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ОТРИМАННЯ БАГАТОКОМПОНЕНТНИХ ХРОМОВАНИХ ПОКРИТТІВ НА ДЕТАЛЯХ, ЯКІ ЕКСПЛУАТУЮТЬСЯ В АГРЕСИВНИХ УМОВАХ ЕЛАСТОМЕРНОГО ВИРОБНИЦТВА

Дана стаття присвячена дослідженню технології отримання багатокомпонентних хромованих покриттів на деталях, які експлуатуються в агресивних умовах еластомерного виробництва. Зокрема, розглядається використання методу саморозповсюджуючого високотемпературного синтезу (SHS), що дозволяє отримувати покриття з високою корозійною стійкістю завдяки утворенню пасивних оксидних плівок на поверхні. Проведено аналіз актуальності проблеми підвищення надійності та довговічності деталей в умовах агресивного впливу, який свідчить про необхідність впровадження ефективних методів захисту машин та установок. Стаття розглядає методику отримання багатокомпонентних хромованих покриттів з використанням технології SHS, а також вплив режиму теплового самовоспалення з розбавленням порошкової суміші на ефективність отримання покриттів і їх корозійну стійкість. Проведено дослідження корозійної стійкості отриманих покриттів в агресивних середовищах, таких як водний розчин соляної кислоти, азотна кислота та сірчана кислота, що мають концентрацію 15%. На основі результатів досліджень зроблено висновок про ефективність застосування багатокомпонентних хромованих покриттів для підвищення корозійної стійкості деталей, які експлуатуються в агресивних умовах еластомерного виробництва. Дана стаття має практичне значення для підвищення довговічності та надійності машин і установок, особливо в умовах еластомерного виробництва, де важлива стійкість деталей до агресивних середовищ та корозії.

Ключові слова: саморозповсюджувальний високотемпературний синтез, корозійна стійкість, хромовані покриття, еластомерні матеріали, кремній, бор, матриця.

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OBTAINING MULTI-COMPONENT CHROME COATINGS ON PARTS THAT ARE USED IN AGGRESSIVE CONDITIONS OF ELASTOMER PRODUCTION

This research is devoted to the study of the technology for obtaining multicomponent chrome coatings on parts that operate under aggressive conditions of elastomeric production. In particular, the use of the self-propagating high-temperature synthesis (SHS) method is considered, which allows obtaining coatings with high corrosion resistance due to the formation of passive oxide films on the surface. The urgency of the problem of increasing the reliability and durability of parts under aggressive conditions is analyzed, which indicates the need to introduce effective methods of protecting machines and installations. The article considers the methodology for obtaining multicomponent chrome coatings using SHS technology, as well as the effect of thermal spontaneous combustion with dilution of the powder mixture on the efficiency of coating production and their corrosion resistance. The corrosion resistance of the obtained coatings in aggressive environments, such as an aqueous solution of hydrochloric acid, nitric acid, and sulfuric acid with a concentration of 15%, was studied. Based on the research results, it is concluded that the use of multicomponent chrome coatings is effective for improving the corrosion resistance of parts that operate in aggressive conditions of elastomer production. This article is of practical importance for increasing the durability and reliability of machines and installations, especially in the conditions of elastomer production, where the resistance of parts to aggressive environments and corrosion is important.

Key words: selfpropagating high-temperature synthesis, corrosion resistance, chrome coatings, elastomeric materials, silicon, boron, matrix.

Formulation of the problem. Formulation of the problem in the context of the study under discussion includes the following aspects. First of all, with the development of technologies, there is a growing need to improve the reliability and durability of machine parts, devices and installations, especially those operating under vulcanization conditions of elastomer production. The role of surface hardening processes is becoming critical to ensure the longevity of machines and mechanisms due to the growing demands of the industry, including high loads, temperature fluctuations and aggressive environments. The SHS method, based on diffusion chromium plating, is proving to be effective in increasing the durability of various components as it changes the chemical composition, structure and properties of metal surface layers, which increases their resistance to wear, corrosion and other types of degradation. A comparative analysis with other diffusion saturation methods shows the advantages of SHS coatings, as they can have material properties that increase wear or corrosion resistance compared to the substrate, and also have strong adhesive strength to powders. In this regard, it is also important to take into account the microstructure of SHS coatings, which determines their mechanical and chemical properties, and to solve problems related to the control of diffusion processes and coating homogeneity, which is important for practical applications in industrial environments [1, 3].

