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THERMODYNAMIC MODELING OF FORMATION TITANIUM COATINGS UNDER SHS CONDITIONS

ТЕРМОДИНАМІЧНЕ МОДЕЛЮВАННЯ ФОРМУВАННЯ БАГАТОКОМПОНЕНТНИХ ТИТАНОВИХ ПОКРИТТІВ В УМОВАХ СВС

This research focuses on modeling the thermodynamic processes of producing chrome coatings using self-propagating high-temperature synthesis (SHS). We consider the kinetic regularities of chemical processes, as well as the influence of temperature and diffusion factors on chemical reactions in the gas phase. A method for optimizing the composition of powder mixtures to obtain coatings with increased wear resistance is presented. The composition of the gas phase of the reaction products of the SHS system was analyzed by thermodynamic modeling, which allowed us to consider in detail the mechanisms of coating formation on metal surfaces. The research included mathematical modeling, factor analysis, and experimental methods, including X-ray diffraction and metallographic analysis. Analysis of the phase composition and microstructure of the resulting coatings. Depending on the chemical composition of the substrate, in the near-surface zone, carbides $(Cr, Fe)_{23}C6$ *or* $(Cr, Fe)_7C_3$ *doped with titanium can be formed, followed by* Fe_2Ti, Cr_2Ti, *and an α-solid solution of Ti and Cr in α-iron.*

***Keywords**: titanium coatings, powder mixtures, thermodynamic modeling, composition optimization, wear resistance, phase composition.*

Дане дослідження спрямоване на моделювання термодинамічних процесів отримання хромованих покриттів з використанням саморозповсюджувального високотемпературного синтезу (СВС). У роботі розглянуті кінетичні закономірності хімічних процесів, а також вплив температури та дифузійних факторів на хімічні реакції у газовій фазі. Представлено методику оптимізації складу порошкових сумішей для отримання покриттів із підвищеною *зносостійкістю. Проведено аналіз складу газової фази продуктів реакцій СВС-системи шляхом термодинамічного моделювання, що дозволило детально розглянути механізми формування покриттів на металевих поверхнях. Дослідження включало математичне моделювання, факторний аналіз та експериментальні методи, що включали рентгеноструктурний та металографічний аналізи. Визначено оптимальні співвідношення легуючих елементів (хрому, титану, алюмінію) для формування стійких покриттів на сталі. Проведено аналіз фазового складу та мікроструктури отриманих покриттів. Залежно від хімічного складу підкладки, в при поверхневій зоні можливе утворення карбідів (Cr, Fe)$_{23}$C$_6$ или (Cr, Fe)$_7$C$_3$, легований титаном, нижче розташований Fe$_2$Ti, Cr$_2$Ti, α-твердий розчин Ti та Cr у α-залізі; на сталі 45 — (Cr,Fe)$_{23}$C$_6$, легований титаном, α-твердий розчин хрому в залізі з включеннями Cr$_2$Ti. Дослідження показали, що покриття, отримані у системі СВС, мають вищу зносостійкість порівняно з покриттями, отриманими в ізотермічних умовах. Висновки роботи свідчать про переваги використання системи СВС для поліпшення якості та тривалості служби отриманих покриттів.*

***Ключові слова**: титанові покриття, порошкові суміші, термодинамічне моделювання, оптимізація складу, зносостійкість, фазовий склад.*

Problem's Formulation

To increase the resistance of steel surfaces in high temperature conditions, effective protective coatings need to be developed. The method of choice for this purpose is vacuum fusion with SHS. The objective is the research and development of protective coatings on steel substrates produced by the SHS method to increase their resistance and efficiency at high temperatures. To achieve this goal, it is necessary to conduct thermodynamic and mathematical modeling of the process of obtaining protective coatings to determine the optimal compositions of powder mixtures and the phase composition of coatings. Multicomponent coatings based on titanium are widely used to protect parts of mechanisms and assemblies operating in difficult operating conditions. In order to increase the wear resistance, microhardness, and corrosion resistance of steel products, various methods of saturating the surface of parts with several carbide-forming elements, namely titanium and chromium, are often used.

Analysis of recent research and publications

Before starting our own research, we analyzed the latest publications and publications on the development of protective coatings for steel. This analysis revealed several key areas and trends in the field. An alternative strategy for producing protective coatings is a process known as self-propagating high-temperature synthesis (SHS). In this process, exothermic reactions between the starting reagents are locally initiated, generating a significant amount of heat that promotes the propagation of the front of physical and chemical transformations and the formation of synthesis products. The development of SHS technologies makes significant changes in the traditional production of powder and composite materials, increasing labor productivity and opening up prospects for the creation of new technical means for different operating conditions [1,2].

