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MODELING THE PHASE COMPOSITION OF PROTECTIVE COATINGS USING FUNCTIONALLY ACTIVE CHARGES

МОДЕЛЮВАННЯ ФАЗОВОГО СКЛАДУ ЗАХИСНИХ ПОКРИТТІВ З ВИКОРИСТАННЯМ ФУНКЦІОНАЛЬНО-АКТИВНИХ ШИХТ

Our research focuses on the development of protective coatings for carbon-carbon composite materials (CCCM) using functionally active charges (FAC) obtained under nonstationary temperature conditions. The optimal compositions of titanium-doped powder coatings were modeled to increase heat resistance and study the phase composition. Chemical-thermal methods, methods of saturation from the liquid phase, and the method of saturation in an active gas environment are analyzed. Particular attention is paid to the chemical interaction and formation of carbide phases, which are important for the stability of coatings under high temperature conditions. Experimental studies have determined the compositions of powder mixtures that provide high heat resistance and evaluate the effect of chromium, silicon, titanium, and aluminum on the physical and mechanical properties of coatings. The regression equations were calculated to estimate the dependence of the wear resistance of coatings on the autoinitiation parameters and the content of alloying elements. The analysis of the results includes the construction of three-dimensional graphical dependencies for optimizing the composition of powdered FAC in Cr-Al-Ti systems. The protective coating consists of the TiC carbide phase and the Al_2Cr3, $CrAl_2$, TiAl phases, forming two zones: the inner one with titanium carbide and the outer one, the composition of which depends on the alloying elements in the FAC. These coatings have shown high heat resistance and excellent wear resistance, which makes them promising for use in high-temperature conditions.

Keywords: *protective coatings, carbon-carbon composite materials, heat resistance, synthesis, optimization, chemical and thermal treatment.*

Наше дослідження спрямоване на розробку захисних покриттів для вуглець-вуглецевих композиційних матеріалів (ВВКМ) з використанням функціонально активних шихт (ФАШ), отриманих при нестаціонарних температурних умовах, що забезпечують підвищені експлуатаційні характеристики. Основною метою є моделювання оптимальних складів порошків для захисних покриттів, легованих титаном, для підвищення жаростійкості робочої поверхні. У ході дослідження проаналізовано різні методи отримання захисних покриттів, включаючи хіміко-термічні методи та методи насичення з рідкої фази, для виявлення їхніх особливостей у взаємодії з матрицею ВВКМ та змін у механічних властивостях.

Крім традиційних методів, досліджено метод насичення поверхні твердою фазою в активному газовому середовищі за допомогою ФАШ, отриманих при нестаціонарних температурних умовах. Цей метод забезпечує високоякісні покриття, скорочує час обробки та дозволяє працювати при високих температурах залежно від складу ФАШ. Велика увага приділена проблемам, пов'язаним з хімічною взаємодією та формуванням карбідних фаз, які є важливими для забезпечення стійкості покриттів у високотемпературних умовах.

Експериментальні дослідження включають факторний експеримент для визначення складів порошкових сумішей, які забезпечують високу жаростійкість. Розглянуті різні незалежні змінні, такі як вміст хрому, кремнію, титану та алюмінію, з урахуванням їхнього впливу на фізико-механічні властивості покриттів. Наведено рівняння регресії для оцінки залежностей жаростійкості покриттів від параметрів автоініціації та вмісту легуючих елементів. Аналіз результатів дослідження включає побудову тривимірних графічних залежностей для оптимізації складу порошкової ФАШ в системах Cr-Al-Ti.

При легуванні титаном захисне покриття складається з карбідної фази TiC та фаз Al_2Cr_3, $CrAl_2$, TiAl. Захисне покриття має дві зони: внутрішню, яка містить карбід титану, і зовнішню зону, склад якої залежить від вибору легуючих елементів у ФАШ.