Analysis of recent research and publications. An analysis of recent research and publications in the field of obtaining chromium coatings on parts that operate under aggressive conditions of elastomeric production using the self-propagating high-temperature synthesis method allows us to identify the following key aspects.

Recent studies confirm the high efficiency of the SHS method in forming chrome coatings on metal parts. This method can significantly increase the resistance of parts to aggressive environments and ensure their long-term operation. New research aims to optimize SHS processes to achieve maximum uniformity and quality of chrome coatings. This includes developing new formulations, controlling process parameters, and analyzing the impact of microstructure on coating properties.

Research focuses on the microstructure of SHS chrome coatings and its impact on mechanical, thermal and corrosion properties. It is important to ensure the correct microstructure to form high-quality chrome coatings. Comparative studies with other coating methods allow us to find out the advantages and disadvantages of the SHS method in specific operating conditions and compare its effectiveness [4,5].

Recent studies have focused on the practical applicability of the SHS method in industrial environments. It is important to develop technologies that would be efficient, cost-effective and have a wide range of applications in aggressive elastomer production conditions [2].

Setting objectives. Research into the self-propagating high-temperature synthesis method for obtaining chromium coatings on parts used in aggressive elastomeric production conditions has the following goals and objectives. First of all, the main goal is to develop optimal process parameters and formulations for the SHS process to produce high-quality and efficient chrome coatings on metal parts. This includes studying the effect of processing conditions, temperature parameters, powder composition and gasification mode on the quality and properties of coatings. Another important aspect is the study of the microstructure of the resulting coatings and their properties, such as strength, hardness, resistance to abrasive wear, as well as thermal conductivity and electrical conductivity. This makes it possible to assess the effectiveness of the coating in the conditions of its operation and determine the possibility of its use in specific production conditions.

The third task is to optimize the SHS process to meet practical requirements and in accordance with the technological capabilities of the production. This includes implementing the most effective solutions for equipment, operating modes and process control to ensure consistent coating quality at the industrial level. In addition, it is important to conduct a comparative analysis of the effectiveness of the SHS method with other coating technologies to determine its competitiveness and applicability in practical conditions of elastomer production. The overall result of the study provides for specific practical recommendations for the implementation of the obtained results in production, which will improve the quality and efficiency of elastomeric products with chrome coatings in aggressive operating conditions.

Presenting main material. 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. Diffusion chromium plating using the CVS method is an effective method of increasing the durability of various parts, which changes the chemical composition, structure and properties of the metal surface layers.

Modern composite materials, such as rubber and rubber-based natural and synthetic rubber, play an important role in the metallurgical, textile and chemical industries. The use of such materials allows for the creation of products for structural and tribotechnical applications with improved damping properties, high elasticity and corrosion resistance. The use of rubber instead of metal also helps to reduce the weight of structures and machines, shortens the time for manufacturing parts (even of complex configurations) and increases corrosion resistance [6]. The pressing process was carried out using a hydraulic press of the "vulcanization 100-400 2E" type with plates measuring 400x400 mm for new elastomeric materials based on a copolymer of vinyl di-fluoride and hexopropylene, ethylene-propylene rubber.

Rubbers consist of a mixture of substances, the main component of which is natural or synthetic rubber. It is important to note that pure rubber has low mechanical, thermal, chemical and electrical properties. To improve these characteristics, fillers such as clay, carbon black, modified montmorillonite octadecylamine, silica (SiO₂), aluminosilicate hollow microspheres, carbon black, and others are effectively used [3].

The materials used for press tooling in the production of elastomeric products, such as steel 20, steel 45, U8, 40X, 40X16M, were investigated. Mixtures of powders with dispersity from 60 to 250 microns of the following materials were used as reaction agents. When determining the necessary dispersity of reagents, we were guided by the studies, which showed that the maximum completeness of transformation is achieved when using a reaction mixture with a fraction of 100-120 microns. The press tooling to be processed is shown in Fig. 1.

