, NH_3, Si, SiCl, $SiCl_2$, $SiCl_3$, $SiCl_4$, SiJ). This mechanism of transition to the gas phase plays a key role in the formation of highly effective chrome protective coatings that must be used when pressing new elastomeric materials.

References

[1] Sereda, B.P., Bannykov, L.P., Nesterenko, S.V., Kruglyak, I.V., Gaidaienko, O.S., & Sereda, D.B. (2019). Surface hardening of materials operating under complex influence of aggressive substances: Monograph. Kamianske: Dnipro State Technical University.
[2] Sereda, B. (2021). High-performance chrome coatings to protect against wear and corrosion. Steel Properties and Applications in Conjunction with Materials Science and Technology, 39–41.
[3] Voevodin, V.N., Zmyi, V.I., & Rudenky, S.G. (2017). High-temperature heat-resistant coatings for the protection of refractory metals and their alloys (review). Powder Metallurgy, 03(04), 100-117.
[4] Dombrovsky, Yu.M., & Stepanov, M.S. (2011). New aspects of chemical-thermal treatment of metals in powder media. Bulletin of DSTU, (8), 1217–1221.
[5] Savulyak, V.I., & Shenfeld, V.Y. (2016). Surfacing of high-carbon wear-resistant coatings: Monograph. Vinnytsia: VNTU.
[6] Kovalevsky, S.V. (2013). New combined methods of processing working surfaces of machine parts (using neural network analysis): Monograph. Kramatorsk: DDMA.
[7] Khizhnyak, V.G., Arshuk, M.V., & Datsiuk, O.E. (2014). Diffusion coatings involving titanium, aluminum, and silicon on steel 12X18H10T. Scientific News. Kyiv: NTUU "KPI", (5), 84–88.
[8] Sakhnienko, M.D., Ved, M.V., Karakurkchi, G.V., Yermolenko, I.Y., & Zyubanova, S.I. (2013). Resource-saving technology for restoring worn parts. Integrated Technologies and Energy Saving, (2), 9–13.
[9] Vasmer, E. (2022). Preparation and characterization of composites containing natural rubber, waste rubber, and cellulose nano-crystals. Master's degree in Advanced Materials Science and Engineering.
[10] Kumar, V., Alam, M.N., Manikkavel, A., Song, M., Lee, D.-J., & Park, S.-S. (2021). Silicone rubber composites reinforced by carbon nanofillers and their hybrids for various applications: A review. Polymers, 13(14), 2322.
[11] Kozub, Y.G., & Solodey, I.I. (2019). Utilization of the finite element method for computing the thermoelastic state of pneumatic tires. Strength of Materials and Theory of Structures, (102), 232–242.

Список використаної літератури

1. Поверхневе зміцнення матеріалів працюючих в умовах комплексного впливу агресивних речовин: монографія. Б.П. Середа, Л.П. Банніков, С.В. Нестеренко, І.В. Кругляк, О.С. Гайдаєнко, Д.Б. Середа. Кам'янське: Дніпровський державний технічний університет, 2019. 170 с.
2. Sereda B. High-performance chrome coatings to protect against wear and corrosion Steel Properties and Applications in Conjunction with Materials Science and Technology 2021, P. 39–41.
3. Воеводин В.Н., Змий В.И., Руденький С.Г. Высокотемпературные жаростойкие покрытия для защиты тугоплавких металлов и их сплавов (обзор). Порошковая металлургия. Киев: ИПМ им. И.Н. Францевича НАН Украины. 2017. 03(04). С. 100–117.
4. Домбровский Ю.М., Степанов М.С. Новые аспекты химико-термической обработки металлов в порошковых средах. Вестник ДГТУ. 2011. № 8(59). С. 1217–1221
5. Савуляк В.І., Шенфельд В.Й. Наплавлення високовуглецевих зносостійких покриттів. Монографія. Вінниця: ВНТУ, 2016. 24 с.
6. Нові комбіновані методи оброблення робочих поверхонь деталей машинобудування (із застосуванням нейросітьового аналізу) : монографія / С. В. Ковалевський [та ін.]. Краматорськ : ДДМА, 2013. 196 с.
7. Хижняк В.Г., Аршук М.В., Дацюк О.Е. Дифузійні покриття за участю титану, алюмінію та кремнію на сталі 12Х18Н10Т. Наукові вісті. К.: НТУУ «КПІ», 2014. № 5 (97). С. 84–88.

8. Сахненко М.Д. Ресурсозаощаджувальна технологія відновлення зношених деталей / М. Д. Сахненко, М. В. Ведь, Г. В. Каракуркчі, І. Ю. Єрмоленко, С. І. Зюбанова // Інтегровані технології та енергозбереження. 2013. № 2. С. 9–13.
9. Vasmer, E. Preparation and characterization of composites containing natural rubber, wastes rubber and cellulose nano-crystals. Master's degree in Advanced Materials Science and Engineering. 2022. 94 p.
10. Kumar, V., Alam, M.N., Manikkavel, A., Song, M., Lee, D.-J., Park, S.-S. Silicone Rubber Composites Reinforced by Carbon Nanofillers and Their Hybrids for Various Applications: A Review. Polymers. 2021. №13(14), 2322. https://doi.org/10.3390/polym13142322
11. Kozub, Y.G., Solodey, I.I. Vykorystannya MSE dlya obchyslennya termopruzhnogo stanu pnevmatychnykh shyin [Utilization of the finite element method for computing the thermoelastic state of pneumatic tires]. Opir materialiv i teoriya sporud. 2019. № 102. P. 232–242.

Надійшла до редколегії 05.03.2024