Obtaining of wear-resistant carbide coatings on high-carbon steels under SHS conditions

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Abstract
Offered promising methods of applying protective wear-resistant coatings - technology for producing powder coatings by in a high-temperature synthesis (SHS). This kind of protection is the most promising and less costly, since it does not require changes in the technology of materials. In the work studies the production of wear-resistant carbide coatings for high-carbon steels under SHS conditions. High-carbon steels such as steel 50 and U8A. The high hardness of the resulting alloy coating and the ability to retain lubricant on the surface leads to an increase in the resistance of these parts to wear. Tests on the friction machine MT-5 (friction under conditions of shock-dynamic loading) showed that the best wear resistance is provided by protective coatings doped with Si, the wear value was -28 · 10^{-4} g/m², while at doping with boron - 38 · 10^{-4} g/m², and when doping with titanium - 60 · 10^{-4} g/m².

Introduction
For machine parts, working in high temperatures and wear, of great importance are the properties of the surface layer. To harden the surface layer using various methods of chemical-thermal treatment (CTT).

One of the effective methods CTT, allowing to improve the wear resistance and heat resistance of the products is the saturation of powder media. Thus saturating the contents of the main elements in the powder mixture reaches 80 %, and the duration of the process varies from 4 to 12 hours. Such a prolonged high-temperature isothermal exposure can lead to overheating of the product, which significantly affects the structure and mechanical properties of the parts, the disadvantages of the traditional processes of chemical-heat treatment is their high power consumption, which leads to higher cost products.

In this regard, topical application of a new technology, based on the method of self-propagating high temperature synthesis (SHS) combined with chemical gas reactions. The essence of the SHS is to carry out exothermic reactions in the mode of propagation of the combustion wave with the formation of combustion products in the form of compounds and materials of practical value and possessing valuable characteristics. The process may be conducted in the mode of combustion or heat of combustion, and is characterized by intensive application of coatings due to the presence of temperature gradient in the system, in a powdered medium.
The treatment efficiency is determined by a timing process parameters and thermophysical characteristics of SHS mixtures. It is therefore of interest to reveal the mechanism of influence on the processes of heat of ignition.

The object of this work is to develop optimal formulations of powder SHS mixtures for application protective coatings in the mode of combustion and thermal ignition, the study of the influence of doping chromolithograph coatings on the performance properties of parts during the course of the process of diffusion saturation during transient temperature conditions. Analysis of technological parameters of SHS-process, structure, phase, chemical composition and properties of coatings obtained by SHS-mixtures, and to evaluate the quality of the formed protective coatings.

**Materials and methods of research**

Multicomponent protective coating was applied to samples of brass LGMc-3-1, carbon-carbon composite (CCC) and began mass assignment (steel 50, U8A).

Chemical heat treatment was carried out in the reactor of the open type (P=105 PA) in the operating temperature range 900-1050 °C (for brass 750-850) and duration of isothermal holding 30÷60 minutes.

For the preparation of the reaction SHS mixtures used powders of oxides of chromium and aluminum oxide, metal iodine the dispersion of 200-350 microns. The coating was performed in the mode of thermal ignition of SHS-process. Surface preparation of the samples consisted of the successive stages of grinding, polishing and degreasing in acetone.

Initiating the process of saturation was carried out by pre-heating in a resistance furnace to a temperature of the start of ignition. Temperature during the SHS process was controlled by a chromel-alumel thermocouple in a protective case that is entered directly in the volume of the charge, and is connected to the potentiometer.

The tests for the MT-5 friction machine were carried out under the conditions of a boundary thorny slip with lubrication by an automotive tractor oil. The counterbody was made of SH15 steel with heat treatment, to a hardness of 60-62 HRC. The load on the test sample was P = 50N. The average speed of the moving sample is 0.19 m / s.

The structure of coatings was investigated on metallographical microscope Neophot-2 and subjected to radiographic analysis. The microstructure was revealed by etching in 3% alcoholic solution of picric acid. To identify the grain boundaries of the ferrite used a 4% alcoholic solution of nitric acid.

**Theory and analysis of the results**

Our method allows to obtain a uniform thickness coating on the parts of complex configuration, is relatively simple technology. The essence of the method lies in the fact that after the passage of the combustion wave, the samples deposited metal layer, which is then deposited alloying components. Were the conditions for the deposition of coatings from titanium, chromium, boron, molybdenum or their silicides. It was also found that the presence of the SHS mixture of an additive
metal J₂ contributes to a better separation of the spent charge from the details. A feature of the reactions of formation of the protective compounds of the elements is their relatively low thermal effect and low adiabatic temperature reactions (compared with other SHS systems). Because of this system for the synthesis of intermetallics be unable to burn at room initial temperature of the initial mixture of powders of metals. For the synthesis of intermetallic compounds is necessary to raise the temperature of the synthesis due to the preheating of the charge for carrying out the synthesis in the mode of thermal ignition. As a result, the initial temperature of the charge becomes one of the main options to control the synthesis of intermetallics in the technology SHS.

Analysis of reactions occurring upon ignition of SHS mixtures and the results of experiments and metallographic investigations allowed determining the mechanism of formation of complex coatings based on titanium. Thermal process of the formation of coatings in the mode of thermal ignition can be divided into five successive stages:

- inert heating the reaction mixture to the ignition temperature;
- thermal self-ignition;
- heating products;
- isothermal exposure;
- cooling.

