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THERMODYNAMIC ANALYSIS OF PHASE TRANSFORMATIONS IN PROTECTIVE COATINGS OBTAINED USING FUNCTIONALLY ACTIVE CHARGES

ТЕРМОДИНАМІЧНИЙ АНАЛІЗ ФАЗОВИХ ПЕРЕТВОРЕНЬ У ЗАХИСНИХ ПОКРИТТЯХ ОТРИМАНИХ З ВИКОРИСТАННЯМ ФУНКЦІОНАЛЬНО-АКТИВНИХ ШИХТ

Research is focused on the creation of protective coatings for carbon-carbon composite materials (CCCM) using functionally active charges (FAC) synthesized under non-stationary temperature conditions. The main task is to optimize the composition of titanium-doped powder mixtures in order to increase the heat resistance of the working surface of materials. In the course of the work, we analyzed various methods of applying protective coatings, including chemical and thermal treatments and liquid phase saturation, to determine their interaction with the CCCM matrix and their effect on the mechanical properties of the material. In addition to the classical approaches, special attention is paid to the study of the method of saturation of the surface with a solid phase in an active gas environment using FAC formed under non-stationary temperature conditions. This technology demonstrates high efficiency due to the possibility of obtaining high-quality protective layers, reducing the processing time and ensuring operation at elevated temperatures. The research focuses on the study of chemical processes of interaction between the coating and the substrate, in particular on the formation of carbide phases, which play a key role in ensuring the heat resistance of coatings.

The experimental part of the work includes the calculation of the composition of the saturated FAS for the chromium-aluminum titanium plating process for the Cr-Al-Ti system. To calculate the equilibrium composition of the system products, a thermodynamic analysis of possible reactions was performed for the temperature range of 400—1600 K, which showed that the decomposition products of the activators react with the oxide film on aluminum, before the reduction reaction begins, to form gaseous compounds. In the process of titanium alloying, protective coatings are formed consisting of the TiC carbide phase, as well as the intermetallics Al_2Cr_3, $CrAl_2$, and TiAl. The coating has a distinct two-zone structure: the inner zone is saturated with titanium carbide, while the outer zone is formed by alloying elements present in the composition of the FAC.

***Keywords**: carbon-carbon composite materials, protective coatings, functionally active blends, heat resistance, synthesis, thermodynamic modeling, chemical and thermal treatment.*

Дослідження спрямоване на створення захисних покриттів для вуглець-вуглецевих композиційних матеріалів (ВВКМ) з використанням функціонально активних шихт (ФАШ), синтезованих у нестаціонарних температурних умовах. Основним завданням є оптимізація складу порошкових сумішей, легованих титаном, з метою підвищення жаростійкості робочої поверхні матеріалів. У процесі роботи проведено аналіз різних методів нанесення захисних покриттів, зокрема хіміко-термічних обробок та насичення з рідкої фази, для визначення їх особливостей взаємодії з матрицею ВВКМ та впливу на механічні властивості матеріалу. Окрім класичних підходів, особлива увага приділена дослідженню методу насичення поверхні твердою *фазою в активному газовому середовищі із застосуванням ФАШ, сформованих у нестаціонарних температурних умовах. Ця технологія демонструє високу ефективність завдяки можливості отримання якісних захисних шарів, скорочення тривалості обробки та забезпечення роботи при підвищених температурах. Дослідження зосереджені на вивченні хімічних процесів взаємодії між покриттям і основою, зокрема на утворенні карбідних фаз, які відіграють ключову роль у забезпеченні термостійкості покриттів.*

Експериментальна частина роботи включає розрахуємо склад насичуємої ФАШ для проведення процесу хромоалюмотитанування для системи Cr-Al-Ti. Для розрахунків рівноважного складу продуктів системи було проведено термодинамічний аналіз можливих реакцій для діапазону температур 400—1600 К, який показав, що продукти розкладання активаторів реагують із окісною плівкою на алюмінії, до початку реакції відновлення, з утворенням газоподібних з'єднань. У процесі легування титаном формуються захисні покриття, що складаються з карбідної фази TiC, а також міжметалідів Al_2Cr_3, $CrAl_2$ і TiAl. Покриття має чітко виражену двозонну структуру: внутрішня зона насичена карбідом титану, тоді як зовнішня зона утворюється за рахунок легуючих елементів, присутніх у складі ФАШ.

