DOI:
UDC 621.793.6

D. Sereda, Candidat of Technical Sciences, Associate Professor, seredabp@ukr.net
D. Kruhliak, Candidat of Technical Sciences, Associate Professor
I. Belozor, graduate student
D. Kiforuk, graduate student
A. Prolomov, graduate student
Dniprovsky State Technical University, Kamianske

PHYSICAL AND MECHANICAL MODELING OF OBTAINING PROTECTIVE COATINGS FOR PARTS DOPED WITH SILICON, TITANIUM AND BORON

The paper considers the preparation of borated, siliconized, and titanized coatings under non-stationary temperature conditions. Thermodynamic analysis and physical and mechanical modeling of the formation of coatings on copper alloys at each stage of coating deposition under SHS conditions have been carried out. The concentrations of gaseous products are determined, to calculate the equilibrium compositions of powder SHS-charges in the mode of thermal spontaneous combustion, we found data on two thermodynamic properties: enthalpy of H_m *and Gibbs energy of* G_T*.*

Keywords*: brass, corrosion, self-propagating high-temperature synthesis, protective coating*

В роботі розглянуто отримання борованих, силіційованих та титанованих покриттів при нестаціонарних температурних умовах. Проведено термодинамічний аналіз та фізико-механічне моделювання формування покриттів на мідних сплавах, на кожній із стадій нанесення покриттів в умовах СВС. Визначено концентрації газоподібних продуктів, для розрахунків рівноважних складів порошкових СВС-шихт у режимі теплового самозаймання знаходили дані по двом термодинамічним властивостям: энтальпії H_m *і енергії Гиббса* G_T*.*

Ключові слова*: латунь, корозія, саморозповсюджуваний високотемпературний синтез, захисне покриття*

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]

$$2/\mathrm{m}\mathrm{Me}_n\mathrm{O}_m + 4/3m\mathrm{Al} = 2n/m\mathrm{Me} + 2/3m\mathrm{Al}_2\mathrm{O}_3 \tag{1}$$

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 ΔZ^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 $\mathrm{Al_2O_3}$. The required amount of ballast impurity introduced into the SHS charge is found from the heat balance equation [15]:

$$Q_{физ} + Q_{хим} = Q_c + Q_n, \tag{2}$$

where $Q_{физ}$ — heat capacity of the mixture at the temperature of initiation of the reaction, kJ; $Q_{хим}$ — heat released during the reduction reactions, kJ; Q_c — heat that went to heat SHS-charge, kJ; Q_n — heat loss, kJ.

In the expanded form the equation of heat balance acquires the following look:

$$\left(m^I_{Me_{v1}O_{z1}}\Delta H^I_{Me_{v1}O_{z1}} + m^{II}_{Me_{v2}O_{z2}}\Delta H^{II}_{Me_{v2}O_{z2}} + ..m^N_{Me_{vn}O_{zn}}\Delta H^N_{Me_{vn}O_{zn}}\right)\left(1-q_n\right) = (m^I_{Me}C_p^{,,} + m^{II}_{Me}C_p^{,,} + \ldots + m^{II}_{Me}C_p^{,,} +$$

$$+\sum m'_{Al2O3}C_p^{,,} + m'_{Me^I_{v1}O_{z2}}C_p^{,,} + m'_{Me^{II}_{v1}O_{z2}}C_p^{,,} + m'_{Me^N_{vn}O_{zn}}C_p^{,,} + m_б C_p^{,,})\left(T_2 - T_1\right), \tag{3}$$

where $m^i_{Me_{vi}O_{zi}}$ — mass of oxide involved in the reduction reaction, kg; $m'_{Me^I_{vi}Oi_{zi}}$ — mass of oxide not involved in the reduction reaction, kg; m^i_{Me} — mass of the element formed as a result of recovery, kg; $m_б$ — the required amount of ballast impurity, kg; $\Delta H^i_{Me_{vi}O_{zi}}$ — thermal effect of $Me_{vi}O_{zi}$ 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; $q_п$ — 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 ± 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 ΔH^0 and ΔS^0 and 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:

$$Cr_2O_3+2Al = 2Cr + Al_2O_3 \tag{1}$$

2. Disintegration reactions of the gas carrier:

$$I_2 \rightarrow 2I \tag{2}$$

$$NH_4Cl \rightarrow NH_3 + HCl \tag{3}$$

$$2NH_3 \rightarrow N_2 + 3H_2 \tag{4}$$

$$NH4F \rightarrow NH3 + HF \tag{5}$$

$$HF \rightarrow H + F \tag{6}$$

3. Chemical transport reactions:

$$Cr + 2F = CrF_2 \tag{7}$$

$$Cr + F_2 = CrF_3 \tag{8}$$

$$CrF_2 + \tfrac{1}{2}F2 = CrF_3 \tag{9}$$

$$Si + F_2 = SiF_4 \tag{10}$$

$$Si + 4HCl \leftrightarrow SiCl_4 + 2H_2 \tag{11}$$

$$Si + 2HCl \leftrightarrow SiCl_2 + H_2 \tag{12}$$

$$Cr + I_2 = CrI_2 \tag{13}$$

$$Cr + 3I = CrI_2 \tag{14}$$

$$Al + 3/2Cl_3 = AlCl_3 \tag{15}$$

$$Al + I \leftrightarrow AlI \tag{16}$$

$$2\,Cr + 3\,Cl_2 = 2CrCl_3 \tag{17}$$

$$2SiI_2 \leftrightarrow Si + SiI_4 \tag{18}$$

$$Si + 2I_2 \leftrightarrow SiI_4 \tag{19}$$

$$Cr + Cl_2 \leftrightarrow CrCl_2 \tag{20}$$

$$Cr + Cl_2 \leftrightarrow CrCl_2 \tag{21}$$

$$2Al+ 3I_2 = Al_2I_6 \tag{22}$$

4. Exchange reactions with structural material:

$$4Fe + AlI_3 \leftrightarrow Fe_3Al + FeI \tag{23}$$

$$2Fe + AlI \leftrightarrow FeAl + FeI \tag{24}$$

$$4Fe + BI_3 \leftrightarrow FeB + FeI_3 \tag{25}$$

$$4Fe + BI_3 \leftrightarrow FeB + Fe_3I \tag{26}$$

$$Cu + 2I \leftrightarrow CuI_2 \tag{27}$$

$$CrI_2 + 3Cu \leftrightarrow CuCr + 2CuI \tag{28}$$

$$4Cu + AlI_3 \leftrightarrow Cu_3Al + CuI \tag{29}$$

$$7Cu + 2AlI_3 \leftrightarrow CuAl_2 + 6CuI \tag{30}$$

$$2Cu + AlI \leftrightarrow CuAl + CuI \tag{31}$$

$$SiI_2 + 3Cu \leftrightarrow CuSi + 2CuI \tag{32}$$

$$TiI_4 + 8Cu \leftrightarrow Cu_4Ti + 4CuI \tag{33}$$

$$TiI_4 + 6Cu \leftrightarrow Cu_2Ti + 4CuI \tag{34}$$

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 can not 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 $H_{т}$ 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.

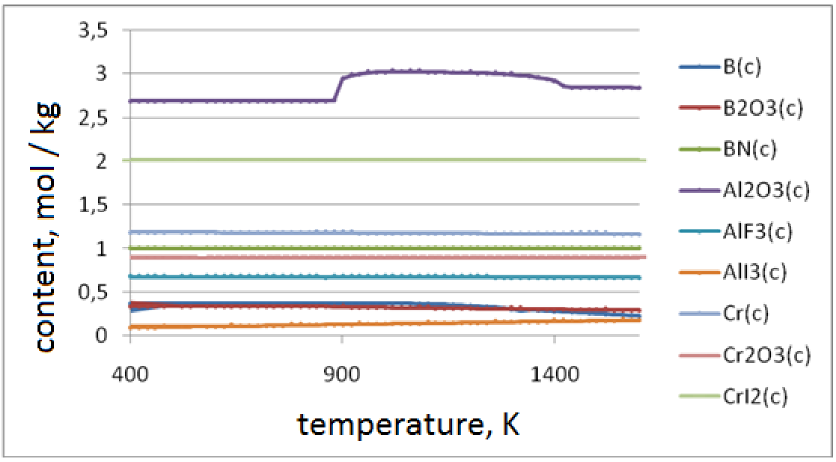

Fig. 1. Content of condensed products in SHS-charge, in the mode of thermal spontaneous combustion, for the system doped with boron

