FORMATION OF CHROMATED COATINGS ON A PRESS TOOLING IN THE PRODUCTION OF RUBBER PRODUCTS FOR ROCKET AND SPACE TECHNOLOGY

B. Sereda, A. Udod

Dnipro State Technical University, 2 Dniprobudivska St., Kamianske, 51900, Ukraine.

Abstract. This research analyzes the influence of residual stresses formed as a result of the process of self-propagating high-temperature synthesis on the mechanical properties and durability of structural materials and protective coatings. The main emphasis is placed on the analysis of the relationship between residual stresses and adhesive strength and durability of the obtained coatings. 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 cushioning, flexibility, and elasticity, which makes them able to handle dynamic loads and adapt to various forms of deformation without losing structural properties. Research was carried out on parts of press tooling used for manufacturing of rubber-technical products in rocket-space engineering. It was found that residual stresses formed during the SHS process have a significant effect on the adhesion properties of protective coatings. Residual stresses appear after SHS treatment under conditions of thermal self-ignition of SHS charges. At the cooling stage of the SHS process, residual compressive stresses appear as a result of the elastic interaction of the alloyed titanium coating and the structural material, which have different sizes and coefficients of thermal expansion. The maximum values of adhesion strength of titanium coatings on steel 45 were 120-150 MPa when alloyed with aluminum and 180-210 MPa when alloyed with chromium. This research emphasizes the importance of residual stress control for improving the strength and durability of protective coatings obtained under SHS conditions and their possible role in extending the service life of structures and equipment. Additional research in this direction may contribute to process optimization and product quality improvement in the aerospace industry.

Key words: SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS, SILICON, BORON, CHROMIUM, COATINGS, ELASTOMERIC MATERIALS, WEAR RESISTANCE, MICROHARDNESS

FORMУВАННЯ ХОРОМОВАНИХ ПОКРИТТІВ НА ПРЕСОВОМУ ОСНАЩЕНІ ПРИ ВИРОБНИЦТВІ ГУМО-ТЕХНІЧНИХ ВИРОБІВ ДЛЯ РОКЕТНО-КОСМІЧНОЇ ТЕХНІКИ

Б.П. Середа, А. М. Удод

Дніпровський державний технічний університет, вул. Дніпровбудівська 2, м. Кам'янське, 51900, Україна.

Анотація. У цьому дослідженні аналізується вплив залишкових напружень, що формуються в результаті процесу саморозповсюджуваного високотемпературного синтезу, на механічні властивості та стійкість конструкційних матеріалів і захисних покриттів. Основний акцент робиться на аналізі взаємозв'язку залишкових напружень з адгезійною міцністю і стійкістю отриманих покриттів. Композити на основі каучуків можуть виявитися конкурентоспроможними та в перспективі замінити традиційні матеріали в ряді застосувань, оскільки їх властивості перевершують традиційні гумові. Композити на основі гум часто мають меншу щільність порівняно з традиційними матеріалами, такими як метал. Це дозволяє зменшити вагу виробів, що важливо в різноманітних галузях, де легкість є ключовою характеристикою. Гумові композити характеризуються амортизацією, гнучкістю та еластичністю, що робить їх дієтою працювати при динамічних навантаженнях та пристосовуватися до різних форм і деформацій без втрати структурних властивостей. Дослідження проводили на деталях пресового оснащення ракетно-космічних виробів, що використовуються для виготовлення гумових виробів у ракетно-космічній техніці. Встановлено, що залишкові напруження, які утворилися під час процесу СВС, суттєво впливають на адгезійні властивості захисних покриттів. Залишкові напруження з'являються після СВС-обробки в умовах теплового самозапалювання СВС-шихт. На стадії охолодження СВС-процесу, в результаті пожежної взаємодії легованого титанового покриття і конструкційного матеріалу, що мають різні розміри.
Introduction

In modern industry of production of rubber-technical products for rocket-space technology, the problem of providing high strength and durability of protective coatings used on parts of press tooling is urgent. One of the main factors affecting the mechanical properties and durability of coatings is residual stresses arising in the process of self-propagating high-temperature synthesis (SHS).

Residual stresses can have both positive and negative effects on the adhesion and durability of coatings, depending on their magnitude and distribution. Therefore, it is necessary to study in more depth the relationship between the formation of residual stresses and the mechanical properties of coatings on press tooling in order to develop methods to optimize the application process and improve the quality of the resulting protective coatings [1-2].

Purpose of this research is to analyze the influence of residual stresses on the adhesive strength and durability of protective coatings on parts of press tooling used in rocket and space technology, as well as the development of recommendations for optimizing technological processes to improve the quality and durability of structures.