***Ключові слова**: захисні покриття, вуглець-вуглецеві композиційні матеріали, жаростійкість, синтез, оптимізація, хіміко-термічна обробка.*

Problem's Formulation

Research is focused on determining the optimal parameters for obtaining protective coatings for CCCM for the purpose of analyzing the phase composition of protective coatings and increasing the service life at high temperatures. The main objectives of the study are to develop FAC for the creation of alloyed titanium protective coatings that provide optimal resistance to oxidation, erosion and gas flows. Various coating methods, such as chemical-thermal treatment and liquid-phase saturation, were analyzed to determine their effectiveness and impact on the mechanical properties of the material. It is also important to establish the optimal composition of the coating, taking into account the content of alloy impurities such as silicon, titanium, aluminum and chromium, to ensure the formation of protective oxide membraness and preserve the strength of the material structure.

In this context, experimental research will be conducted to determine the optimal parameters of coating heat treatment, as well as to establish the relationship between the composition of functionally active blends and the mechanical properties of the resulting protective coatings. Particular attention is paid to the analysis of chemical reactions and processes occurring during coating formation, in particular, the formation of oxide phases and structural changes in the material.

Analysis of recent research and publications

The practical utilization of carbon-carbon composite materials faces significant challenges due to susceptibility to oxidation, erosion, and burnout in gas streams. Addressing these issues necessitates the development of effective protective coatings to enhance performance and extend service life. Promising materials for such coatings include refractory compounds like carbides, borides, nitrides, and silicides, known for their oxidation resistance, high hardness, and exceptional wear resistance. These coatings offer vital protection against high temperatures and harsh environments, safeguarding CCCM integrity. Composite materials combining carbon or graphite matrices with reinforced carbon or graphite fibers, boast exceptional properties including low specific gravity, high mechanical strength even at extreme temperatures, and superior thermal shock resistance [1].

The widespread use of CCCM spans diverse fields, notably in solid rocket engines where temperatures can exceed 2500 °C. Here, materials must withstand abrasive particles present in combustion products, emphasizing the importance of ablative and erosion resistance. Similarly, during spacecraft re-entry into the Earth's atmosphere, surface temperatures can soar above 5000 °C, necessitating materials with exceptional heat resistance. Decades of research and development in CCCM have propelled scientific and technological advancements globally, particularly in composite materials. This progress owes much to the development of carbon fibers and other high-temperature fibrous materials, which significantly influence CCCM properties. Thus, meticulous selection and application of reinforcing fibers stand as pivotal aspects in the ongoing evolution and application of these remarkable composites. The main method of this work is to identify the optimal functionally active charge, which can be used to obtain light chromium chrome plating on CCCM at non-stationary temperature conditions [2—3].

Various methods have been explored for producing protective coatings, each with distinct advantages and drawbacks. A challenging aspect involves coating saturation with silicon from the liquid phase, causing chemical interactions with the CCCM matrix and uneven carbide phase formation, thus altering mechanical characteristics. Nonetheless, several technologies have been devised for applying protective coatings to carbon materials, including chemical-thermal treatment and liquid-phase saturation methods [4]. The diffusion method of surface saturation from the solid phase in an active gas medium during FAC, acquired under non-stationary temperature conditions, has emerged as a promising chemical and thermal treatment method for CCCM. This technique offers high-quality coating surfaces, shorter processing times, and the ability to attain high temperatures, depending on FAC mixture composition. Adjusting the amount and content of alloying additives enables the production of coatings with diverse chemical compositions to meet specific engineering requirements.

Chromoaluminized coatings have gained traction for enhancing heat resistance in aerospace equipment parts. Chromoaluminized saturation, whether simultaneous or sequential, of metals and alloys with chromium and aluminum is primarily employed to improve wear, heat, and corrosion resistance of parts [5-6]. Chromium aluminizing methods include solid-phase, vapor-phase, gas-phase, and liquid-phase techniques, comprising simultaneous and sequential approaches, as well as solid-simultaneous and slip-based methods. These techniques offer versatility in creating coatings with customized properties suitable for demanding applications in aerospace and other sectors. Doping chromium-plated coatings with titanium, silicon, and boron holds promise for significant performance enhancement. The addition of these elements, combined with high corrosion and heat resistance, yields more versatile coatings with increased surface hardness, scale resistance, and corrosion resistance due to the formation of additional silicon and titanium oxides [7—8].

