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DEVELOPMENT OF RATIONAL CHARGES FOR THE PRODUCTION OF CHROMIUM ALLOYED SILICON COATINGS IN THE CONDITIONS OF SHS

РОЗРОБКА РАЦІОНАЛЬНИХ ШИХТ ДЛЯ ОТРИМАННЯ ХРОМОВАНИХ ПОКРИТТІВ ЛЕГОВАНИХ КРЕМНІЄМ В УМОВАХ SHS

Development and optimization of a technological process for the formation of multicomponent chromium-based coatings obtained by self-propagating high-temperature synthesis (SHS) to improve the performance of press tooling parts under high temperatures is considered in this research. The coatings formed under SHS conditions have a unique multilevel structure that provides excellent performance properties that are significantly superior to those obtained by other methods. The research included the use of powder mixtures with different particle size distributions to form protective layers on steel samples. Thermodynamic modeling and studies of reaction kinetics confirmed the possibility of obtaining coatings with the required properties at different temperature conditions. Metallographic analysis revealed high adhesion, uniformity of the coatings and their resistance to cracking. The structure of the silicon-doped coatings revealed the phases FeAlCr)$_{23C6}$, (FeCr)7C3, (FeAlCr)$_{5Si3}$, an ordered solid solution of Fe_3Al with the addition of Cr, as well as an б-solid solution of Al, Cr, and Si in the Fe structure. The developed technology has shown effectiveness in protecting the elements of press tooling operating under thermal effects and aggressive environments, which contributes to the durability and reliability of press tooling in the production of rubber products.

***Keywords**: synthesis, chromium, coating, silicon, aluminum, press tooling.*

У роботі розглянуто розробку та оптимізацію технологічного процесу формування багатокомпонентних покриттів на основі хрому, отриманих методом саморозповсюджуваного високотемпературного синтезу (SHS) для підвищення експлуатаційних характеристик деталей пресового оснащення під впливом високих температур. Покриття, сформовані в умовах SHS, мають унікальну багаторівневу структуру, яка забезпечує чудові експлуатаційні властивості, що значно перевершують аналоги, отримані іншими методами. Дослідження включали використання порошкових сумішей з різним гранулометричним складом для формування захисних шарів на зразках зі сталі. Термодинамічне моделювання та дослідження кінетики реакцій підтвердили можливість отримання покриттів з необхідними властивостями за різних температурних режимів. Металографічний аналіз виявив високу адгезію, рівномірність покриттів та їхню стійкість до тріщиноутворення. У структурі легованих кремнієм покриттів було виявлено фази $(FeAlCr)_{23}C_6$, $(FeCr)_7C_3$, $(FeAlCr)_5Si_3$, впорядкований твердий розчин Fe_3Al з додаванням Cr, а також б-твердий розчин Al, Cr і Si у структурі Fe. Розроблена технологія пока-

зала ефективність у захисті елементів пресового оснащення, які працюють в умовах термічного впливу та агресивних середовищ, що сприяє підвищенню довговічності та надійності пресового оснащення при виробництві гумотехнічних виробів.

Ключові слова*: синтез, хром, покриття, кремній, алюміній, пресове оснащення.*

Problem's Formulation

Coatings obtained by self-propagating high-temperature synthesis (SHS) have unique characteristics due to their specific structure. The SHS process forms a thin film of the applied substance, similar to a gas-phase deposition process, as well as an extensive transient diffusion zone resembling diffusion saturation. Due to this multilevel structure, coatings obtained under SHS conditions exhibit superior performance properties, standing out markedly from similar deposition technologies. They are characterized by improved coating material properties (such as increased resistance to wear and heat compared to the base material) and strong adhesion between powder layers, where particles of one substance are uniformly covered by a layer of another material. This structure creates a significant contact area for the reactants, especially when fine particles are used, which enhances the reactivity of the coating. At the same time, micron-sized particles can remain stable and sufficiently active under these conditions [1].

When the coating particles are not fused, reactions between reactants proceed through the solid phase, mainly due to reaction diffusion processes. Although low mass transfer coefficients in the solid phase can slow down the reaction, this disadvantage can be compensated by increasing the contact surface area, which is especially important when fine powders are used [2]. A significant role is played by high temperature, which intensifies the processes in the diffusion zone and promotes the reaction. Under certain conditions, it is possible to achieve the so-called "solid flame" regime, in which all components, including intermediates, remain in the solid state, ensuring purity and directionality of the reaction [3—4].

