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OBTAINING CHROME COATINGS ON STRUCTURAL MATERIALS WORKING IN CONDITIONS OF VULCANIZATION OF NEW HUMOTECHNICAL PRODUCTS

This work investigated the possibility of obtaining protective coatings, under conditions of self-propagating high-temperature synthesis, on parts of equipment for vulcanizing new rubber products. Research is focused on finding effective ways to strengthen the working surfaces of conditionally important elements of equipment operated in aggressive environments, in particular, press tooling. Given the high requirements for wear and corrosion resistance of such parts, special attention was paid to the choice of composition and coating process parameters. To achieve this goal, various composite materials and application methods were used, and a set of studies was conducted to investigate the properties of the resulting coatings. The results obtained indicate the possibility of successful application of chrome coatings alloyed with silicon, boron, and aluminum for further strengthening and protection of vulcanization equipment parts. The conducted research is relevant for the development of new production technologies and improving the efficiency of operation of press equipment for vulcanization of rubber products

Key words: *self-propagating high-temperature synthesis, silicon, boron, chromium, coatings, elastomeric materials, wear resistance, microhardness.*

Formulation of the problem. Given the rapid development of technology in Ukraine, the issues of increasing the reliability and durability of machine parts, devices and installations operating under conditions of vulcanization of rubber products have become so urgent. The role of surface hardening processes in the durability of machines and mechanisms has become especially important at the present stage, as the development of machine-building industries is associated with an increase in loads, temperatures and aggressiveness of the environments in which critical parts operate. An effective method of increasing the durability of various parts, which changes the chemical composition, structure and properties of the metal surface layers, is chromium plating using the SHS method [1-4]. An analysis of the literature shows that there are currently many methods of diffusion saturation of the steel surface with chromium and other elements, among which the common one is to perform the saturation process at high temperatures, when the free energy reserve of the system is large enough for diffusion in the solid phase.

Analysis of recent research and publications. This paper analyzes the latest research and publications in the field of formation of protective coatings on metal surfaces under hydrocarbon conditions. In particular, the use of self-propagating high-temperature synthesis (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 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 compared to their analogues, as 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[5-8].

Obtaining innovative chrome coatings on structural materials operating under conditions of vulcanization of rubber products has proven to be an urgent task in the context of the rapid development of technology in Ukraine. Given the increasing loads and aggressive environment in which critical parts operate, the effectiveness of surface hardening methods has become critical. In particular, diffusion silicification has proven to be an effective method of increasing the durability of various parts by changing their chemical composition, structure and properties [9-11].

Based on the analysis of literature sources, it became known that there are many methods of diffusion saturation of the steel surface with chromium. They include processes that occur at high temperatures, when the free energy of the system is large enough for diffusion in the solid phase. Various methods are used to produce chromium-based coatings, such as in the environment of molten electrolytes, in the gas phase, using powder masses in a neutral or reducing atmosphere.

According to [1-12], there are many methods for diffusion saturation of the steel surface with silicon. Their main common aspect is the implementation of the saturation process at high temperatures, when the free energy of the system is sufficiently large for diffusion to occur in the solid phase. It has been found that self-propagating high-temperature synthesis (SHS) has made it possible to relate the structure of materials formed during combustion to the kinetics of fast exothermic reactions. It is noted in [8] that a solid flame in its pure form is a rare phenomenon and can occur only in systems with a very developed contact surface of the reactants. The study of gaseous SHS coatings shows that they have better characteristics than their analogues, as they have the properties of the applied material and high adhesive strength. It is known that pure rubber is characterized by low mechanical, thermal, chemical and electrical properties.

Setting objectives. The purpose of this study is to develop and improve technologies for obtaining protective coatings on metal surfaces using self-propagating high-temperature synthesis (SHS). The paper investigates in detail the processes of combustion and formation of protective coatings under SHS conditions, and considers the possibilities of using various components to obtain improved coating properties. The main goal is to optimize the process parameters in order to achieve the most effective coating characteristics.