Formulation of the study purpose

Research is focused on finding the optimal parameters for obtaining protective coatings for CCCMs in order to analyze their phase composition and improve their durability at high temperatures. Objectives include the development of FAC for alloyed titanium coatings that are resistant to oxidation, erosion, and gas flows. Various coating methods, such as chemical heat treatment and liquid phase saturation, were evaluated for their effectiveness and impact on mechanical properties. Determining the ideal coating composition, which takes into account the impurities of alloys such as silicon, titanium, aluminum and chromium, is vital for the formation of protective oxide membranes and maintaining the structural integrity of the material. Experimental studies will determine the optimal parameters of heat treatment of coatings and investigate the correlation between the composition of the functionally active charge and the mechanical properties of the resulting coatings. Particular attention is paid to the analysis of chemical reactions and processes during the formation of coatings, especially the formation of oxide phases and structural changes in the material.

Presenting main material

The research findings and their subsequent discussion were pivotal. Analyzing the reactions occurring in non-stationary temperature conditions, coupled with experimental results and metallographic studies, led to the formulation of a scheme for developing protective coatings. The process of forming such coatings under thermal autoignition conditions can be delineated into five distinct stages: inert heating of the FAC mixture to the autoignition temperature, thermal autoignition, heating of the parts, isothermal aging, and cooling. The heat resistance test is performed in an electric furnace at a temperature of 1000 °C for 25 hours. The heat resistance characteristic is the change in the sample weight.

The selected independent variables for the experiment were the chromium, silicon, titanium and aluminum content of the FAC mixture. CCCM was chosen as the starting material and I_2 and NH_4F were used as process activators for all systems. It was observed that the introduction of more than 5 % of gas transport agent into the mixture resulted in significant distortion of the sample surface, while less than 1% did not activate all gas transport reactions.

To achieve a 100 % composition of powdered FAC mixtures, Al_2O_3 was utilized as the final product. Regression analysis was conducted to establish equations representing the dependency of wear resistance of protective coatings on the regime of thermal autoignition and the content of alloying elements. The resulting equations are as follows:

$$Y_4 = 60,311 - 0,6X_1 + 4,1X_2 - 0,6X_3 + 0,1111X_1^2 - 3,3889X_2^2 + 4,1111X_3^2 + 2,375X_1X_3 + 0,375X_1X_3 + 2,125X_2X_3.$$

The adequacy of the models was assessed, revealing their capability to predict response function values across a wide range of factor values. This ensures their applicability for predicting responses within the specified upper and lower level bounds. To identify the optimal heat resistance parameters of the coatings, the regime and FAC compositions were analyzed. Three-dimensional graphical dependencies were constructed to visualize these relationships effectively (fig. 1). These graphical representations facilitate a clearer understanding of the interplay between different factors and their impact on heat resistance properties. The test samples were weighed every 5 hours during testing using analytical scales VLR-200, which provided an accuracy of 10^{-4} g. The duration of the entire testing process was 25 hours.

The gas transport method of coating with the help of FAC allows for the production of CCCM with enhanced physical and mechanical properties, all without requiring high energy costs and time-intensive processes.