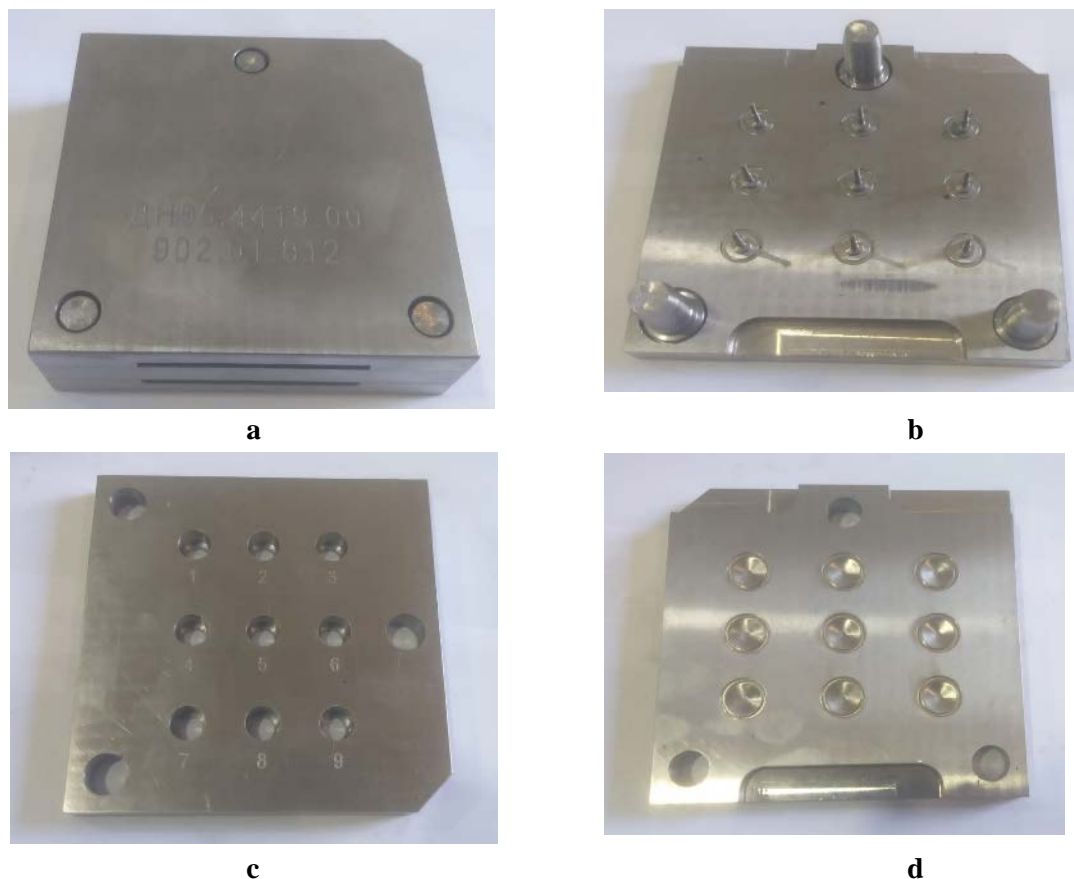


Fig. 1. General view of the press tooling: a- appearance of the complete tooling, b- punch, c- press spacer, d- die.

Coatings obtained in self-propagating high-temperature synthesis processes have unique properties related to the associated gas-transport reactions. These coatings consist of a film of the applied product, similar to gas-phase deposition, as well as a broad transient diffusion (gradient) zone, as in diffusion saturation. Due to these features, gas-phase SHS coatings have better characteristics compared to other methods [7,8]. They can have properties of the applied material, such as being more wear-resistant or corrosion-resistant than the substrate, and have high adhesion strength powders. In such powders, the particles of one substance are coated with a layer of another, which provides a large specific contact surface for the reactants at sufficiently small particle sizes. The micron sizes under such conditions are satisfactory, and the interaction between the reactants occurs in the solid phase in the reaction diffusion regime if the particles do not melt. The low values of mass transfer coefficients in the solid phase can be compensated by a large contact surface. In this case high temperature is an important factor intensifying the process.