The influence of temperature, isothermal holding time, and component concentration on the thickness, structure, and properties of the resulting coatings was investigated. The results of the study allow us to develop recommendations for the improvement and practical application of technologies for the formation of protective coatings on metal surfaces. The knowledge gained in this work has significant practical potential and can be used in industrial production to improve the properties of metal structures and increase their service life.

Presenting main material. The coatings coated in SHS-processes, when accompanying gas-transport reactions take place, are very peculiar. They consist of a film of the applied product, as in gas-phase sedimentation (GP), and a wide transition diffusion (gradient) zone, as in diffusion saturation. As a consequence, gas-transport SHS - coatings have the best features of their counterparts - 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 in such conditions are satisfactory. If the particles do not melt, then the interaction between the reactants occurs solid-phase 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 in which all substances (not only initial and final, but also intermediate substances) are in the solid state.

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 can solve the heat balance equation of the systems under consideration.

In the work, samples from mass-produced steels 20, steel 45, U8, 40X, 40X16M were used for coating. As reaction agents, mixtures of powders with a dispersion of 60-250 microns of the following materials were used: chromium, silicon, boron, aluminum oxide, aluminum, iodine, ammonium fluoride. In determining the required dispersion of reagents, we were guided by studies that showed that the maximum transformation completeness is observed when using a reaction mixture with a fraction of 100-120 microns. The protective coatings on the samples under SHS conditions were obtained using the developed pilot plant DSTU12, consisting of the following main functional systems: reaction equipment; system for monitoring and controlling technological parameters; gas utilization system.

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 400x400 of new elastomeric materials based on a copolymer of vinyl dl-fluoride and hexopropylene, ethylene-propylene rubber, containing carbonized fiber from PAN (polyacrylonitrile), stone (granite) flour, aluminosilicate microspheres as Np. 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 include clay, carbon black, modified montmorillonite octadecylamine (organo-MMT), silica (SiO_2), aluminosilicate hollow microspheres (ASM), industrial carbon.

The existence of temperature limits to which the propagation of the combustion front is possible introduces certain restrictions on the use of the combustion mode as a technological mode. On the contrary, the thermal autoignition mode is free from these limitations. By diluting the initial powder mixture with an inert substance up to 85-90% wt. %, it is possible to reduce the maximum temperature of the process to the technologically necessary temperatures.

The main compounds in the gas phase in the temperature range of 400 - 1600 K are as follows: SiCl, $SiCl_2$, $SiCl_3$, $SiCl_4$, SiJ_2, SiJ_3, AlJ, AlJ_2, AlCl, $AlCl_2$, $CrCl_2$, CrF, CrF_2, CrF_4, BF_3, $TiCl_2$, $TiCl_3$, $TiCl_4$, as well as iodine in atomic and molecular form.

With increasing temperature, the amount of products in the gaseous phase increases and condensed products are released. Characteristically, in the temperature range of 400-1600 K the share of condensed phase decreases, which is associated with the evaporation of the carriers used. Simultaneously, starting from the temperature of 800 K, the decomposition of reaction products occurs, which confirms the appearance of decomposition products and a sharp increase in the number of moles of gas. The gaseous products interact with the elements of the powder system (Al, Si, B, Ti, W, Cr) and transfer them to the gas phase (appearing SiCl, $SiCl_2$, $SiCl_3$, $SiCl_4$, SiJ_2, SiJ_3, AlCl, $AlCl_2$, $AlCl_3$, BF_3, CrF, CrF_2, CrF_4, $TiCl_2$, $TiCl_3$, $TiCl_4$, AlJ and others). At temperatures above 800 K, the fraction of condensed phase practically does not change. This fact suggests that in the temperature range of 800-1600 K reactions with the release of condensed phase occur, but without changing the number of moles, which is characteristic of decomposition reactions, disproportionation, or eCrChange with the substrate, i.e. essentially there is a chemical transport of elements.