Ключові слова: *вуглець-вуглецеві композиційні матеріали, захисні покриття, функціонально активні шихти, жаростійкість, синтез, термодинамічне моделювання, хіміко-термічна обробка.*

Problem's Formulation

Under conditions of intensive use of machine components and technological tools, the physical and mechanical characteristics of the surface layer, in particular its hardness, wear resistance and resistance to external factors, play a key role. That is why methods of surface modification of materials have gained considerable popularity in modern mechanical engineering and metallurgy. To strengthen the surface layers of structural and alloy steels, various technologies for forming functional coatings are widely used to ensure a long service life of products. The main objective of the process of applying such protective coatings is to achieve high adhesion between the coating and the base material, as well as to create a continuous, porous and stable layer capable of operating effectively in an aggressive environment.

Currently, the most common methods of obtaining protective coatings are electroplating by electrolysis, gas-thermal spraying (metallization), thermodiffusion saturation using powder materials, immersion of products in molten metal, and cladding. Depending on the way the protective layer interacts with the substrate, adhesive and diffusion coatings are distinguished [1]. One of the most popular surface hardening technologies is chemical heat treatment (CHT), which involves the simultaneous exposure of high temperatures and active chemicals to the surface of the product. Within this approach, the processes of saturation of steels with elements such as titanium, chromium and boron are of particular importance, which contributes to the formation of high-strength and wear-resistant coatings [2].

However, it is worth noting that traditional chemical heat treatment methods have a number of significant drawbacks. These include high energy intensity of processes, considerable duration of operations and limited possibilities for creating multicomponent coatings with a high concentration of various elements in the surface layer. In this context, technologies for obtaining wear-resistant coatings based on FAC show significant advantages [3]. They can significantly reduce the time of coating formation while ensuring its high quality and functional efficiency. Such methods minimize energy costs and allow obtaining coatings with the required characteristics under conditions of intensive equipment operation.

Analysis of recent research and publications

In high-temperature operational environments, the use of carbon-carbon composite materials (CCCM) has become increasingly relevant due to their exceptional properties. To protect these materials from severe oxidation, the study proposes advanced methods for applying heat-resistant protective coatings via thermal self-ignition processes [4—5]. This protection method is highly promising and cost-effective because it does not require alterations to existing CCCM production technologies.

Furthermore, the resulting protective layer forms a thin film that interacts with the carbon matrix and fibers without compromising the material's overall mechanical properties.

As high-temperature materials, CCCMs exhibit a range of unique characteristics, such as enhanced strength at elevated temperatures, low specific weight, and ease of mechanical processing. Due to these attributes, CCCMs are classified as ultra-pure materials, available in various types and grades with densities ranging between 1.45 and 2.23 t/mі. Additionally, they display pronounced anisotropy in mechanical properties depending on the fiber reinforcement direction [6—7].

Despite these advantages, CCCMs face significant challenges when used in aerospace applications, particularly regarding their insufficient erosion and oxidation resistance. A primary factor contributing to the suboptimal performance of CCCMs is residual porosity, an inherent aspect of their production. Even the application of an ultra-thin heat-resistant coating can substantially enhance the material's operational capabilities by mitigating this issue.

The performance and durability of these coatings largely depend on the protective oxide layer formed on the surface, which prevents the diffusion-driven degradation of the coating. During high-temperature interactions with oxygen, oxides of easily oxidizable components within the coating (those with high oxygen affinity) predominantly form. Consequently, heat-resistant coatings often incorporate elements such as Cr, Ti, Al, Si, and Zr, which exhibit high oxygen affinity and generate refractory oxides (e.g., Al_2O_3, SiO_2) on the surface [8—9].