SHS produces high-temperature compounds of various chemical compositions (carbides, nitrides, silicides, chalcogenides, intermetallics, hydrides) and reduced metals. It also makes it possible to produce inorganic materials with various physical properties (powdered, sintered - solid and porous, cast), as well as products of various shapes and sizes. The method can be used to grow single crystals from molten combustion products. One of the most promising applications of the SHS phenomenon is modern technologies for applying protective coatings, including wear-resistant ones. The purpose of this research is to analyze the developments using SHS in wear-resistant coating technologies, systematize these data and determine the prospects for the development of these technologies [3—5].

Formation of the purpose of the research

The purpose of our research is to develop effective protective coatings based on the SHS method to improve the resistance of steels in aggressive operating conditions. We aim to determine the optimal conditions of the coating process by compiling a mathematical model based on thermodynamic principles to predict the phase composition of the resulting coatings. We also have the objective of investigating the influence of various factors, such as charge chemistry and process parameters, on the microstructure and properties of the coatings. We aim to determine the optimal charge parameters and compositions that will provide the best durability and performance of the coatings under service conditions.

In addition, we have conducted experimental studies, including factor analysis, to evaluate the effect of various factors on the properties of the resulting coatings. Based on these results, we intend to optimize the coating process and charge compositions to achieve the best results in improving the durability of steels.

Presenting main material

Thermodynamic modeling of thermochemical processes, which consists in the thermodynamic analysis of the equilibrium state of systems as a whole (full thermodynamic analysis). Thermodynamic systems are defined as conditionally distinguished material areas whose interaction with the environment is reduced to the exchange of heat and work. The use of thermodynamic modeling allows us to quantitatively simulate and predict the composition and properties of complex heterogeneous, multielement, multiphase systems over a wide range of temperatures and pressures, taking into account chemical and phase transformations [6,7]. This makes it possible to effectively study thermochemical processes in existing high-temperature installations and optimize their conditions, predict the results of high-temperature interactions, dramatically reduce the time and cost of research, and successfully systematize theoretical and experimental information.

The calculation of the thermodynamic equilibrium of arbitrary systems (determination of all equilibrium parameters, thermodynamic properties, chemical and phase composition) is carried out by minimizing the isobaric-isothermal potential or maximizing the entropy of the system, taking into account all potentially possible individual substances q in equilibrium. Computational methods developed on the basis of the variational principles of thermodynamics [8] suggest that:

1. Of all the permissible values of moles Mq of individual substances in a thermodynamic system, those that minimize the thermodynamic potential of the system correspond to equilibrium values;

2. Of all the permissible values of energy Ui contributed by each independent component (atom), those that maximize the total contribution of energy of individual atoms to the system correspond to equilibrium values.

The constituent parts of a system are all possible and existing substances in different aggregate states formed from the elements included in the system under study. The components of a thermodynamic system are the substances that are minimally necessary for the composition of this system. The number of components is equal to the number of substances present in the system minus the number of independent reactions that bind these substances. In thermodynamic modeling, condensed individual substances are compounds with a multiple of the number of atoms that form them.

Substances with fractional stoichiometric coefficients are considered solutions. Condensed phases include compounds in solid (crystalline or amorphous) and liquid states. Individual substances that have the same chemical formula but are part of different phases are considered to have different constituents. The constituents of the gas phase are molecules, radicals, atoms, ions and electron gas.

Thermodynamic modeling of processes consists in the thermodynamic analysis of the equilibrium state of systems as a whole (full thermodynamic analysis). Thermodynamic systems are defined as conditionally distinguished material areas whose interaction with the environment is reduced to the exchange of heat and work. The calculation of the thermodynamic equilibrium of arbitrary systems (determination of all equilibrium parameters, thermodynamic properties, chemical and phase composition) is carried out by minimizing the isobaric-isothermal potential or maximizing the entropy of the system, taking into account all potentially possible individual substances in equilibrium.

The kinetic regularities of chemical processes in the SPS depend on both temperature and diffusion factors. Assuming that at the warm-up stage the inhibition of diffusion processes in the gas phase is small, and the rate of temperature change is small compared to the rate of gas-phase chemical reactions, it can be assumed that at each temperature the equilibrium composition of reaction products is determined. In this case, by calculating the equilibrium composition of reaction products for a number of temperatures, one can follow the chemical picture of the process development [9—10].