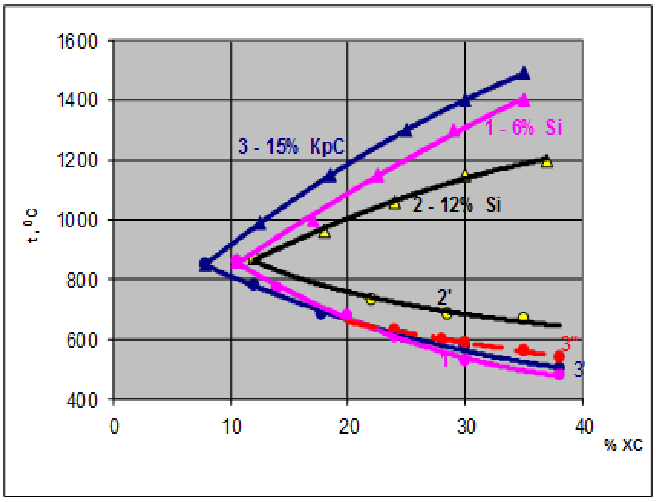

Figure 1 – Dependence of autoignition temperature (t*) and maximum temperature (tm) on CrC content for the system nCrC + 8Si + 6Al + LAl_2O_3 + 2 NH_4Cl + $1J_2$: 1, 1' - 6% wt., Si; 2, 2' - 12% wt., Si and for the system: nCrC + 15SiC + 6 Al + lAl_2O_3 + 2 NH_4Cl + $1J_2$, curves 3, 3', 3"

Aluminum powder, chromium oxide, chromium oxide, aluminum oxide, aluminum oxide, crystalline silicon, silicon oxide, ammonium chloride, and metallic iodine were used to obtain chromoaluminosiliconized coatings. To carry out the joint surface saturation of chromium, aluminum, and silicon, the content of crystalline silicon was selected up to 7% wt%, and the siliceous component (SiC) up to 20%. As can be seen from the literature [11], at higher silicon content, predominantly silicification takes place. The dependence of ignition temperature (t*) and maximum temperature (tm) on CrC is shown in fig. 1. The use of silicon component (curve 3) leads to the occurrence of double ignition (3', 3"), which is caused by the beginning of the reaction of aluminum reduction by silicon oxide. The overall temperature rise of the process, when using the silicon component is higher than using only the chromium component, which indicates the higher thermal characteristics of the mixture. Optimal compositions of SHS - mixtures for chromoalumosilicification, obtained because of graphical optimization for the thermal autoignition condition.

The influence of process temperature and isothermal holding time on the thickness of the siliconized layer doped with chromium and aluminum. The variation of the layer depth as a function of temperature and saturation time deviates from the exponential and parabolic law characteristic of purely diffusion kinetics. This is probably due to the fact that the absolute value of concentrations and the ratio between the number of diffusion atoms of chromium, aluminum and silicon changes with increasing temperature, which in turn leads to a change in the limiting concentrations that cause phase recrystallization, and also changes the diffusion rate of each of the elements.

Powders of aluminum oxide, chromium oxide, crystalline silicon, silicon oxide, silicon oxide, titanium, aluminum, and crystalline iodine were used to obtain multicomponent chromium-doped coatings doped with Si, Al B, and Ti. When the surface was saturated with chromium, aluminum and titanium, the content of crystalline silicon was: 7.5% wt. and SiC 15% wt. At higher silicon content, predominantly silicification takes place. The dependence of autoignition temperature (t*) and maximum temperature (tm) on CrC content is shown in Fig. 1. As can be seen, when using SiC, there is an increase in the maximum temperature and the occurrence of the point of secondary temperature rise, which is due to the reaction of aluminum reduction by silicon oxide. The optimal amount of gas-transporting agent: J_2 - 2%, NH_4Cl - 3%.

Microhardness of multicomponent chromium alloyed layers doped with silicon, aluminum on technical iron and steel 20 is within 7100 - 8200 MPa, on steel 45 and U8A it reaches 15000 - 16800 MPa, which is associated with the formation of carbide phases of chromium type $(Cr,Fe)_3C_2$. The character of microhardness variation by thickness of protective layers is shown in fig. 2.