Among various methods, diffusion saturation from a solid phase within an active gaseous environment, utilizing functionally active charges under non-stationary temperature conditions, stands out as one of the most promising approaches for CCCM chemical-thermal treatment. This technique ensures superior coating quality, reduces processing time, and allows for operation at elevated temperatures depending on the FAC composition. By adjusting the type and concentration of alloying additives, this method facilitates the production of coatings with diverse chemical compositions, meeting specific technical requirements.

Presenting main material

Carbon-carbon materials are a broad class of composite materials that are a combination of a carbon or graphite matrix that is reinforced with carbon or graphite fibers. Such materials have a number of outstanding properties such as low specific gravity, high mechanical strength even at extremely high temperatures, and excellent thermal shock resistance.

The advantages of carbon-carbon materials are very important in comparison with alternative temperature resistant structural materials such as pyrocarbons, polycrystalline graphite, tungsten, tantalum, molybdenum, and others. These properties are especially valuable in conditions of extreme temperatures and high-speed gas flows, which are characteristic of rocket and space technology.

The use of carbon-carbon materials has a wide range of applications, including solid rocket engines. For example, in such engines, gas stream temperatures can reach 2500 °C or higher. Solid propellant combustion products can also contain abrasive particles, which emphasizes the importance of ablative and erosion resistance of materials in critical situations.

Calculate the composition of the saturated FAS for the process of chromium-aluminum-titanium (Cr-Al-Ti). The degree of chromium oxide reduction is determined by the value of the isobaric potential.

The reaction begins with the reduction of Cr_2O_3, oxide, and as its concentration in the mixture decreases and the oxide strength equalizes, the synthesis of the TiAl phase begins. The average temperature of the initiation of the synthesis reaction, obtained from experimental data T *, is ~ 580—650^o C (853—973 K). The average value of the isobaric potentials of Cr_2O_3 and TiAl formation in the temperature range of 853—1273 K is -527,184 and -64,83 kJ/mol, which corresponds to the degree of reduction of Cr_2O_3 — 85 %. The amount of chromium oxide involved in the reduction reaction is determined by the formula:

$$m_{Cr_2O_3} = 0{,}85 m''_{Cr_2O_3}, \tag{1}$$

where $m''_{Cr_2O_3}$ — initial Cr_2O_3 content in the charge, % by weight.

The amount of aluminum m_{Al}, required for reduction $m_{Cr_2O_3}$ and synthesis m_{TiAl}, the amount of chromium m_{Cr}, phase m_{TiAl} and aluminum oxide m_{Al2O3} formed are calculated using the corresponding stoichiometric reaction equations.

The amount of chromium oxide that does not participate in the reaction:

$$m'_{Cr_2O_3} = m''_{Cr_2O_3} - m_{Cr_2O_3}, \tag{2}$$

To carry out the chromium-aluminum titanium process, it is necessary that the ratio of chromium and TiAl phase in the mixture satisfies the following conditions:

$$Cr_2O_3{:}TiAl \geq 20 : 80\% \text{ by weight.} \tag{3}$$

At a ratio in the saturating mixture of Cr_2O_3:TiAl= 20 : 80% by weight, the maximum temperature of the process will be $T_м = 2130$ K, excluding heat losses.

During the process, the reaction products are heated from the initiation temperature T_1 to the maximum permissible charge temperature T_2 mainly due to the heat released during the reaction ($Q_{хим}$). The heat losses during the process will be as follows:

$$Q_П = \left[m_{Cr_2O_3}\Delta H_{Cr_2O_3} + m_{TiAl}\Delta H_{TiAl}\right]\cdot q_П, \tag{4}$$

where $\Delta H_{Cr_2O_3}$ and ΔH_{TiAl} — thermal effects of the reactions of Cr_2O_3 reduction and TiAl synthesis, respectively, kJ/kg; $q_п$ —share of heat from exothermic reactions used to cover heat losses.