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. Organization of SHS, is to create a suitable powder mixture and environment, which provide exothermicity of the interaction at local initiation (start) of the reaction. The reaction then begins to propagate spontaneously, forming a combustion wave, and ends with the cooling of the synthesized product. Depending on the type of chemical reaction, three main classes of SHS processes are distinguished: direct synthesis from elements; direct synthesis from compounds and exchange reactions; metallothermal SHS, including reduction stages. As a result of such SHS processes, various chemical compounds such as carbides, borides, silicides, nitrides, intermetallides, chalcogenides, and others are formed. Depending on the aggregation state of reactants and reaction products, SHS processes can be categorized into gasless, low-gas, filtration and metallothermal [5—6]. The selection of a suitable SHS-system is based on the principles of technological combustion, with the main criterion being the formation of the target product as a result of the exothermic reaction. It is important to note that the thermal effect is important only insofar as it ensures the maintenance of the combustion process necessary for the continuous flow of the reaction and the formation of the protective coating

Formulation of the research problem

Development and optimization of the technological process of creating multi-component coatings based on chromium, designed to improve the performance characteristics of press tooling parts under conditions of high temperatures. This approach is aimed at improving the thermal stability and durability of surfaces, which allows to increase the service life and reliability of equipment subjected to strong thermal impact.

Presenting main material

Application of protective coatings under SHS conditions was carried out using a specially designed pilot plant model DSTU12. This plant is a complex equipment, including not only a reactor for coating, but also a high-precision system of control and regulation of process parameters, as well as a gas utilization system that provides safe removal of the resulting gaseous products. To form protective coatings on the samples made of 40X steel, powder mixtures of different particle size distribution were used, with the dispersity range from 60 to 250 microns. The charge included such elements as chromium, silicon oxide, aluminum oxide, aluminum, iodine and ammonium fluoride. These components were selected in order to provide the necessary adhesion, corrosion resistance and thermal stability, which increases the protective properties of the coating during the operation of the press tooling.

The process of pressing rubber-technical products was carried out on a hydraulic vulcanizing press model 100—400 2E with a working area of plates 400×400 mm. New elastomeric materials based on copolymer of vinylidene fluoride and hexopropylene and ethylene-propylene rubber, containing carbonized fiber based on polyacrylonitrile (PAN), stone (granite) flour and aluminosilicate microspheres were used [7—8]. This press is designed to create pressure on the sample with simultaneous temperature effect, which allows the process of vulcanization of rubber products in molds at a maximum force of up to 1000 kN.

Investigations of microstructure of structural materials with protective coating were carried out on cross sections using REM 106I. For thermodynamic modeling of chemical reactions in the SHS process, the equilibrium composition of system products was calculated using TERRA. In the development of optimal compositions of powder reaction SHS-charge, providing sufficient coating thickness and high durability, used methods of mathematical planning of the experiment with the implementation of full factor analysis according to plan 2^3.

The analysis of reaction products makes it possible to build a model of the process of formation of protective coatings under SHS conditions. Based on the calculations of adiabatic combustion temperatures in such systems, it is possible to solve the heat balance equation for each specific composition, which makes it possible to optimize the process parameters and predict the characteristics of the resulting coatings. For thermodynamic modeling of chemical reactions in the process of self-propagating high-temperature synthesis, the calculation of the equilibrium composition of the system products was performed using the TERRA program. Fig. 1 shows the content of gaseous silicon compounds in the SHS charge for the Cr-Al-Si system.