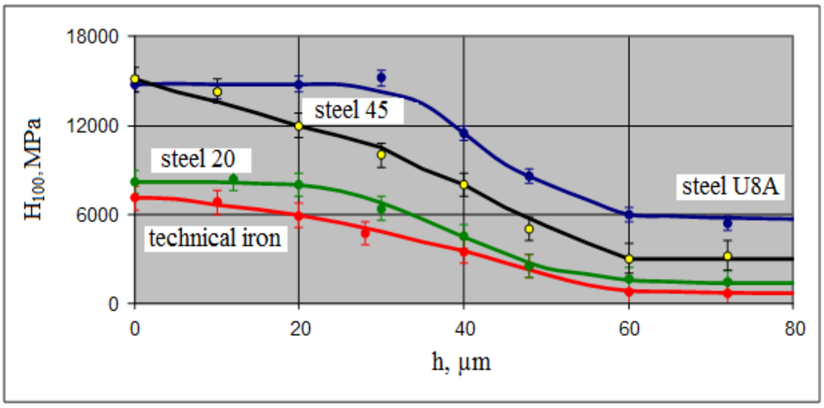

Figure 2 – Variation of microhardness of chrome layers doped with silicon and aluminum as a function of layer depth: $t_п = 1000\ ^0C$, $t_в = 60$ min.

Conclusions. After analyzing the latest research and publications on chromium plating, the purpose of this study was to develop and improve methods for protecting metal structures used in the vulcanization of rubber products using innovative chrome coatings. The main attention was paid to the study of surface hardening and diffusion saturation processes, in particular the use of self-propagating high-temperature synthesis. The experimental results showed that the obtained coatings have increased strength and resistance to aggressive environments, and are able to maintain their properties for a long time. The research objectives included analyzing the effect of various methods of diffusion saturation of the steel surface with silicon on the formation of the coating structure and its properties, developing the optimal composition and process mode, and studying the mechanisms of interaction between the system components during the formation of the protective layer. We obtained a chromium-alloyed coating alloyed with silicon, aluminum, titanium, and boron. The aim of the study was to strengthen the working surfaces of parts operated in aggressive conditions on equipment for vulcanization of products made of new elastomeric materials based on a copolymer of vinyl develfluoride and hexopropylene, ethylene-propylene rubber. The surface microhardness of boron-doped multicomponent chrome layers is 20000-22000 MPa, which is due to the presence of the FeB phase. The microhardness of the Fe2B alloyed phase is 15000-16000 MPa. The obtained results indicate that silicon is displaced from the boride zone to the sublayer of the α-phase, alloying only the Fe2B phase. Based on the results, it can be concluded that chrome coatings are effective in protecting metal structures under conditions of vulcanization of rubber products. The data obtained provide a basis for the transition from theoretical calculations to practical applications in industry, ensuring an increase in the quality and service life of press tooling.

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ОТРИМАННЯ ХРОМОВИХ ПОКРИТТІВ НА КОНСТРУКЦІЙНИХ МАТЕРІАЛАХ, ЩО ПРАЦЮЮТЬ В УМОВАХ ВУЛКАНІЗАЦІЇ НОВИХ ГУМОТЕХНІЧНИХ ВИРОБІВ

У даній роботі досліджувалася можливість отримання захисних покриттів, в умовах саморозповсюджувального високотемпературного синтезу, на деталях обладнання для вулканізації нових гумотехнічних виробів.. Дослідження спрямоване на пошук ефективних шляхів зміцнення робочих поверхонь умовно важливих елементів обладнання, що експлуатуються в агресивних умовах, зокрема, пресової оснастки. Враховуючи високі вимоги до зносостійкості та корозійної стійкості таких деталей, особлива увага приділялася вибору складу та параметрів процесу отримання покриття. Для досягнення цієї мети було використано різні композиційні матеріали та методи нанесення, а також проведено комплекс досліджень з вивчення властивостей отриманих покриттів. Отримані результати свідчать про можливість успішного застосування хромованих покриттів, легованих кремнієм, бором, алюмінієм для подальшого зміцнення та захисту деталей вулканізаційного обладнання. Проведені дослідження, є актуальними для розробки нових технологій виробництва та підвищення ефективності експлуатації пресової оснастки для вулканізації гумотехнічних виробів.

Ключові слова: *саморозповсюджувальний високотемпературний синтез, кремній, бор, хром, покриття, еластомерні матеріали, зносостійкість, мікротвердість.*