Problem’s Formulation

About development new productions in Ukraine, it is important to increase the reliability and durability of parts of machines and units operating in conditions of wear, alternating loads, high temperatures, speeds and pressures, as well as aggressive corrosive environments, the properties of the surface layer are important. In many cases, the most rational solution to the problem is a combination of durable structural material with temperature, wear and chemically resistant coatings on work surfaces. Therefore, the issue of improving the performance of parts by creating protective coatings is relevant. Among the methods of surface hardening are widely used chromium-plated coatings obtained by various methods of chemical heat treatment [1—5].

However, all known methods are energy-intensive and long. In this regard, the development of new methods of chemical heat treatment is relevant for Ukraine, which allows to regulate the composition and structure of protective coatings, to provide the necessary performance characteristics with a minimum time of their formation. Such technologies are based on the phenomenon of self-propagating high-temperature synthesis [6—7].

Formulation of the study purpose

Physico-chemical modeling to establish the mechanisms of formation of doped CPS, which is based on the results of the study of the gas phase by thermodynamic analysis of thermal spontaneous combustion reactions SHS-charges, studies of kinetic schemes of chemical transformations in the studied SHS-charges, study of the dependence of burning rate and from cholesterol, B, Ti, Si. as well as studies of the temperature characteristics of the regime of thermal spontaneous combustion of powder SHS-charges [8—9].

Presenting main material

For the thermodynamic analysis of the SHS process of forming alloy protective coatings, a universal calculation program of multicomponent heterogeneous TERRA systems was used, created
on the basis of ASTRA-4 program [10—12] under WINDOWS environment and developed for high-
temperature processes. Unlike traditional methods of calculating equilibrium parameters in chemical
thermodynamics using Gibbs energy, the equilibrium constants and the law of acting masses of
Goldberg and Vague, the universal program of thermodynamic calculations TERRA is based on the
entropy maximum for isolated thermodynamic systems. It is characterized by a maximum entropy
relative to thermodynamic degrees of freedom, which include concentrations of system components,
temperature, pressure, etc.

Among the various factors influencing the mechanism of coating formation in SHS conditions
are the initial conditions preceding the diffusion of elements into the material, which directly or
indirectly depend on physicochemical saturation factors (thermodynamic characteristics of phases in
the system of interacting elements; thermodynamic characteristics of saturated environment). Consider
the most important of them.

The interaction of metal oxides with aluminum can be represented in general by the equation [13]
\[ 2m_{Me,OMe} + 4/3mA_l = 2m_{Me} + 2/3Al_2O_3 \] (1)

The main condition for the spontaneous course of this reaction is the higher thermodynamic
strength of aluminum oxides in comparison with oxides of renewable metals. The strength of oxides
of different metals is characterized by the value of the isobaric potential \( \Delta Z^0 \) in the interaction of these
metals with oxygen. The greater the difference in the values of the isobaric potentials of the formation
of alumina and the reducing element (metal), the more complete and vigorous the reduction reactions.

To reduce the temperature, a “ballast” additive is introduced into the SHS charge, which absorbs
part of the heat of the reduction reaction. The most convenient and cheapest ballast additive is alumina
Al_2O_3. The required amount of ballast impurity introduced into the SHS charge is found from the heat
balance equation [15]:
\[ Q_{\text{mix}} + Q_{\text{wall}} = Q_c + Q_a, \] (2)

where \( Q_{\text{mix}} \) — heat capacity of the mixture at the temperature of initiation of the reaction, kJ; \( Q_{\text{wall}} \) —
heat released during the reduction reactions, kJ; \( Q_c \) — heat that went to heat SHS-charge, kJ; \( Q_a \) —
heat loss, kJ.

In the expanded form the equation of heat balance acquires the following look:
\[ \left( m'_{Me,OMe} \Delta H^i_{Me,OMe,OMe} + m''_{Me,OMe} \Delta H^ii_{Me,OMe,OMe} + \ldots m^n_{Me,OMe} \Delta H^n_{Me,OMe,OMe} \right) (1 - q_n) = m'_{Me} C'_p + m''_{Me} C'_p + \ldots m^n_{Me} C'_p + \right. \\
\left. + \sum m_{Al2O3} C''_p + m'_{Me,OMe} C''_p + m''_{Me,OMe} C''_p + m^n_{Me,OMe} C''_p + m_b C''_p \right) (T_2 - T_1), \] (3)

where \( m'_{Me,OMe} \) — mass of oxide involved in the reduction reaction, kg; \( m'_b \) — mass of oxide not
involved in the reduction reaction, kg; \( m''_{Me,OMe} \) — mass of the element formed as a result of recovery, kg; \( m_b \)
— the required amount of ballast impurity, kg; \( \Delta H^i_{Me,OMe,OMe} \) — thermal effect of Me,OMe reduction reaction,
kJ/kg; \( C'_p \) — average heat capacity of the corresponding component of the mixture in the temperature
range \( T_1 - T_2 \), kJ/(kg·deg); \( T_1 \) and \( T_2 \) — respectively, the temperature of initiation of the reduction reaction
and the maximum allowable temperature of the process, K; \( q_n \) — coefficient of heat loss.