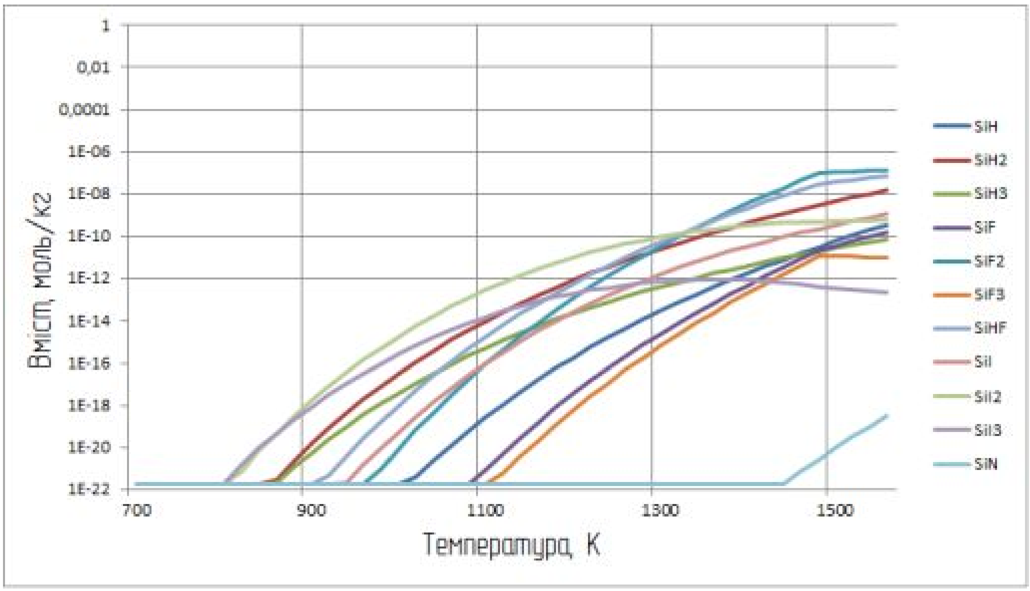


Fig. 1. Content of gaseous silicon compounds in the reactor for the system: Cr-Al-Si

As the temperature increases, the amount of products in the gaseous phase increases, and condensed products are formed. In the temperature range from 400 to 1600 K, a decrease in the proportion of the condensed phase is observed due to the vaporization of the carriers used. With increasing temperature, starting from about 800 K, the decomposition of reaction products occurs, which leads to the formation of decomposition products and a sharp increase in the number of molecules in the gas phase.

The gaseous products begin to actively interact with elements of the powder system such as aluminum, silicon and chromium, converting them to the gas phase. This leads to the formation of gaseous compounds (SiH, SiH_2, SiH_3, SiF, SiF_2, SiF_3, SiHF, SiI, SiI $_2$, SiI_3, and others).

A composite plan is a combination of a full or fractional factor plan and some additional plan. The latter is often the so-called star plan. If the centers of both plans coincide, the composite plan is called the central plan. Third-order composite plans, which include a full factorial experiment, make it possible to calculate regression coefficients characterizing triple effects. The presence of triple interaction effects in the regression equation can sometimes be considered as a fact that indicates changes in the mechanism of the process when moving from one value of the factors to another.

Following parameters were chosen as variables in the experiment: chromium compound content (SiC), titanium content, energetic component content (EC). Methods of mathematical planning of the experiment with full factor analysis according to the plan were used in the development of optimal compositions of powder SHS-loading, providing sufficient coating thickness and high durability 2i. The response surface of the obtained mathematical models is represented by three-dimensional graphical dependencies (Fig. 2).

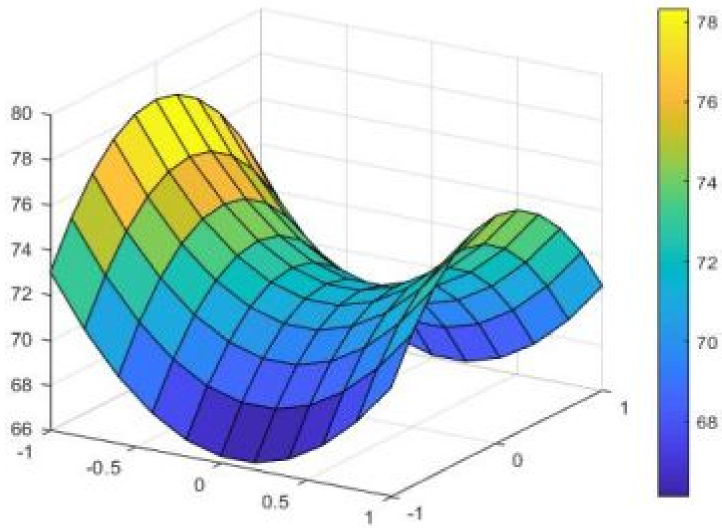


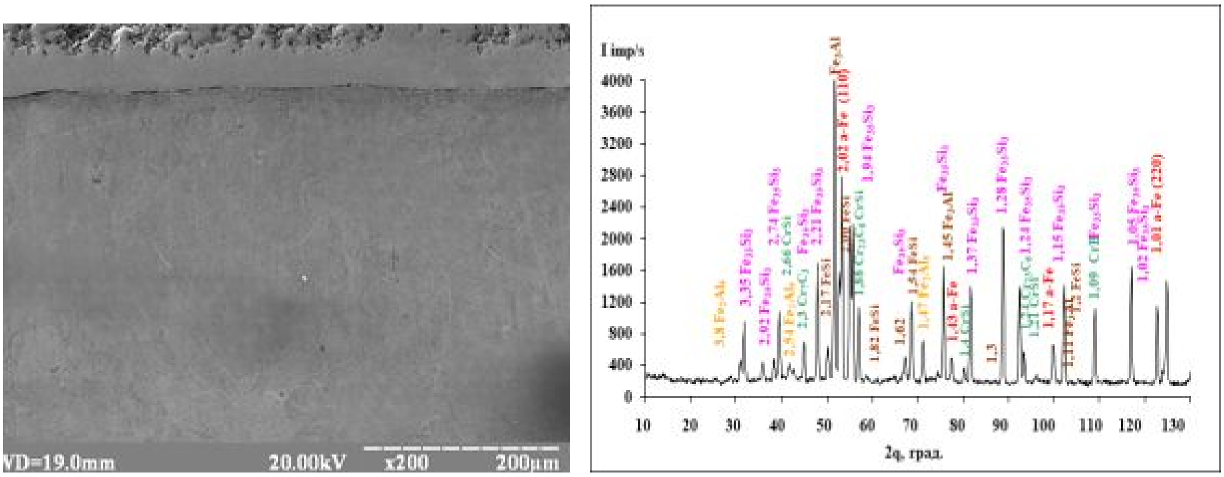
Fig. 2. Optimization of wear resistance for the system Cr-Al-Si