Determination of reaction products allows modeling the process of formation of protective layers under SHS conditions. On the basis of calculation of adiabatic temperatures of SHS system combustion it is possible to solve the heat balance equation, which is important for optimization and control of the process of protective coatings application. For the application of protective coatings on samples under SHS conditions the developed pilot plant DDTU12 was used, which includes the main functional systems: reaction equipment, system of control and regulation of technological parameters, as well as the system of gas utilization. This ensured efficient and controlled deposition of coatings with specified characteristics and quality.

The existence of temperature limits to which the combustion front can spread limits the use of combustion in technological processes. This is due to the fact that certain conditions, such as the presence of oxygen and sufficiently high temperatures, are required to sustain combustion. However, the thermal self-ignition mode is not subject to these limitations. By diluting the initial powder mixture with an inert substance to 85-90% by weight, it is possible to reduce the maximum process temperature to the values required by the technology. This approach allows more flexible process control and provides the necessary conditions without the risk of exceeding temperature limits.

Thus, the use of thermal auto-ignition mode with powder mixture dilution with an inert substance is an effective way to optimize processes, especially in areas where precise temperature control and avoidance of possible combustion limitations are important.

The following compounds predominate in the gas phase at temperatures between 400 and 1600 K: SiCl, SiCl₂, SiCl₃, SiJ₂, SiJ₃, AlCl, AlCl₂, AlCl₃, BF₃, CrF, CrF₂, CrF₄, TiCl₂, TiCl₃, TiCl₄, AlI, as well as iodine in atomic and molecular states. With increasing temperature, an increase in the number of products in the gaseous phase as well as the formation of condensed products is observed. However, the fraction of condensed phase decreases in the range of 400-1600 K due to vaporization of the carriers used. At temperatures above 800 K, the decomposition of reaction products occurs, indicating the appearance of decomposition products and a sharp increase in the number of gaseous molecules. The gaseous products interact with the elements of the powder system (Al, Si, B, Ti, Cr), transferring them to the gas phase.

At temperatures above 800 K, the proportion of the condensed phase practically does not change, indicating reactions with the formation of the condensed phase without changing the total number of molecules. This fact indicates the chemical transport of elements in the range of 800-1600 K. To increase corrosion resistance, a coating containing elements that form passive films is required. When tested in a 20% aqueous solution of hydrochloric acid, the best resistance is shown by protective coatings alloyed with chromium and titanium, which have the following weight loss rates: 23.5 and 21.5 g/m². Corrosion test results for 8 days are shown in Table 1.

Table 1

Corrosion resistance of steel 45 with protective coatings in aqueous acidic environments

Corrosive environment	Type of coating	Weight loss (10 ⁻⁴ g/m ²)							
		Test time, days							
		1	2	3	4	5	6	7	8
20% HNO ₃	Uncoated	87	152	230	300	363	468	547	631
	Cr-Al-Si	5,8	10,8	18	23	27	31	35	38
	Cr-Al-Ti	6,3	13	19	24	28	33	38	44
	Cr-Al-B	5,6	11	14,7	18	23	28	33,6	37,8
20% HCl	Uncoated	56	90	121	166	218	280	340	401
	Cr-Al-Si	6,7	10,3	11,7	15	18,3	20,9	25,1	28,2
	Cr-Al-Ti	5,9	9,2	11,1	13,3	15,4	16,9	19,2	21,5
	Cr-Al-B	6,4	10,7	12,5	14,1	16,4	19,1	21,1	23,5
20% H ₂ SO ₄	Uncoated	59	94	130	160	198	220	252	280
	Cr-Al-Si	3,7	4,7	6,6	8,2	9,2	10,9	12,2	13,4
	Cr-Al-Ti	2,9	3,4	4,5	5,6	7,2	8,1	8,8	9,6
	Cr-Al-B	3,9	5	6,4	7,9	9,7	10,8	12,9	14

When tested in a 20% aqueous solution of sulfuric acid, the best resistance is shown by protective coatings alloyed with silicon and titanium, which have the following weight loss rates: 13.4 and 9.6 g/m². When tested in a 20% aqueous solution of nitric acid, titanium and silicon-alloyed protective coatings show good resistance, with the following indicators: 44 and 38 g/m². A comparative analysis of the corrosion resistance of protective SHS coatings and CTH coatings obtained under isothermal conditions shows that they have a weight loss of 1.9-2.2 times less.