Scientific novelty

For the purposes of this research, the objective is to analyze the effect of residual stresses on the mechanical properties and durability of protective coatings on parts of press tooling used to manufacture rubber products in rocket and space technology. The study is aimed at determining the magnitude and distribution of residual stresses in protective coatings on various elements of press tooling, taking into account the specifics of their use in rocket and space technology. Other important tasks include analyzing the effect of residual stresses on the adhesive strength of coatings and their ability to withstand mechanical and thermal loads under extreme conditions, as well as developing methods for optimizing the process of applying protective coatings to increase their reliability and durability [3].

To achieving these objectives, it is proposed to conduct a set of experiments that involves measuring residual stresses in protective coatings using high-precision methods of mechanical stress analysis. In addition, a series of adhesion strength tests will be conducted to determine the stability of coatings under the influence of mechanical and thermal factors [4]. The results of the study will be analyzed using statistical methods and mathematical models to obtain objective conclusions about the impact of residual stresses on the functional properties of protective coatings. This approach will make it possible to understand the mechanisms of deformation, fracture in protective coatings, and develop recommendations for their improvement to increase the efficiency and duration of operation in rocket and space technology.

Presenting main material

Coatings obtained under conditions of self-propagating high-temperature synthesis have special characteristics. They are formed from a film of the applied product, similar to the gas-phase deposition process, and a wide transient diffusion zone, similar to diffusion saturation. These features allow SHS coatings to have superior properties compared to other...
analogs: they can have improved characteristics of the applied material (e.g., improved wear or thermal resistance compared to the base material) and high adhesion strength between layers of powders where particles of one material are covered by a layer of the other [5]. This provides a large contact area for the reagents, especially when small particles are used. Micron particle sizes also remain acceptable under these conditions. If the particles do not melt, reactions between reactants proceed through the solid phase by reaction diffusion. The low values of mass transfer coefficients in the solid phase can be compensated by increasing the contact surface. An important factor is also high temperature, which intensifies the processes. Under certain conditions, it is possible to achieve a pure solid flame regime in which all substances, including intermediates, remain in the solid state [6].

By analyzing the reaction products, we can create a model of the process of formation of protective coatings under SHS conditions. Based on calculations of adiabatic combustion temperatures of SHS systems, we can solve the heat balance equation for the systems under consideration.

Mixtures of powders with different dispersions from 60 to 250 μm were used to apply protective coatings on steel samples such as steel 45, U8, 40X and 40X16M. These powders included elements such as chromium, silicon, boron, aluminum oxide, aluminum, iodine, and ammonium fluoride. The choice of powder dispersion was guided by studies that showed that the optimum powder fraction to maximize reaction completeness was between 100 and 120 μm. The press tooling to be processed is presented in Fig. 1, 2.

The process of applying protective coatings under SHS conditions was carried out at a specially designed pilot plant DDTU12. This plant includes not only reaction equipment, but also a system of control and regulation of process parameters, which ensures safe and efficient coating process.

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Currently, 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. Pressing was carried out on a hydraulic vulcanizing pressing machine 100-400 2E with plate sizes of 400x400 new elastomeric materials based
on a copolymer of vinyl difluoride and hexopropylene, ethylene-propylene rubber, containing carbonized polyacrylonitrile fiber, stone (granite) flour, and 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 [7]. Effective fillers for natural and artificial rubbers are clay, carbon black, modified montmorillonite octadecylamine, silica (SiO$_2$), aluminosilicate hollow microspheres (AHM), technical carbon.

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 [8]. 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 [9-10].

However, it is important to take into account limitations and challenges, such as limited strength compared to metals, possible problems with heat dissipation at high temperatures, and the cost of producing and processing rubber composites. The growth in demand for these materials will depend on technological development, solving these problems and increasing their competitiveness in the market.

Existence of limiting temperatures at which the combustion front can propagate places certain restrictions on the use of the combustion mode in technologies. On the contrary, the thermal autoignition mode is free from these limitations. By diluting the initial powder mixture with an inert substance to 85-90% of the mass, it is possible to reduce the maximum temperature of the process to a technologically necessary level. As the temperature increases, 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 due to vaporization of the carriers used. Simultaneously, starting from the temperature of 800 K, the decomposition of reaction products occurs, which indicates the appearance of decomposition products and a sharp increase in the number of gas molecules.