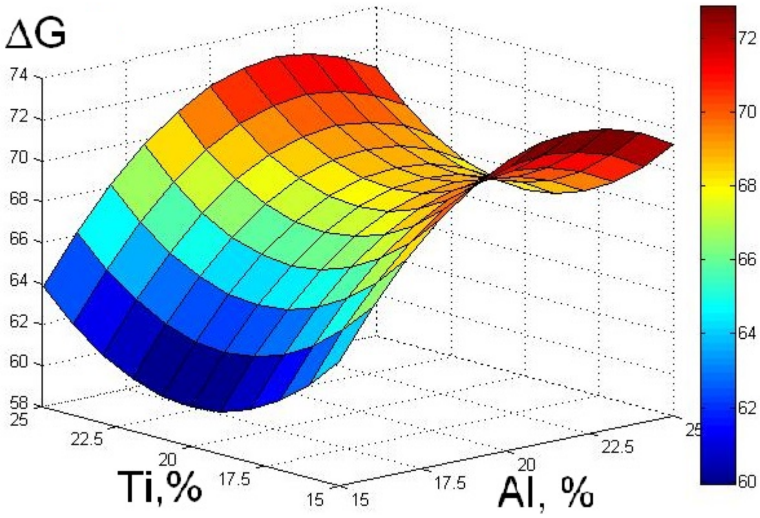


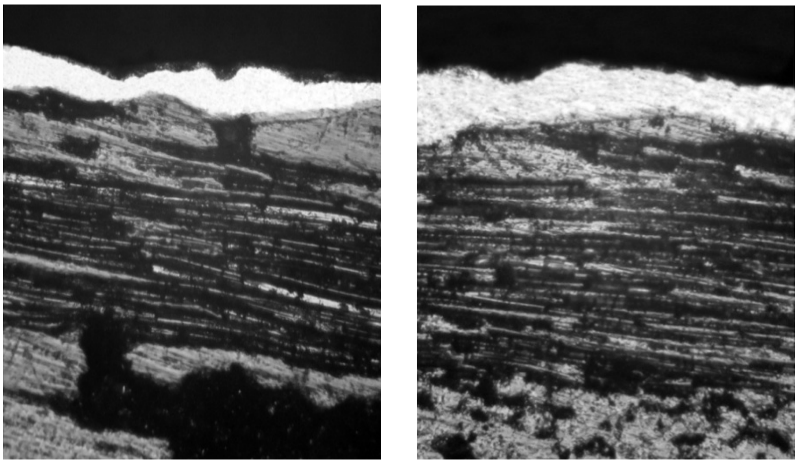
Fig. 1. Effect of Ti and Al content on heat resistance

The temperature of heating the mixture as a result of the reaction depends on the temperature of its previous heating, as well as the amount of heat released as a result of the reduction reaction. At the same time, it should be taken into account that the final heating temperature depends not only on the amount of heat of the reduction reaction, but also on the temperature range in which the reaction itself takes place.

The main element of all heat-resistant coatings is aluminum, which is used to form a protective α–Al_2O_3 oxide membranes. In diffusion coatings, the aluminum content is usually at the level of 15... 25 %. This aluminum content ensures the formation of an α–Al_2O_3 oxide membranes during oxidation. The second most important component of the coatings is chromium, which ensures the formation of the α–Al_2O_3 membranes. The chromium content in high-temperature coatings is usually 7...20 %.

The coatings obtained under FAC conditions, on CCCM with titanium alloying, are diffusion in nature and are characterized by uniformity in thickness. With increasing process temperature, the coating thickness increases (Fig. 2).

The results of X-ray diffraction and metallographic analysis of the coatings on the HCCM showed that in the entire temperature and time interval on the carbon materials under study, the protective coating consists of two zones: the inner zone containing titanium carbide and the outer zone, the composition of which depends on the choice of alloying elements in the HCC charge. When alloyed with titanium, the protective coating is a carbide phase of TiC and phases of: Al_2Cr_3, $CrAl_2$, TiAl (Fig. 3).



a b

Fig. 2. Microstructures of titanium-doped protective coatings at different exposure times: a) 20 min, b) 60 min, x100