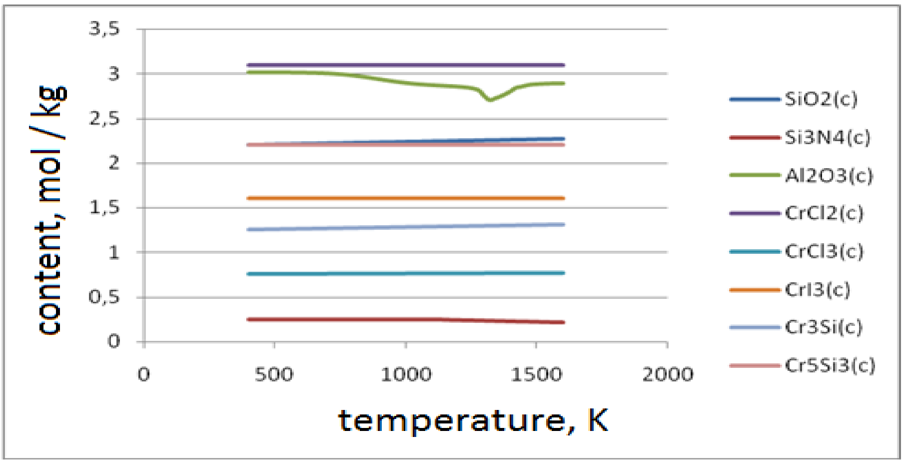

Fig. 2. Content of condensed products in SHS-charge, in the mode of thermal spontaneous combustion, for the system doped with silicon

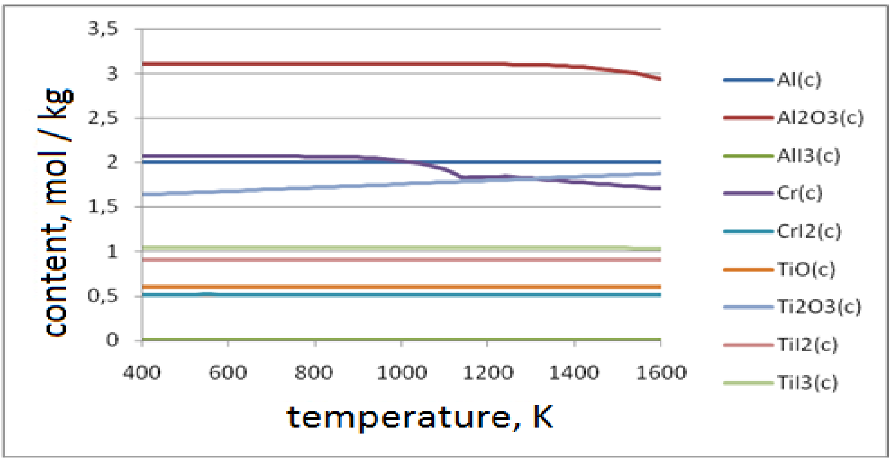

Fig. 3. Content of condensed reaction products in SHS charge, in the mode of thermal spontaneous combustion, for titanium-doped system

Conclusions

It was found that at a temperature of 400—1600 K the decomposition products of activators (I_2, NH_4Cl, and NH_4F) react with the oxide film on aluminum (before the reduction reaction) with the formation of gaseous compounds AlI, AlI_2, Al_2I_6, 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.

References

[1] Merzhanov A.G. (1994). Tverdoe plamya: otkrytiya, koncepcii i gorizonty poznaniya [Solid flames: discovery, concepts and horizons of cognition]. *Combust. Sci. and Technol.*, (4(98)), 307–336.

[2] Lakhtin Yu.M. (1993). Metallurgiya i termicheskaya obrabotka metallov [Metallurgy and heat treatment of metals]. M.: Metallurgy.

[3] Merzhanov A.G., Rogachev A.S. (2003). Fazovye i strukturnye prevrashcheniya pri SVS [Phase and structure transformations during SHS]. *Adv. Sci. Techn.*, (31), 271–282.