The thermodynamic analysis of the equilibrium composition of the system products shows that in the operating temperature range, the main components of the gas phase are iodides and chlorides of titanium, aluminum, and chromium (Fig. 1).

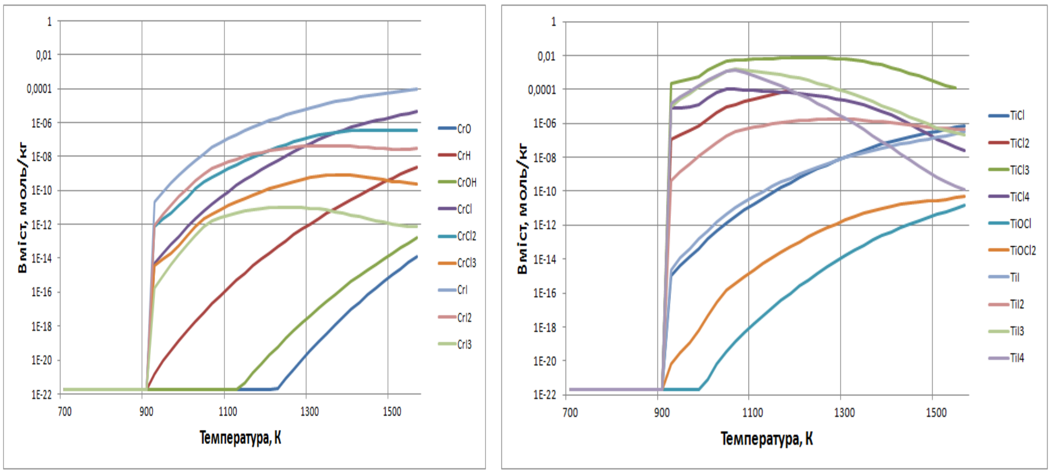

Fig. 1. The content of gaseous chromium and titanium compounds in the reactor in the mode of thermal spontaneous combustion for the Ti-Cr system

Gaseous products, interacting with the elements of the powder charge, convert them into the gas phase, and then chemical transport reactions occur: Al+I ⇔ AlI; Al+2I ⇔AlI_2; Al+3I⇔AlI_3; 2Al+I_2⇒2AlI; 2Al+AlI_3⇔3AlI; 2/3AlI_3+4/3Al⇔2AlI; 2/3AlI_3+1/3Al⇔AlI_2; Al_2I_6⇔2AlI_3; 1/2Ti+I_2⇔1/2TiI_4; Ti+4I⇒TiI_4 ; Cr+2I⇔CrI_2; Cr+3I⇔CrI_3. In titanium chromium plating by the SHS method, both metallic chromium and chromium component (CC) are the source of active chromium atoms. When saturated in mixtures containing CC and titanium or CC, titanium, chromium (provided that the total amount of chromium in the mixture is identical), a greater coating thickness will be obtained when chromium is present in the charge in an unbound state.

The choice of the basic level and variation intervals is based on the fact that the introduction of CC less than 10% by weight leads to a disruption of the combustion wave of thermal self-ignition. The amount of CC is selected based on the study of changes in the characteristic temperatures of the SHS process. To obtain a 100 percent composition of powdered SHS charges, Al2O3 is used as a ballast impurity. The resulting equation characterizing the effect of the technological regime and the composition of the charges on the parameters for optimizing physical, mechanical, and operational properties is as follows: $\Delta J_1 = 21{,}4 + 9{,}2\ XC + 2{,}4Ti - 4{,}4\ Cr - 0{,}2\ XC^2 - 0{,}21Cr^2 - 0{,}12\ XCCr$. The response surface of the obtained mathematical models is represented by three-dimensional graphical dependencies (Fig. 2).