Duration of the first stage largely depends on the mixture composition and its thermal characteristics. On stage inert heating of the evaporation and dissolution of the gas used media by the reaction.

\[
I_2 \rightarrow 2I
\]

At this stage, the diffusion layer is not yet formed. In the second stage (thermal ignition) runs the main exothermic reduction reaction of chromium oxide:

\[
\frac{1}{2} \text{Cr}_2\text{O}_3 + \text{Al} \rightarrow \text{Cr} + \text{Al}_2\text{O}_3
\]

The temperature in the reactor rises sharply to a maximum process temperature \( t_m \). The formation of gaseous compounds and saturating the transfer of the main elements to the substrate:

\[
\text{M} + \frac{m}{n} \text{G}_p \rightarrow \text{MG}_m,
\]

M – is the applied element, \( \text{G}_p \) – halogen, \( \text{MG}_m \) – volatile halide.

It is necessary to move the element and the substrate were in different temperature zones. The presence in the gas phase as \( I \), and \( I_2 \) indicates the flow in the investigated temperature range the following chemical transport reactions:

\[
\text{Al} + I \leftrightarrow \text{AlI} \\
\text{Al} + 2I \leftrightarrow \text{AlI}_2 \\
\text{Al} + 3I \leftrightarrow \text{AlI}_3
\]
2Al + I₂ → 2AlI
2Al + AlI₃ ↔ 3AlI
2/3AlI₃ + 4/3Al ↔ 2AlI
2/3AlI₃ + 1/3Al ↔ AlI₂
Cr + I₂ → CrI₂
Al₂I₆ ↔ 2AlI₃
1/2Ti + I₂ ↔ 1/2TiI₄
Ti + 4I → TiI₄

At the stage of thermal ignition for the SHS compositions containing an excess of aluminum, when the maximum temperatures possible liquid transport mechanism saturating elements in the diffusion zone (chrome and aluminum are dissolved and transferred to the substrate).

On the surface of the deposited powder in the steel products possible at this stage, the flow of heterogeneous exchange reactions with the iron substrate. In the third stage (heating products) is the equalization of temperature on the volume of the reactor. The process temperature is reduced to the calculated saturation temperature. Begins the formation of the coating.

At the stage of isothermal holding occurs diffusion coating growth. During the cooling phase, the formation of the diffusion layer occurs less intensively, due to the decrease of diffusion coefficients saturating elements. The grain size of the coating depends on the cooling rate. Studies show that the maximum growth rate of the coatings is observed in the initial stages of the SHS process. This can be explained by the fact that the austenite formed during sharp temperature increase at the stage of thermal ignition is characterized by high density of dislocations. Therefore, its diffusion susceptibility increases.

Adjusting the temperature conditions of the process, you can control both the rate of growth of the layers and their structure. The thickness of the formed coatings is influenced by the composition of the charge, the length and isothermal holding temperature and the chemical composition of the substrate.

Form a continuous plated layer, almost needle-like structure, below which are equiaxed grain Cu₃Al. When the content in the mixture to 12 wt%. aluminum coatings are composed of a solid solution of chromium-based chemicals and CuCr₂ eutectic, with a chromium concentration ~ 2% doped with aluminum (Fig.1, a).

When chromium aluminum titanium coating on steel U8 consists of solid solutions FeAl, Fe₃Al, a titanium alloy and area of a solid solution of Ti and Al in α-Fe (Fig.1).
Fig. 1 - Microstructure of multicomponent coatings: doped silicon on the material – a) brass; b) stainless steel 50; c) steel U8, d) CCC

When chromium aluminum titanium coating carbon–carbon materials, on the border of the formed carbide layer, which smoothes the difference between the coefficients of linear expansion between the substrate and the metal coating, and also provides better diffusion transfer of atoms in the coating. In the case of titanium diffusion exchange goes through the formation of intermetallic titanium (Fig.1, d). Is formed on the surface layer of intermetallic TiAl₃ and TiAl thickness of 15-20 microns with a hardness of 1100-1300 N. The main part of a hardening layer with a thickness of 30-50 μm has a hardness of 300 to 500 N. The magnitude of residual stresses is 150-200 N/mm².

When tested in conditions of sliding friction, the best wear resistance, among the coatings under consideration are chromoaluminium-titanium and chromoaluminium-coated coatings. Their wear resistance is 1,8-2,1 times higher than that of coatings obtained under isothermal conditions. This can be explained by a higher microhardness, which is for coatings obtained in isothermal conditions: for chromoaluminoboronation it is 14000-14500 MPa, for chromoaluminosilication12500-13000 MPa, for chromoalumotation of 15000-15500 MPa, and under SHS conditions it reaches the corresponding values for chromoaluminoboron 15000-16000 MPa.
Tests on the friction machine MT-5 (friction under conditions of shock-dynamic loading) showed that the best wear resistance is provided by protective coatings doped with Si, the wear value was \(-28 \cdot 10^{-4}\) g/m\(^2\), while at doping with boron - \(38 \cdot 10^{-4}\) g/m\(^2\), and when doping with titanium - \(60 \cdot 10^{-4}\) g/m\(^2\).

**Conclusions**

1. The obtained protective coatings doped silicon and titanium under stationary temperature conditions, ensures high stability of the treatment results in limited duration of the process.

2. For the intensification of the processes of diffusion saturation and reduce energy consumption at the stage of inert warm-up may be recommended introduction to the composition of the reaction mixtures the excess aluminum (10 to 15%).

3. Tests on the friction machine MT-5 (friction under conditions of shock-dynamic loading) showed that the best wear resistance is provided by protective coatings doped with Si, the wear value was \(-28 \cdot 10^{-4}\) g/m\(^2\), while at doping with boron - \(38 \cdot 10^{-4}\) g/m\(^2\), and when doping with titanium - \(60 \cdot 10^{-4}\) g/m\(^2\). Their wear resistance is 1,8-2,1 times higher than that of coatings obtained under isothermal conditions.

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