[4] Khusid B.M. Mansurov V.A., Ubortsev A.D., Shulman Z.P. (1993). Fazovye i himicheskie prevrashcheniya v samorasprostranyayushchejsya volne ekzotermicheskoj reakcii v smesi organicheskih poroshkov [Phase and chemical transformations in the self-propagating wave of an exotermal reaction in a mixture of organic powders]. *Soc., Faraday Trans.*, (4(89)), 727–732

[5] Borisenok G.V., Vasiliev L.A., Voroshnin L.G. (1981). Himiko-termicheskaya obrabotka metallov i splavov [Chemical-thermal treatment of metals and alloys]. Directory. Moscow: Metallurgy

[6] Sereda B., Sereda D., Sereda I. (2017). Ustanovlenie svyazi mezhdu harakteristikami mikrostruktury i zharostojkost'yu silikatnyh pokrytij, poluchennyh v usloviyah SVS [Establishment of the relationship between the microstructure characteristics and the heat resistance of silicate coatings obtained under SHS conditions]. *Material science and technology. Pittsburgh. Pennsylvania USA.* 412–416

[7] Sereda B., Belokon Y. Kruglyak I. (2019). Modelirovanie processov proizvodstva splavov na osnove TiAl i CiAl v usloviyah SVS dlya aviakosmicheskoj promyshlennosti. [Modeling of

processes for the production of bassed alloys TiAl and NiAl in the conditions of SHS for aerospace applications]. *Material science and technology. Portland, Orgon.* USA. 137–142

[8] Sereda B., Sereda D. (2016). Razrabotka receptur zashchitnyh pokrytij na osnove bora dlya agregatov, rabotayushchih pri vysokih temperaturah v metallurgii [Development of Protective Coatings Formulations Based on Boron for Units Operating at High Temperatures in Metallurgy]. *Material science and technology. Salt Lake City, Utah USA*. 931–934.

[9] Sereda B., Palehova I., Gaydaenko A. (2019) Sovremennye tribologicheskie pokrytiya. Poluchenie pokrytij na osnove titana v usloviyah SVS [Advanced tribological coatings titanium based coatings obtaining under SHS Conditions]. *Material science and technology. Portland, Orgon, USA.* 380–387.

[10] Gurvich L.V., Veits I.V., Medvedev V.A. (1978-1982) Termodinamicheskie svojstva individual'nyh veshchestv [Thermodynamic properties of individual substances] (In 4 volumes, Reference edition) M: Science

[11] Edilbaev A.I. (2008) Issledovanie vozmozhnosti obezzhelezivaniya margancevyh koncentratov [Investigation of the possibility of deironing manganese concentrates]. *Bulletin of the National Engineering Academy of the Republic of Kazakhstan*. Almaty – 2008, (4), 125–133.

[12] Sinyarev G.B., Vatolin N.A., Trusov B.G., Moiseev R.K. (1982). Ispol'zovanie komp'yuterov dlya termodinamicheskih raschetov metallurgicheskih processov [The use of computers for thermodynamic calculations of metallurgical processes]. M.: Nauka.

[13] Lyakishev N.P., Pliner Yu.L., Ignatenko G.F., Lapko S.I. (1978). Alyumotermiya [Alumothermy]. M.: Metallurgy".

[14] Pliner Yu.L., Ignatenko G.F. (1967). Vosstanovlenie oksidov metallov alyuminiem [Reduction of metal oxides with aluminum]. M.: Metallurgy.

[15] Frank-Kamenetskiy D.A. (1987). Diffuziya i teploperedacha v himicheskoj kinetike [Diffusion and heat transfer in chemical kinetics]. M.: Nauka.

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

Середа Д., Кругляк Д., Бєлозір І., Кіфорук Д., Проломов А.