Aking into account the above, the heat balance equation of the reaction of Cr_2O_3 reduction and TiAl synthesis in the expanded form takes the following form:

$$\left[m_{Cr_2O_3}\Delta H_{Cr_2O_3} + m_{TiAl}\Delta H_{TiAl}\right]\left[1 - q_П\right] = \left[m_{Cr}C''_p + m_{Ti}C''_p + \sum m'_{Al_2O_3}C''_p + \right.$$

$$\left. + m'_{Cr_2O_3}C''_p + m'_{TiAl}C''_p + m_б C''_p\right]\left[T_2 - T_1\right], \tag{5}$$

where C''_p — average heat capacity at the corresponding component of the mixture in the temperature range of 873—2130 K, kJ/(kg-grad); $m_б$ — amount of ballast admixture, kg.

The fraction of the heat of exothermic reactions that is used to cover heat losses is determined from equation:

$$q_П = \frac{\left[T_{np} - T_2\right]\left[m_{Cr}C''_p + m_{Ti}C''_p + \sum m'_{AL_2O_3}C''_p + m'_{Cr_2O_3}C''_p + \right.}{m_{Cr_2O_3}\Delta H_{Cr_2O_3} + m_{TiAl}\Delta H_{TiAl} + \left[m''_{Cr_2O_3}C'_p + \right.} \rightarrow$$

$$\rightarrow \frac{\left. m'_{TiAl_2}C''_p + m_б C''_p\right]}{\left. + m''_{TiAl_2}C'_p + \sum m_{Al}C'_p + m_б C'_p\right]\cdot T_1}, \tag{6}$$

where C'_p — average heat capacity at the corresponding component of the mixture in the temperature range of 298—853 K, kJ/(kg-grad)).

The joint solution of equations (5) and (6) gives the value of q_p for temperatures of 973, 1073, 1173, and 1273 K, equal to 0.51, 0.47, 0.42, and 0.38, respectively. The average value in the temperature range of 973—1273 K is 0.55. To reduce the reaction temperature of Cr_2O_3 reduction and TiAl synthesis for 973, 1073, 1173, and 1273 K, it is necessary to introduce 51, 47, 42, and 38 % of the ballast impurity reduction and TiAl synthesis for 973, 1073, 1173, and 1273 K, it is necessary to introduce 51, 47, 42, and 38% of the ballast impurity
Al_2O_3 into the charge, respectively.

The application software package “ASTRA” was used to calculate the equilibrium composition of the products of the studied system. During the calculations, the database of thermodynamic properties of individual compounds was used, which contains detailed information on entropy, enthalpy, specific heat, Gibbs free energy, and the heat of formation of more than 1500 substances. To ensure the mandatory presence of the gas phase, 1 % argon was added to the initial composition of the model. In all cases, the pressure was assumed to be equal to atmospheric pressure (0.098 MPa), which allowed for calculations in a wide range of changes in the input components depending on temperature.

The results of the thermodynamic analysis of possible reactions in the temperature range of 400—1600 K demonstrated that the products of thermal decomposition of activators (I_2, NH_4Cl) actively interact with the oxide film on the aluminum surface, which precedes the reduction reactions and is accompanied by the formation of gaseous compounds such as AlI, AlI_2, Al_2I_6, CrF_2, CrI_2, CrI_3, $TiCl_3$, $TiCl_4$, TiI_2, etc. As the temperature increases, the amount of gaseous products increases, and condensed phases are released in parallel (Fig. 1, 2).

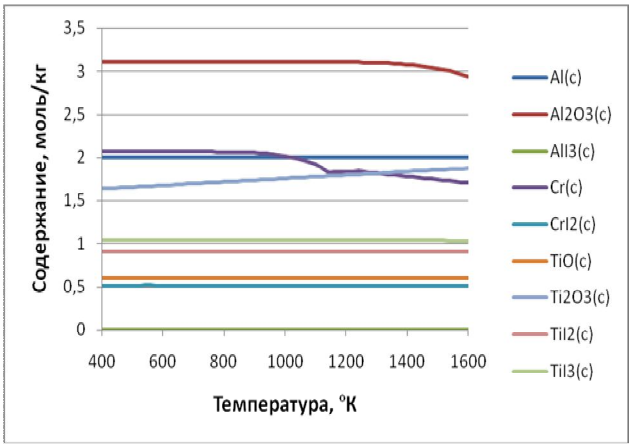

Fig. 1. Content of condensed reaction products in the FAC for the system Cr-Al-Ti:

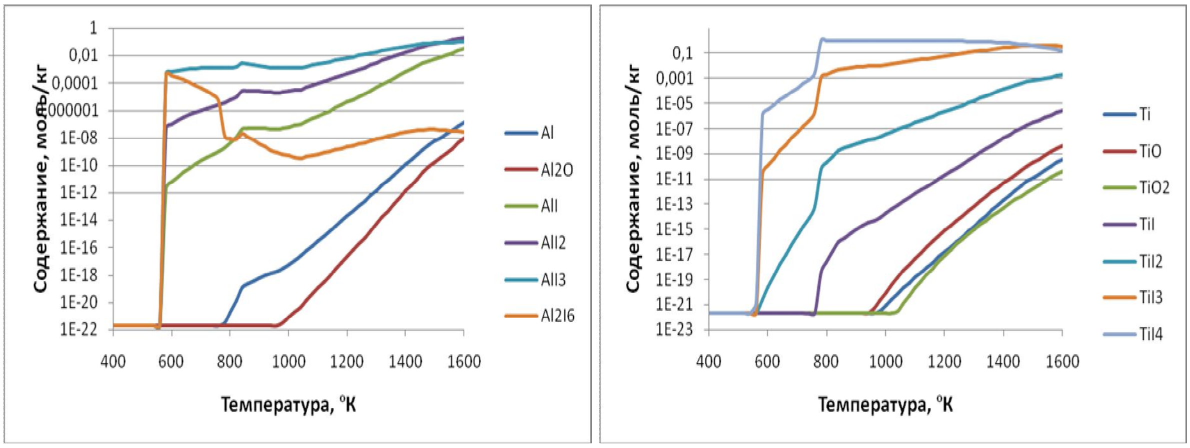

Fig. 2. Content of gaseous aluminum and titanium compounds in the FAC for the system Cr-Al-Ti:

In the temperature range of 1200—1800 K, the main components of the gas phase are iodides, fluorides, and chlorides of elements such as chromium, aluminum, boron, titanium, and silicon. These compounds play a key role in the formation of the protective coating, contributing to the formation of the necessary heat-resistant phases and providing increased resistance of the material to high temperature exposure.

Characteristically, in the temperature range of 400—1600 K, the fraction of the condensed phase decreases, which is associated with the evaporation of a single gas transportation medium. At the same time, starting from temperatures of 400 K, its decomposition occurs, as evidenced by the appearance of decomposition products in the system and an increase in the number of gas moles. At temperatures above 750—800 K, the proportion of the condensed phase in the system begins to increase, while the amount of the gas phase does not change. Gaseous products, interacting with the elements of the powder charge, convert them to the gas phase. This fact suggests that in the temperature range of 600—1600 K, reactions occur with the release of the condensed phase, but without changing the number of gas molecules, which is characteristic of decomposition, disproportionation, dissociation or exchange reactions with the surface of the material being processed, i.e., in fact, chemical transport reactions occur. The specific quantitative composition of the proposed systems cannot be specified within the framework of thermodynamic calculations, so it is necessary to experimentally select the composition that ensures the optimal mode of the process.

Simultaneously, starting from a temperature of 800 K, the reaction products decompose, which is confirmed by the appearance of decomposition products and a sharp increase in the number of gas moles. The gaseous products interact with the elements of the powder system (Al, Si, B, Ti, and Cr) and convert them into the gaseous phase.

Simultaneously with the determination of the concentration of gaseous products, data on two thermodynamic properties were found to calculate the equilibrium compositions of powdered FAC in the mode of thermal spontaneous combustion: enthalpy H_t and Gibbs energy G_T. The enthalpy was chosen to determine the thermal effect of the chemiяёcal reactions under consideration; at $D_H < 0$, the reaction will proceed with heat release, and at $D_H > 0$ — with heat absorption. To calculate the equilibrium of chemical reactions in the studied system, as well as to determine the equilibrium compositions of the components involved in these reactions, the equilibrium constants of all independent reactions possible in these blends were determined.