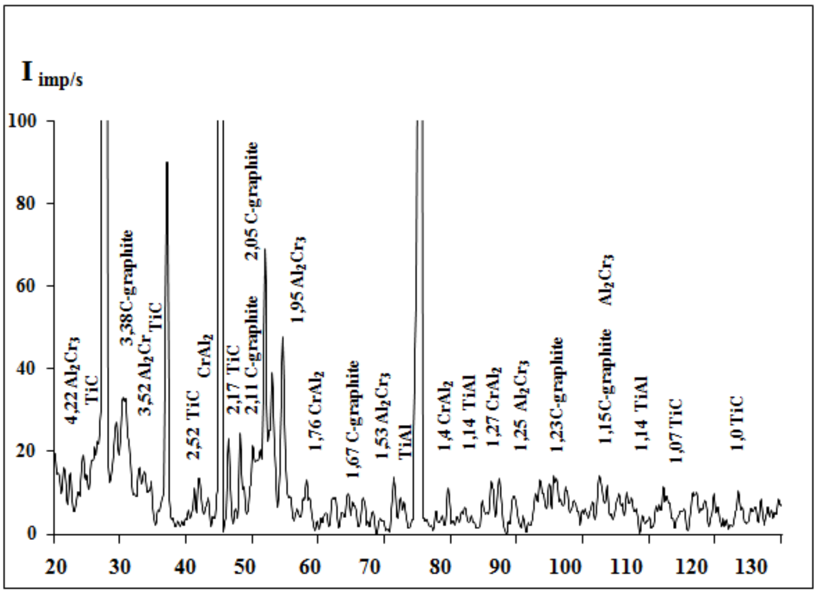


Fig. 3. Diffractogram of a sample of the CCCM with a protective coating

When saturated with chromium, aluminum, and titanium, solid substitution solutions are formed. The activation energy Q in γ-iron exceeds 250.8 kJ/g-atom. Therefore, using the non-stationary stage of the process, we obtain not only a high temperature but also an increased concentration of diffusing elements on the surface of materials.

Protective coatings produced under isothermal conditions tend to have more porous surfaces, characterized by the presence of the FeAl phase, allowing oxygen to penetrate the steel surface. In contrast, the heat resistance of coatings alloyed using FAC is superior. This improvement is attributed to the higher concentrations of chromium, aluminum, silicon, and titanium, which facilitate the formation of protective oxide layers such as SiO_2, TiO_2, Cr_2O_3, and Al_2O_3.

A notable feature of the high heat resistance of FAC-obtained coatings is the stepwise formation of protective layers. Initially, a CrAl protective coating is created, followed by alloying with titanium, chromium, and silicon to form heat-resistant phases like TiAl and CrSi2. This multistep process greatly enhances the coatings' ability to endure high temperatures and harsh conditions.

Conclusions

The results of X-ray diffraction and metallographic analysis of coatings on carbon materials showed that, across the entire temperature-time range, the protective coating consists of two zones: an inner zone containing titanium carbide and an outer zone, whose composition depends on the choice of alloying elements in the SHS mixture. When alloyed with titanium, the protective coating comprises TiC carbide phase and phases such as Al_2Cr_3, $CrAl_2$, and TiAl. Upon saturation with chromium, aluminum, and titanium, solid substitution solutions are formed. The activation energy Q in γ-iron exceeds 250.8 kJ/mol. Protective coatings produced under isothermal conditions tend to have more porous surfaces (with the FeAl phase present), allowing oxygen to penetrate to the steel surface. Compared to isothermal coatings, the heat resistance of coatings alloyed using FAC is higher, due to the higher concentrations of chromium, aluminum, silicon, and titanium, which contribute to the formation of protective oxide layers such as SiO_2, TiO_2, Cr_2O_3, and Al_2O_3. A significant aspect of the high heat resistance of coatings produced using FAC is the sequential formation of protective layers. Initially, a CrAl protective coating is formed, followed by doping with titanium, chromium, and silicon to introduce heat-resistant phases like TiAl and CrSi2. This multistep process significantly enhances the coatings' ability to withstand high temperatures and harsh conditions.

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