Analysis of heat losses conducted by Lyakishev N.P. and Pliner Yu.L. [135—136] shows that the fluctuations of heat loss under different conditions of metal-thermal reduction are so large that the use
of different processes in thermal calculations, or a single amount of heat loss leads to additional error
that significantly exceeds the allowable calculations. Thus, according to the heat balances available in
the literature [135—136], heat losses during metal-thermal reduction range from 8 to 25.3 % of the
total heat input. If we take into account the average heat loss of 16.6 %, the error in determining the
melt temperature for different technological schemes will be \( \pm 200 \) °. Therefore, a necessary part of
the thermal calculations of aluminothermic charges should be an estimate of the amount of heat loss characteristic of the accepted conditions of the process.

To determine the amount of gas transport agent in the saturating charge, we perform
thermodynamic calculations to determine the composition of the gas phase and the possibility of gas-
phase reactions in the temperature range 400—1600 K with different activators. Ammonium chloride, ammonium fluoride, iodine, and others can be used as activators of the saturation process. The specific choice of an activator was determined depending on the possibility of transferring their components to the processed materials and the scheme of the saturation process, both in the combustion mode and in the mode of thermal spontaneous combustion.

Introduced into SHS-charge activators, in the absence of ballast additives, contributes to a sharp (300—400°C) decrease in the temperature of initiation of reduction reactions. This feature can be explained by the activation of the reducing agent surface due to the interaction of the decomposition products of the activator with the oxide film on aluminum by the following thermodynamically probable reactions (the calculation was performed under the assumption that $\Delta H^0$ and $\Delta S^0$ and do not change with temperature):

As a result of thermodynamic calculations of the equilibrium composition of the reaction products, we can assume the following kinetic scheme of chemical transformations in the studied SHS-charges:

1. The combustion reaction of the chromium component:
   $$\text{Cr}_2\text{O}_3 + 2\text{Al} = 2\text{Cr} + \text{Al}_2\text{O}_3$$ (1)

2. Disintegration reactions of the gas carrier:
   $$\text{I}_2 \rightarrow 2\text{I}$$ (2)
   $$\text{NH}_4\text{Cl} \rightarrow \text{NH}_3 + \text{HCl}$$ (3)
   $$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$$ (4)
   $$\text{NH}_4\text{F} \rightarrow \text{NH}_3 + \text{HF}$$ (5)
   $$\text{HF} \rightarrow \text{H} + \text{F}$$ (6)

3. Chemical transport reactions:
   $$\text{Cr} + 2\text{F} = \text{CrF}_2$$ (7)
   $$\text{Cr} + \text{F}_2 = \text{CrF}_3$$ (8)
   $$\text{CrF}_2 + \frac{1}{2}\text{F}_2 = \text{CrF}_3$$ (9)
   $$\text{Si} + \text{F}_2 = \text{SiF}_4$$ (10)
   $$\text{Si} + 4\text{HCl} \leftrightarrow \text{SiCl}_4 + 2\text{H}_2$$ (11)
   $$\text{Si} + 2\text{HCl} \leftrightarrow \text{SiCl}_3 + \text{H}_2$$ (12)
   $$\text{Cr} + \text{I}_2 = \text{CrI}_2$$ (13)
   $$\text{Cr} + 3\text{I} = \text{CrI}_3$$ (14)
   $$\text{Al} + 3/2\text{Cl}_3 = \text{AlCl}_3$$ (15)
   $$\text{Al} + \text{I} \leftrightarrow \text{AlI}$$ (16)
   $$2\text{Cr} + 3\text{Cl}_3 = 2\text{CrCl}_3$$ (17)
   $$2\text{SiI}_2 \leftrightarrow \text{Si} + \text{SiI}_4$$ (18)
   $$\text{Si} + 2\text{I}_2 \leftrightarrow \text{SiI}_4$$ (19)
   $$\text{Cr} + \text{Cl}_2 \leftrightarrow \text{CrCl}_2$$ (20)
   $$\text{Cr} + \text{Cl}_2 \leftrightarrow \text{CrCl}_2$$ (21)
   $$2\text{Al} + 3\text{I}_2 = \text{Al}_3\text{I}_6$$ (22)