Gaseous products interact with elements of the powder system (Al, Ti, Cr), transferring them to the gas phase (AlJ, AlJ$_2$, AlCl, AlCl$_2$, CrCl$_2$, CrF, CrF$_2$, CrF$_4$, TiCl$_2$, TiCl$_3$, TiCl$_4$ etc.). At temperatures above 800 K, the fraction of condensed phase practically does not change, indicating that reactions with the release of condensed phase in the range of 800-1600 K without changing the number of molecules, which is characteristic of decomposition, disproportionation or exchange reactions with the substrate, which is the essence of chemical transport of elements.

Residual stresses appear after SHS treatment under conditions of thermal self-ignition of SHS charges. At the fifth stage of the SHS process, during cooling, residual compressive stresses appear as a result of the elastic interaction of the alloy titanium coating and the structural material, which have different sizes and coefficients of thermal expansion.

Tensile residual stresses in the surface layers are particularly harmful for metal products operating under alternating load, as such stresses contribute to fatigue failure (fatigue cracks usually originate on the surface of the product). The harmful effect of residual stresses is also reflected in an increase in the overall chemical activity of the metal.

Research has revealed that the saturation mode affects the nature and level of
residual stress distribution between the layers. The study of the adhesion strength of the coatings showed that the highest adhesion strength is achieved in coatings with the addition of aluminum. For example, on steel 45, the adhesion strength increases from 4.3 MPa (with the addition of titanium) to 5.6 MPa (with the addition of aluminum). Compared to coatings produced under isothermal conditions, this figure increases by 1.25-1.31 times. These results correlate with the overall brittle fracture index.

The results obtained are relevant for further research in the development of new materials and production technologies aimed at improving the efficiency and reliability of materials in high-tech industries, in particular in the rocket and space industry.

Fig. 3 shows the results of studies of the distribution of residual stresses along the thickness of the alloyed titanium coating obtained under SHS conditions on steel 45. It was found that compressive stresses occur on the surface of steel 45, reaching 120-150 MPa when alloyed with aluminum, and 180-210 MPa when alloyed with chromium.

Research of the distribution of residual stresses over the thickness of the protective coating on structural materials revealed that compressive stresses occur on their surface.

Table 1 shows the results of studies of the adhesion strength of alloyed protective chromium coatings obtained in the developed SHS blends and obtained under isothermal conditions on samples of steel 45 ($t = 10500{\text{C}}, \tau = 60 \text{ min}$) developed SHS blends and under isothermal conditions.

<table>
<thead>
<tr>
<th>Type of coating</th>
<th>Adhesion of coatings obtained under SHS conditions, MPa</th>
<th>Adhesion of coatings obtained under isothermal conditions, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-Ti</td>
<td>4.3</td>
<td>3.5</td>
</tr>
<tr>
<td>Cr-Al</td>
<td>5.6</td>
<td>4.4</td>
</tr>
</tbody>
</table>

As can be seen from the table, the highest adhesion strength of the alloyed chromium protective coating obtained by alloying with aluminum.

Research shows that the saturation mode affects the magnitude and nature of the layer-by-layer distribution of residual stresses. The study of the adhesive strength of the coatings revealed that the highest adhesive strength was obtained for aluminum-alloyed coatings. On steel 45, it increases from 4.3 (with Ti alloying) to 5.6 MPa (Al alloying), compared to coatings obtained under isothermal conditions, this figure increases by 1.25-1.31 times. These results correlate with the total brittle fracture score.

**Conclusions**

The conclusion of this research emphasizes the importance of analyzing the residual stresses arising from the process of self-propagating high-temperature synthesis on the mechanical properties and durability of structural materials and protective coatings. The study showed that these stresses can significantly affect the strength and resistance of materials under dynamic and cyclic loads, in particular under demanding operating conditions typical of rocket and space technology.
The main objectives of the research were to determine the effect of residual stresses on the adhesion strength and mechanical properties of protective coatings applied to parts of press tooling used to manufacture rubber products in rocket and space technology. Experimental testing and optimization of the coating process allowed us to draw important conclusions about improving the reliability and durability of protective coatings in operating conditions.

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The results obtained are relevant for further research in the development of new materials and production technologies aimed at improving the efficiency and reliability of materials in high-tech industries, in particular in the rocket and space industry.

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Відомості про авторів

Borys Sereda. Ukraine.
Dniprovsky State Technical University.
Head of the department of automobiles and transport and logistics systems, Doctor of Technical Sciences, Professor.
Sphere of interests – materials science, self-propagating high-temperature synthesis.
ORCID: 0000-0002-9518-381X seredabp@ukr.net

Andrey Udod. Ukraine
Postgraduate student of the Department of automobiles and transport and logistics systems
Sphere of interest – protective coatings on press tooling parts.