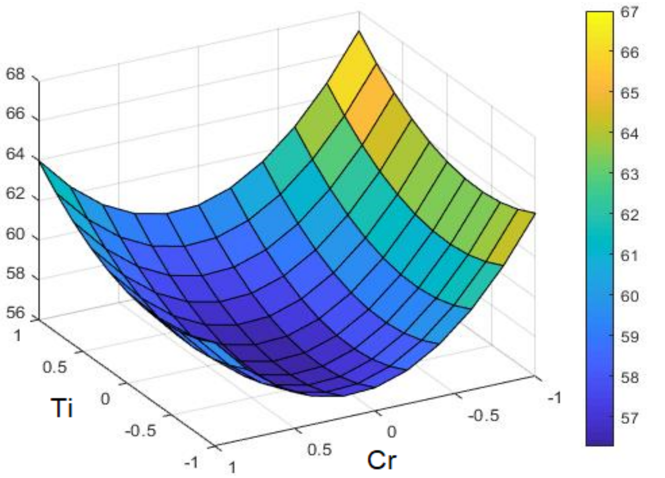

Fig. 2. Influence of Ti and Cr content (% wt.) in the SHS charge on wear resistance

The rational content of titanium is 24—26 % by weight and chromium is 4—7 % by weight (for the Ti-Cr system), thus, these values of titanium and chromium content allow obtaining minimal wear rates of steels with alloy protective coatings. As a result of X-ray diffraction and metallographic analyses, it was found that a continuous, homogeneous coating was formed on the steel surface (Fig. 3).

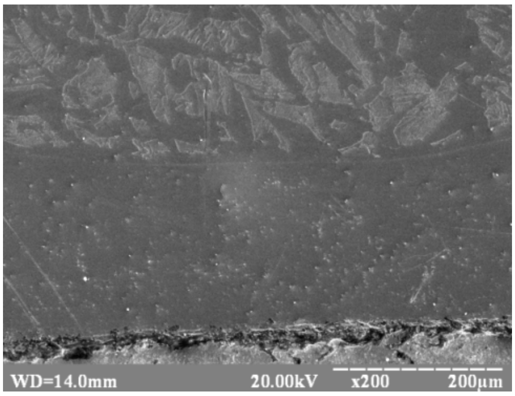

Fig. 3. Microstructure of titanium-chromium coatings obtained by the SHS method on steel 45 x 200

The phase composition of the zones depends significantly on the carbon content of the steel. Under these saturation conditions, chromium is characterized by a higher diffusion coefficient than titanium and, due to its smaller atomic radius, forms solid solutions of embedding more easily. Therefore, it penetrates the substrate to a greater depth than titanium. Depending on the chemical composition of the substrate, carbides may form in the near-surface zone (($(Cr, Fe)_{23}C_6$ or $(Cr, Fe)_7C_3$, alloyed with titanium, below is the Fe_2Ti, Cr_2Ti, α- solid solution of Ti and Cr in α-iron; on steel 45 — $(Cr,Fe)_{23}C_6$, doped with titanium, an α-solid solution of chromium in iron with Cr_2Ti inclusions. Wear resistance was evaluated on samples of 45 steel with titanium-chromium SHS coatings and coatings obtained under isothermal conditions.

Conclusions

The thermodynamic analysis of the equilibrium composition of the SWS system products was carried out, and the main components of the gas phase in the processing process were determined. Using the methods of mathematical modeling, the optimal compositions of powdered SWS blends for the production of wear-resistant titanium coatings alloyed with chromium were determined. The analysis of the phase composition and microstructure of the obtained coatings revealed the key features of their structure and structure. The phase composition of the zones significantly depends on the carbon content of the steel. Under these saturation conditions, chromium is characterized by a higher diffusion coefficient than titanium, and due to its smaller atomic radius, it is easier to form solid solutions of the embedding. Therefore, it penetrates the substrate to a greater depth than titanium. Depending on the chemical composition of the substrate, carbides may form in the near-surface zone $(Cr, Fe)_{23}C_6$ or $(Cr, Fe)_7C_3$, alloyed with titanium, below is the Fe_2Ti, Cr_2Ti, α- solid solution of Ti and Cr in α-iron; on steel 45 — $(Cr,Fe)_{23}C_6$, doped with titanium, an α-solid solution of chromium in iron with Cr_2Ti inclusions.

Identification of the optimal proportions of alloying elements such as chromium, titanium, and aluminum in the course of experimental research has become an important step in improving the process of obtaining coatings with improved resistance and service life. Mathematical modeling and thermodynamic analysis of the processes occurring during the formation of coatings provided important information on the kinetics of reactions, as well as the effect of temperature and diffusion processes on the characteristics of coatings. This allows for a deeper understanding of the mechanisms of coating formation and the development of more accurate and efficient methods for their production. An equation was obtained that characterizes the effect of the technological regime and composition of the blends on the parameters for optimizing physical, mechanical and operational properties.

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