The results obtained can be explained by the formation of alloyed phases on the surface, which leads to surface passivation in aggressive environments. It is also possible to assume the influence of electrochemical inhibition of anodic dissolution of metals at a higher concentration of alloying elements of

alloyed protective coatings compared to coatings obtained under isothermal conditions, which indicates the absence of microcracking.

It is known that mechanical stresses (in this case, compressive residual stresses) affect the corrosion behavior of metals due to the structural material receiving additional energy due to the fact that the level of residual stresses in coatings obtained under conditions of thermal spontaneous combustion of SHS charges is higher. As a result, the probability of microcracking of passive oxide films decreases, which leads to an increase in corrosion resistance. A comparative analysis of the corrosion resistance of protective SHS coatings and CTH coatings obtained under isothermal conditions shows that they have a weight loss of 1.9-2.2 times less.

The conducted research allows us to conclude that one of the main factors affecting the performance of equipment is its corrosion resistance under the aggressive influence of the corrosive environment of elastomeric products production.

Conclusions. Several important conclusions were drawn during the study of the self-propagating high-temperature synthesis SHS method for obtaining chromium coatings on parts that operate under aggressive conditions of elastomer production. The SHS method is an effective and promising way to produce high-quality coatings, including chrome, on metal parts. It was found that optimal process parameters, such as processing modes, temperature, and powder composition, significantly affect the quality and properties of the resulting coatings. A detailed analysis of the microstructure allows us to determine the optimal conditions for coating formation. When tested in a 20% aqueous solution of sulfuric acid, the best resistance is shown by protective coatings alloyed with silicon and titanium, which have the following mass loss rates: 13.4 and 9.6 g/m².

When tested in a 20% aqueous nitric acid solution, titanium- and silicon-alloyed protective coatings show good resistance, with values of 42 and 37 g/m². A comparative analysis of the corrosion resistance of protective SHS coatings and CTH coatings obtained under isothermal conditions shows that they have a weight loss of 1.9-2.2 times less. The chromium coatings obtained by the SHS method are highly resistant to abrasive wear, corrosion and mechanical stress, which makes them effective for use in elastomeric production. The high level of stability and efficiency of the SHS process confirms the possibility of implementing this method at elastomeric products manufacturing enterprises to improve the quality and service life of parts. Thus, the study of SHS for obtaining chromium coatings in the context of elastomeric production is a relevant and promising area that will further improve the quality and efficiency of elastomeric production.

References

1. 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.
2. 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.
3. Поверхневе зміцнення матеріалів працюючих в умовах комплексного впливу агресивних речовин: монографія. Б.П. Серєда, Л.П. Банніков, С.В. Нестеренко, І.В. Кругляк, О.С. Гайдаєнко, Д.Б. Серєда – Кам'янське: Дніпровський державний технічний університет, 2019. – 170с.
4. Sereda B., Sereda D. 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.
5. Konovalenko, A.D., Dragobetsky, V.V. Novyye napravleniya razvitiya SVS–tekhnologiy [New trends in SHS technologies]. *Sistemnyye tekhnologii*. 2003. № 6. P. 68–73.
6. Cheshko, F. Microscopic Study of the Coal Tar Carbonaceous Dispersed Phase. *Chemistry & Chemical Technology*, 2011, 5(3), 355-362.
7. Kiryashkin, A.I., Salamatov, V.G., Maksimov, Y.M., Sosnin, E.A., Tarasenko, V.F., Gabbasov, R.M. Osobennosti spektra opticheskogo izlucheniya v protsessakh goreniya s obrazovaniem kondensirovannykh produktov goreniya [Features of the spectrum of optical radiation in combustion processes with the formation of condensed combustion products]. *Combustion, Explosion, and Shock Waves*. 2010. Vol. 46, №1. P. 132–135.
8. Varma, A., Rogachev, A.S., Mukasyan, A.S., Hwang, S. Combustion synthesis of advanced materials: Principles and applications. In *Advances in Chemical Engineering*. J. Wei (Ed.). New York: Academic Press. 1998. V. 24. P. 79–226.