The results of X-ray diffraction and metallographic analysis of the coatings on the CCCM showed that in the entire temperature and time interval on the carbon materials under research, 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 FAC. When alloyed with titanium, the protective coating is a carbide phase of TiC and phases of: Al_2Cr_3, $CrAl_2$, TiAl (fig. 3).

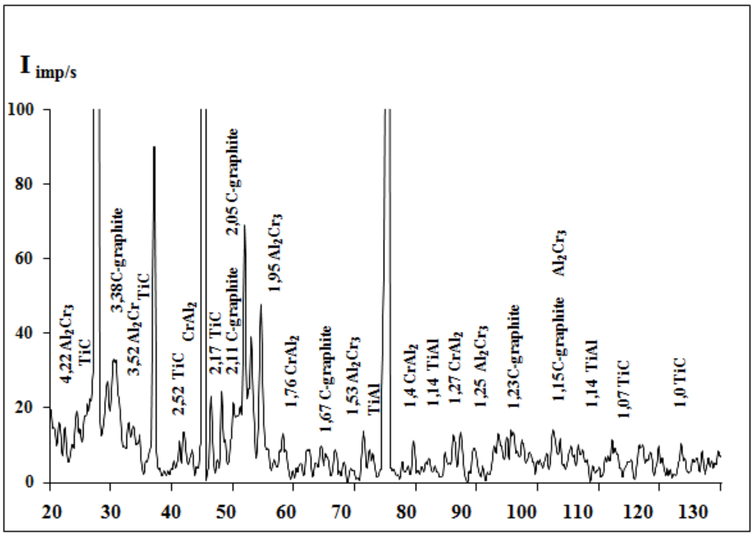

Fig. 3. Diffractogram of a sample of the CCCM with a protective coating

When saturated with chromium, aluminum, and titanium, solid substitution solutions are formed. The activation energy *Q* in б-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 $CrSi_2$. This multistep process greatly enhances the coatings' ability to endure high temperatures and harsh conditions.

Conclusions

The findings from the X-ray diffraction analysis of protective coatings applied to carbon-based materials reveal that these coatings exhibit a distinct two-zone structure across the entire temperature-time spectrum. The inner zone predominantly consists of titanium carbide (TiC), while the composition of the outer zone varies depending on the specific alloying elements incorporated into the FAC. When titanium is used as an alloying element, the resulting protective coating contains TiC carbide phases along with intermetallic compounds such as Al_2Cr_3, $CrAl_2$, and TiAl. Additionally, the saturation process involving chromium, aluminum, and titanium leads to the formation of solid substitution solutions within the material matrix.

The activation energy Q for these processes in г-iron is notably high, exceeding 250.8 kJ/mol. Coatings produced under isothermal conditions tend to exhibit more porous surfaces, primarily due to the presence of the FeAl phase, which facilitates oxygen penetration to the substrate surface, potentially compromising its protective capabilities. In contrast, coatings generated using functional active compositions under dynamic conditions demonstrate significantly improved heat resistance. This enhancement is attributed to the higher concentrations of elements like chromium, aluminum, silicon, and titanium, which promote the formation of stable, protective oxide layers such as SiO_2, TiO_2, Cr_2O_3, and Al_2O_3.

A key factor contributing to the superior heat resistance of FAC coatings lies in their sequential layer formation process. Initially, a CrAl-based protective layer is developed, which is subsequently enriched with additional elements like titanium, chromium, and silicon. This sequential doping introduces heat-resistant phases, including TiAl and $CrSi_2$, thereby enhancing the overall thermal stability and durability of the coating. This multi-phase approach significantly strengthens the coating's capacity to endure extreme temperatures and aggressive environmental conditions, offering robust protection against oxidation and thermal degradation.

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