The obtained equation characterizing the influence of the technological regime and the composition of the charge on the parameters of optimization of physical, mechanical and operational properties, have the following form: $Y_1 = 101,64 – 0,4X_1 – 3,2X_2 – 2,5\ X_3 – 4,5556\ X_1^2 + 1,4444X_2^2 + 5,9444X_3^2 – 4,5X_1X_2 +1X_1X_3 – 1,25X_2X_3$.

Wear resistance for the Cr-Al-Si based system served as the criterion for the optimization evaluation. The choice of the basic level and the intervals of variation is made on the basis that the introduction of EC less than 10 wt. Based on the reserches of the change in the characteristic temperatures of the SHS process, the number of EC, is selected. Al_2O_3 is used as a ballast impurity to produce a one hundred percent composition of the powder SHS charges. According to the results of mathematical modeling of the production of multicomponent protective coatings alloyed with silicon, the following composition of the SHS charge was determined: $18EC + 14SiC + 12Al + 2NH_4Cl + 3NH_4I + 53Al_2O_3$.

Fig. 3 shows the microstructure of silicon-alloyed protective chrome coatings and an X-ray diffractogram of a 40X steel sample.

When obtaining multicomponent silicon-doped chromium coatings, the formed coatings contain the following phases: $(FeAlCr)_{23}C_6$, $(FeCr)_7C_3$, $(FeAlCr)_5Si_3$, an ordered solid solution of Fe_3Al with the addition of Cr, as well as an б-solid solution of Al, Cr, and Si in the Fe structure. Coatings do not contain the brittle FeAl phase, which is present in all coatings obtained under isothermal conditions, which can be explained by the high rate of temperature rise at the stage of thermal spontaneous combustion. This is typical for the processes of electric heating and high-frequency current processing.



a) b)

Fig. 3. Microstructures (x200) of silicon-alloyed protective chrome coatings ($t_п$ – 1000 °C, $ф_в$ = 30 хв.): a — steel 40X; b — X-ray diffractogram of a 40X steel sample, Co-Ka radiation

Conclusions

Research has confirmed the high efficiency of the developed technology for applying multi-component chrome coatings, which was demonstrated in both experimental and theoretical results. The obtained coatings have excellent indicators of wear resistance and thermal stability. Samples from 40X steel, treated by this technology, showed improved performance characteristics in comparison with traditional coatings, which is expressed in a significant reduction of wear and corrosion under the influence of high temperatures and aggressive media. Silicon-doped multi-component chrome coatings showed excellent mechanical properties, such as hardness and shear resistance, due to the carefully selected composition and application technology. When obtaining multicomponent silicon-doped chromium coatings, the formed coatings contain the following phases: $(FeAlCr)_{23}C_6$, $(FeCr)_7C_3$, $(FeAlCr)_5Si_3$, an ordered solid solution of Fe_3Al with the addition of Cr, as well as an б-solid solution of Al, Cr, and Si in the Fe structure. Coatings do not contain the brittle FeAl phase, which is present in all coatings obtained under isothermal conditions, which can be explained by the high rate of temperature rise at the stage of thermal spontaneous combustion.

Concentration of alloying compounds directly depends on the initial composition of the mixture. The results of thermodynamic modeling of reaction products and the study of kinetic laws confirmed the possibility of creating coatings with specified properties at different temperature regimes. Modeling showed that optimally selected powder mixtures and technological parameters contribute to the effective formation of protective layers. Metallographic analysis revealed high quality and uniformity of the obtained coatings, their excellent adhesion to the steel substrate, as well as resistance to cracks and defects. The developed technology was successfully applied for protection of press tooling elements functioning under conditions of thermal impact and aggressive media in the production of rubber products for special purposes.

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