УДК 621.785
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PROTECTIVE COATINGS OBTAINED UNDER CONDITIONS OF SHS FOR WORK IN COKE PRODUCTION

In work discusses methods for the manufacture of protective materials in the thermal self-ignition mode of self-propagating high-temperature synthesis for use in coke-chemical production.

The results of studies of the structures and properties of corrosion-resistant coatings are shown. Analysis of the relevant parameters affecting the structure and operational properties of coatings is presented using various processing methods. According to the test results, it was found that titanium and silicon alloyed coatings have the best corrosion resistance indicators, increasing the service life by 1.5-1.7 times for parts operating under conditions of coke-chemical production.

Keywords: *corrosion-resistant coatings, self propagating high-temperature synthesis, construction material.*

Introduction. Coke chemical production is characterized by a very high aggressiveness of the enterprise atmosphere, thermal effects on the working bodies of machines and structures, the cavity dust abrasiveness, adhesion to the surface of the apparatus of condensate, resins, fuses, etc. For the production environment of the coke-chemical enterprise, the uneven distribution of aggressive substances in the working zone is characteristic. Sources of aggressive impact on the construction material can be divided into sources of energy and chemical influence. The composition and concentration of the components of the operating environment as a result of the physico-chemical processes of coke-chemical production corresponds to moderately and strongly aggressive impacts on building structures of buildings and structures. The maintenance of a constant level of reliability and durability of exploited structures is connected with the effective organization of a technical service, which carries out supervision of structures on its own or through the involvement of specialized organizations.

Surface saturation with aluminum, chromium, zinc and other elements refers to diffusion saturation with metals. The product, whose surface is enriched with these elements, gets valuable properties, which include high heat resistance, corrosion resistance, increased wear resistance and hardness

At present, the main methods of applying a protective coating are galvanic discharges in electrolysis, gas-thermal spraying, or metallization, thermal diffusion saturation in powder, immersion in molten metal, plastering. The adhesive and diffusive metal coatings are distinguished by the type of metal layer protective compound [1-4].

Depending on the method of transferring the diffusion element to the saturated surface, the following basic methods of diffusion metallization are distinguished: immersion into molten metal, if the diffusing element has a low melting point; saturation from molten salts containing diffusing element (with electrolysis and without electrolysis) saturation from the sublimated phase by evaporation of the diffusing element; saturation from the gas phase (contact and non-contact method), consisting of halogen compounds of the diffusing element[4-6].

Among the methods of surface hardening are widely used chromoalyated coatings obtained by various methods of chemical and thermal treatment.

In this connection, the development of new methods of chemical-thermal treatment is actual, it allows to regulate the composition and structure of protective coatings, provide the necessary performance characteristics with the minimum time of their formation. Such technologies are based on the phenomenon of self-propagating high-temperature synthesis [7-10].

Self-propagating high-temperature synthesis (SHS) is a chemical process that occurs with heat release in autowave mode, a type of combustion leading to the formation of solid products. Thermal decomposition of complex reagents, oxidation-reduction reaction, synthesis of simple substances etc may take place as chemical stages SHS. Mixtures for SHS consist of fuel (often metals or volatile compounds), oxidizer, as well as fillers and functional additives; which are introduced to regulate the composition and structure of the base products. Typical reagents - refractory metals (Ti, Zr, Hf, V, Nb, Ta, etc.) and nonmetals (B, C, Si), gases (N2, O2, H2), oxides, metal halides and metal-reducing agents (such as A1 and Mg), metal hydrides, organic and organometallic compounds, mineral raw materials and industrial solid waste [11-12].

Oxygen-free refractory compounds (borides, carbides, nitrides, silicides), intermetallics (aluminides, etc.), chalcogenides, complex oxides (titanates, niobates, tantalates, ferrites, etc.), hydrides, phosphides, and various nonstoichiometric phases, single phase solid solutions of binary compounds (eg, carbonitrides), and others are obtained by SHS method. Organic compounds can be produced also in the SHS mode

By studying the SHS a number of new phenomena were found - (not unique) a number of modes of propagation reaction and hysteretic transition between them, spontaneous homogenization of heterogeneous media associated with the capillary spreading of low-melting component in preflame zone, spin waves as developing of the thermal instability of self-wave processes, the anisotropic effect, which enables the production of polycrystalline products with anisotropy properties, and others. Such new directions in theory and practice of combustion, as gasless combustion (burning of powder mixtures without separation of gaseous products) and filtering burning have been developed. Important advantages of SHS is usage of chemical energy and the absence of external heat sources [13-14].

Inorganic materials (such as powders of refractory compounds, abrasive pastes, nitrided ferroalloys, cermets, ceramics), parts and products of specified sizes and shapes, including those from tungsten carbide (cutting inserts, rolls, dies, etc.), refractories, coatings have been produced with the help of SHS and permanent connection details have also been made.

Materials and methods of research. The purpose of the work was to increase the corrosion resistance of brass Lc40Mc3J in the conditions of SHS. Chemical-thermal treatment was carried out in an open-type reactor (P = 10^5 Pa) in the operating temperature range of 900-1100 ° C. The duration of isothermal exposure varied from 30 to 60 minutes.