4. Exchange reactions with structural material:
   $$4\text{Fe} + \text{AlI}_3 \leftrightarrow \text{Fe}_3\text{Al} + \text{FeI}$$ (23)
   $$2\text{Fe} + \text{Al} \leftrightarrow \text{FeAl} + \text{FeI}$$ (24)
   $$4\text{Fe} + 3\text{Bl}_3 \leftrightarrow \text{FeB} + 3\text{FeI}_3$$ (25)
   $$4\text{Fe} + 3\text{Bl}_3 \leftrightarrow \text{FeB} + 3\text{FeI}_3$$ (26)
   $$\text{Cu} + 2\text{I} \leftrightarrow \text{CuI}_2$$ (27)
   $$\text{CrI}_2 + 3\text{Cu} \leftrightarrow \text{CuCr} + 2\text{CuI}$$ (28)
   $$4\text{Cu} + \text{AlI}_3 \leftrightarrow \text{Cu}_3\text{Al} + \text{CuI}$$ (29)
   $$7\text{Cu} + 2\text{AlI}_3 \leftrightarrow \text{Cu}_3\text{Al}_2 + 6\text{CuI}$$ (30)
   $$2\text{Cu} + \text{Al} \leftrightarrow \text{CuAl} + \text{CuI}$$ (31)
   $$\text{SiI}_2 + 3\text{Cu} \leftrightarrow \text{CuSi} + 2\text{CuI}$$ (32)
   $$\text{TiI}_4 + 8\text{Cu} \leftrightarrow \text{Cu}_4\text{Ti} + 4\text{CuI}$$ (33)
   $$\text{TiI}_4 + 6\text{Cu} \leftrightarrow \text{Cu}_2\text{Ti} + 4\text{CuI}$$ (34)
The calculations and their analysis allow to obtain information about the mechanism of obtaining coatings in the conditions of SHS, and the application of software analysis — to perform an objective assessment of the composition of powder SHS-charges to regulate this process.

The specific quantitative composition of the proposed systems in the framework of thermodynamic calculations cannot be specified, so it is necessary to experimentally choose the composition that provides the optimal mode of the process.

At the same time, starting from a temperature of 800 K, the decomposition of the reaction products takes place, which confirms the appearance of the decomposition products and a sharp increase in the number of moles of gas. Gaseous products interact with the elements of the powder system (Al, Si, B, Ti, and Cr) and convert them into the gaseous phase.

With the determination of the concentration of gaseous products, data on two thermodynamic properties were found for the calculations of the equilibrium compositions of powder SHS charges in the thermal spontaneous combustion mode: enthalpies of $H_T$ and Gibbs energy of $G_T$. The enthalpy was chosen to determine the thermal effect of the considered chemical reactions; at $\Delta H<0$ the reaction will take place with the release of heat, and at $\Delta H>0$ — with heat absorption. To calculate the equilibrium of chemical reactions in the system under study, 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 charges were determined.

![Fig. 1. Content of condensed products in SHS-charge, in the mode of thermal spontaneous combustion, for the system doped with boron](image1)

![Fig. 2. Content of condensed products in SHS-charge, in the mode of thermal spontaneous combustion, for the system doped with silicon](image2)
Fig. 3. Content of condensed reaction products in SHS charge, in the mode of thermal spontaneous combustion, for titanium-doped system

Conclusions

It was found that at a temperature of 400—1600 K the decomposition products of activators (I$_2$, NH$_4$Cl, and NH$_4$F) react with the oxide film on aluminum (before the reduction reaction) with the formation of gaseous compounds AlI, AlI$_2$, CrF$_2$, CrI$_2$, CrI$_3$, BI$_3$, BF$_2$, BF$_3$, TiCl$_3$, TiCl$_4$, TiI$_2$ and others. With increasing temperature, the number of products in the gas phase, condensed products are released.

Experimentally set autoignition temperatures and maximum temperatures from the amount of chromium component in the SHS charge. According to the results of the study of warm SHS processes, it is determined that with increasing the amount of the initial component of spontaneous combustion decreases, and the maximum temperature is chromium-plated, decreases. Increasing the content of boron (silicon, titanium) increases the temperature.

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ФІЗИКО-МЕХАНІЧНЕ МОДЕЛЮВАННЯ ОТРИМАННЯ ЗАХИСНИХ ПОКРИТТІВ
ДЕТАЛЕЙ, ЛЕГОВАНИХ КРЕМНІЄМ, ТИТАНОМ ТА БОРОМ

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Реферат

В роботі розглянуто отримання борованих, силіційованих та титанованих покриттів при нестационарних температурних умовах. Проведено термодинамічний аналіз та фізико-механічне моделювання формування покриттів на мідних сплавах, на кожної із стадій нанесення покриттів в умовах СВС. Визначено концентрації газоподібних продуктів, для розрахунків рівноважних складів порошкових СВС-шихт у різних температурних режимах, підтверджено появу продуктів розкладання і різке збільшення кількості молей газу.

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