Реферат

В роботі розглянуто отримання борованих, силіційованих та титанованих покриттів при нестаціонарних температурних умовах. Проведено термодинамічний аналіз та фізико-механічне моделювання формування покриттів на мідних сплавах, на кожній із стадій нанесення покриттів в умовах СВС. Визначено концентрації газоподібних продуктів, для розрахунків рівноважних складів порошкових СВС-шихт у режимі теплового самозаймання знаходили дані по двом термодинамічним властивостям: ентальпії $H_т$ і енергії Гиббса G_T. Для розрахунків рівноваги хімічних реакцій у досліджуваній системі, а також для визначення рівноважних складів компонентів, що брали участь у цих реакціях, визначали константи рівноваги всіх незалежних реакцій, можливих у даних шихтах. Проведені розрахунки і їх аналіз дозволяють одержати інформацію про механізм отримання покриттів в умовах СВС, а застосування програмного аналізу - виконати об'єктивну оцінку складу порошкових СВС- шихт для регулювання даного процесу. Основними продуктами в газовій фазі, у діапазоні температур 1200-1800 К, є йодиди, фториди, хлориди хрому, алюмінію, бору, титану й кремнію. В результаті розрахунків концентрації газоподібних продуктів СВС- реакцій встановлено, що при температурі 400-750 К відбувається розпад ГТА (NH_4Cl, NH_4F и I_2). З температури 750-900 К, відбувається розпад продуктів реакції, що підтверджується появою продуктів розкладання й різке збільшення кількості молей газу.

Література

1. Лахтін Ю.М. Металургія і термообробка металів: навч. посіб. М.: Металургія, 1993. 448 с.
2. Мержанов А.Г. Твердо полум'я: відкриття, поняття та горизонти пізнання. *Згоряння. наук. і техн.*, 1994. № 4(98). С. 307–336.
3. Мержанов А.Г., Рогачов А.С. Фазові та структурні перетворення під час СВС. *Присл. наук. Техн.*, 2003. № 31. С. 271–282.
4. Хусід Б.М. Мансуров В.А., Уборцев А.Д., Шульман З.П. Фазові та хімічні перетворення в самопоширюваній хвилі екзотермальної реакції в суміші органічних порошків. J. Chem., Soc., Faraday Trans., 1993. № 89. № 4. С. 727–732.
5. Хіміко-термічна обробка металів і сплавів : довідник /Борисенок Г.В., Васильєв Л.А., Ворошнін Л.Г. та інші. М.: Металургія, 1981. 424 с.
6. Sereda B., Sereda D., Sereda I. Establishment of the relationship between the microstructure characteristics and the heat resistance of silicate coatings obtained under SHS conditions. *Material science and technology. Pittsburgh. Pennsylvania USA.* 2017. P.412–416.
7. Sereda B., Belokon Y., Kruglyak I. Modeling of processes for the production of bassed alloys TiAl and NiAl in the conditions of SHS for aerospace applications. *Material science and technology. Portland, Orgon*, USA. P. 137–142.
8. Sereda B., Sereda D. Development of Protective Coatings Formulations Based on Boron for Units Operating at High Temperatures in Metallurgy. *Material science and technology. Salt Lake City, Utah USA*. 2016. P. 931–934.
9. Sereda B., Palehova I., Gaydaenko A. Advanced tribological coatings titanium based coatings obtaining under SHS Conditions. *Material science and technology. Portland, Orgon*, *USA.* 2019. P. 380–387
10. Термодинамічні властивості індивідуальних речовин: Довідкове видання в 4-х т./Л. В. Гурвіч, І. В. Вейц, В. А. Медведєв та ін. М: Наука, 1978–1982.
11. Єдільбаєв А.І. Дослідження можливості знезалізнення марганцевих концентратів. *Вісник Національної інженерної академії РК. Алмати.* 2008. № 4 С. 125–133.
12. Застосування ЕОМ для термодинамічних розрахунків металургійних процесів / [Синярьов Г. Б., Ватолін Н. А., Трусов Б. Г., Мойсеєв Р. К. та ін.]. М.: Наука, 1982. 263 с.
13. Лякішев Н.П., Плінер Ю.Л., Ігнатенко Г.Ф., Лапко С.І. Алюмотермія. М.: Металургія. 1978. 424 с.
14. Плінер Ю.Л., Ігнатенко Г.Ф. Відновлення оксидів металів алюмінієм М.: Металургія. 1967. 248 с.
15. Франк-Каменецький Д.А. Дифузія та теплопередача у хімічній кінетеці. М.: Наука. 1987. 502 с.