Surface preparation of the samples consisted of successive grinding, polishing and degreasing in acetone. Initiation of the process of thermal autoignition was carried out by preheating the resistance in the furnace to the temperature of the beginning of the exothermic reaction (t *).

The tests for corrosion resistance are carried out on cylindrical samples with a diameter of 10 mm and a height of 20 mm. The samples of brass Lc40Mz3J are investigated in 30% - aqueous solutions of hydrochloric, sulfuric and nitric acids at a temperature of 20 ° C. Before and after the test, the samples were washed with acetone, dried and solved on analytical scales for 7 days every 24 hours with accuracy up to 1 mg and the mass loss per unit surface of the sample under the influence of corrosion is calculated [15].

The results of the research and their discussion. Manganese-iron brass LC40Mc3J - brass, designed for casting simple configuration of critical parts and armature of marine shipbuilding, operating at temperatures up to 300 ° C. Manganese-iron brass LC40Mc3J contains,%: Cu 53-58; Fe 0.5-1.5; Mn 3-4; Zn the rest. Mechanical properties for casting, respectively, under pressure and sand, at least: $\sigma_в$ = 392.441 MPa; δ = 10.18%; HB 90, 100

Brasses intensively corrode under the influence of mineral acids (nitric, hydrochloric). Sulfuric acid acts on brass much slower, but in the presence of oxidants {$K_2Cr_2O_7$, $Fe_2(S0_4)_3$}, the corrosion rate increases by two orders of magnitude. Bars are sufficiently stable in solutions of alkalis (with the exception of ammonia) and in concentrated solutions of neutral salts.

Hydrogen sulfide provides strong corrosive action on brass. At the same time, brass with high zinc content (more than 30%) is more stable in the hydrogen sulfide medium than brass with low zinc content. For corrosion resistance research, corrosive materials are used that imitate the intended applications:

- pumps for acid transfer in the production of titanium;
- bearing units on objects of special equipment in rocket space and defense industries;
- for the manufacture of simple configuration of parts for responsible purposes and armature of marine shipbuilding, operating at temperatures up to 300 °C of massive parts, propellers and their blades.

To enhance the corrosion resistance of brass, Lc40Mz3J requires a protective coating containing elements that form passive films. In this case, upon reaching the potential of ionic passivation, oxide films of the composition: Cr_2O_3, Al_2O_3,TiO_2, SiO2 which protect the metal from destruction, are formed.

When tested in a 30% hydrochloric acid aqueous solution, covering doped with silicon and titanium have the best resistance. The metallographic analysis shows that the protective coatings in all samples were uniformly corroded to a small depth, therefore, it is advisable to use covering doped with silicon to work in a 30% hydrochloric acid solution, which, besides good corrosion resistance, also has a high wear resistance.

The results obtained can be explained by the formation of surfaces on the doped phases leading to surface passivation in aggressive media. It is also possible to suppose the effect of electrochemical braking of anodic dissolution of metals at a higher concentration of alloying elements compared to coatings obtained under isothermal conditions.

Table 1

Corrosion resistance of bricks LC40Mc3J with doped coatings when tested in acids.

Corrosive environment	Kind of cover	Mass loss (г/м^2)						
		Test time, day						
		1	2	3	4	5	6	7
30% HNO_3	No cover	86	101	198	286	432	543	620
	Cr-Al-B	7	14	21	25	30	35	37
	Cr-Al-Si	5	12	18	23	26	31	35
	Cr-Al-Ti	4	9	14	20	23	28	32
30% HCl	No cover	92	103	118	130	142	164	180
	Cr-Al-B	3,8	5,2	7,6	12,0	15,1	19,6	24,1
	Cr-Al-Si	1,6	2,8	4,6	7,9	10,3	11,6	13,8
	Cr-Al-Ti	4,2	5,9	8,2	10,1	12,3	14,6	16,7
30% H_2SO_4	No cover	46	58	73	95	122	154	192
	Cr-Al-B	2,1	3,8	5,3	7,5	8,5	10,2	11,7
	Cr-Al-Si	1,8	2,9	4,1	5,7	7,5	9,2	10,8
	Cr-Al-Ti	1,3	2,3	4,1	5,9	8,3	10,1	12,4

Conclusions. Comparative analysis of corrosion resistance of protective coatings obtained in isothermal conditions, shows that they have a weight loss of 1,7-2,1 times more.

It is known that the mechanical stresses (in this case, the compressive residual stresses) affect the corrosion behavior of metals, due to the extraction of the structural material by the fact that the level of residual stresses in coatings obtained under the conditions of thermal self-ignition of the SHS charge is higher. As a result, the probability of micro-bursting of passive oxide films is reduced, resulting in an increase in corrosion resistance.

References

1. Lakhtin Yu.M. Metallurgy and heat treatment of metals. / Yu.M. Lakhtin // - M.: Metallurgy, 1993. - 448 p.
2. Merzhanov A.G. Solid flames: discovery, concepts and horizons of cognition. Combust. Sci. and Technol., 1994, v. 98, № 4-6, p. 307-336.
3. Merzhanov A.G., Rogachev A.S. Phase and structure transformations during SHS.Adv. Sci. Techn. 2003, v.31, pp. 271-282
4. Khusid B.M. Mansurov V.A., Ubortsev A.D., Shulman Z.P.. Phase and chemical transformations in the self-propagating wave of an exotermal reaction in a mixture of organic powders. J. Chem., Soc., Faraday Trans., 1993, v. 89, № 4, p. 727-732
5. Chemical-thermal treatment of metals and alloys. Directory. / Borisenok G.V., Vasiliev L.A., Voroshnin L.G. and others. - Moscow: Metallurgy, 1981.- 424 p.
6. Sereda B. Simulation and modeling of metallurgical phenomena produced on pressing in SHS-condition/ Sereda B., Sereda D., Kovalenko A., Kryglyak I. // Material science and technology - 2017. Pittsburgh. Pennsylvania USA. 2017. - P.727-732
7. Sereda B. Production of highly effective SHS coatings operating in oxidizing and corrosive environments / Sereda B., Sereda D., Kryglyak I. // Material science and technology - 2017. Pittsburgh. Pennsylvania USA. 2017. - P.424-429
8. Establishment of the relationship between the microstructure characteristics and the heat resistance of silicate coatings obtained under SHS conditions/ Sereda B., Sereda D., Sereda I.// Material science and technology - 2017. Pittsburgh. Pennsylvania USA. 2017. - P.412-416

9. Sereda B. Corrosion Resistance and Mechanical Properties Zinc Coating Sheet Steels, Received in Conditions of Self-propagating High Temperature Synthesis / Sereda D., Sereda B. // Material science and technology- 2016. Salt Lake City, Utah USA 2016. - P.825-829.

10. Sereda B. Development of Protective Coatings Formulations Based on Boron for Units Operating at High Temperatures in Metallurgy / Sereda D., Sereda B. // Material science and technology- 2016. Salt Lake City, Utah USA 2016. - P.931-934.

11. Sereda B. Modeling deformation in material processing and laws of phasic by SHS pressing intermetallics alloys / Sereda D., Sereda B. // Material science and technology. Columbus. Ohio, USA 2015. - P.611-617.

12. Sereda B. Aluminized Multifunctional Coating on Steel in SHS Condition./ Sereda D., Sereda B. //Material science and technology. Pittsburgh. Pennsylvania, USA 2014. - P.482-486.

13. Sereda B. Modeling deformation in material processing and laws of phasic by SHS pressing intermetallics alloys / Sereda D., Sereda B. //Material science and technology 2015. Conference and Exhibition. Columbus. Ohio, USA. 1827p. P.611-617 -SCOPUS

14. Sereda B., Sereda D. Kinetiks formation of aluminized multifunctional coating on steel in SHS condition. Material science and technology. Columbus, Ohio, USA. 2011.-P.1667-1671.

15. Zhuk N.P. Course of the theory of corrosion and protection of metals / N.P. Zhuk // - M .: Metallurgy, 1976. - 472 p.

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ЗАЩИТНЫЕ ПОКРЫТИЯ ПОЛУЧЕННЫХ В УСЛОВИЯХ СВС ДЛЯ РАБОТЫ В КОКСОХИМИЧЕСКОГО ПРОИЗВОДСТВЕ

В работе обсуждаются методы изготовления защитных материалов в режиме теплового самовоспламенения самораспространяющегося высокотемпературного синтеза для использования в коксохимическом производстве.

Показаны результаты исследований структур и свойств коррозионно-стойких покрытий. Анализ соответствующих параметров, влияющих на структуру и эксплуатационные свойства покрытий, представлен с использованием различных методов обработки. По результатам испытаний было обнаружено, что покрытия легированные титаном и кремнием, имеют лучшие показатели коррозионной стойкости, увеличивая срок службы в 1,5-1,7 раза для деталей, работающих в условиях коксохимического производства.

Ключевые слова: *коррозионно-стойкие покрытия, самораспространяющийся высокотемпературный синтез, конструкционный материал.*

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ЗАХИСНІ ПОКРИТТЯ ОТРИМАНИХ В УМОВАХ СВС ДЛЯ РОБОТИ В КОКСОХІМІЧНОГО ВИРОБНИЦТВІ

У роботі обговорюються методи виготовлення захисних матеріалів в режимі теплового самозаймання саморозповсюджувального високотемпературного синтезу для використання в коксохімічному виробництві.

Показані результати досліджень структур і властивостей корозійностійких покриттів. Аналіз відповідних параметрів, що впливають на структуру та експлуатаційні властивості покриттів, представлений з використанням різних методів обробки. За результатами випробувань було виявлено, що покриття леговані титаном і кремнієм, мають кращі показники корозійної стійкості, збільшуючи термін служби в 1,5-1,7 рази для деталей, що працюють в умовах коксохімічного виробництва.

Ключові слова: *корозійно-стійкі покриття, саморозповсюджувальний високотемпературний синтез, конструкційний матеріал.*

Стаття надійшла до редакції 13.11.2018