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MODIFICATION OF THE SURFACE OF COPPER ALLOYS WITH ALUMINUM IN THE CONDITIONS OF SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

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The influence of the technological parameters of the SHS process (temperature, holding time and alloying of B, Cr, Ti) on the corrosion resistance of brass with a surface alite layer, which effectively resists β-radiation, was studied. The research was carried out in 30% aqueous solutions of HNO_3, HCl, H_2SO_4. Aluminized coatings doped with silicon, which are obtained under optimal parameters, have 1.7-2.1 times higher corrosion resistance than doped B and Ti. Alloyed coatings have phases CuSi, CuAl, $CuAl_2$, CuTi, Ti_2Cu_3, CuCr, Cu_3Al, Cu_2Al, Al_3Si, and α-phase doped with Cr, Al, Si, B, Ti. When tested in a 30% aqueous solution of nitric acid, the coating doped with titanium and silicon shows a weight loss of 32 and 37 g/m^2, respectively.

INTRODUCTION

Methods for obtaining protective coatings on metal products differ in coating technology, and the main goal of creation is good adhesion to the material, as well as obtaining a continuous, non-porous and protective coating in a given environment.

Currently, the main methods of applying a protective coating are galvanic discharges during electrolysis, thermal spraying or metallization, thermal diffusion saturation in powder, immersion in molten metal, and plaster. Adhesive and diffusion metal coatings differ in the type of protective composition of the metal layer.

Surface saturation with aluminum, chromium, zinc and other elements refers to diffusion saturation with metals. The product, the surface of which is enriched with these elements, acquires valuable properties, including high heat resistance, corrosion resistance, increased wear resistance and hardness [1–5].

Depending on the method of transferring a diffusion element to a saturated surface, the following main methods of diffusion metallization are distinguished: immersion in molten metal, if the diffusion element has a low melting point; saturation from salt melts containing a diffusing element (with and without electrolysis); saturation from the sublimated phase due to the evaporation of the diffusing element; saturation from the gas phase (contact and non-contact method) consisting of halogen compounds of the diffusing element [6, 7].

Among the methods of surface hardening, chromo-alcohol coatings obtained by various methods of chemical and thermal treatment are widely used.

In this regard, it is important for Ukraine to develop new methods of chemical-thermal treatment, which allow 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 (SHS) [8, 9].

Chromoalitizing – simultaneous or sequential saturation of metals and alloys with chromium and aluminum – is mainly used to increase the wear, heat and corrosion resistance of parts. The main methods of chromoalization include: solid, from the vapor phase, gas and liquid. In turn, saturation from the vapor phase is divided into contact and non-contact, gas – simultaneous and sequential, solid – simultaneous from the slip [10, 11].

The solid method includes saturation in powder media. This method consists in the fact that the part on which the coating is created is placed in a container and covered with a powdery mixture. The mixture usually contains: metal or alloy powder, which is the basis of the coating, an activator, which is most often used as halide salts, and a neutral substance, the powder of which is introduced into the mixture to prevent sintering of the metal component. The peculiarity of the method is that the mixture includes an activator, and as a result of its interaction with the metal, a gaseous compound is formed.

Alloying of chrome protective coatings with titanium, silicon and boron makes it possible to dramatically increase operational characteristics and, along with high corrosion and heat resistance, to obtain more universal coatings with high indicators of surface hardness, scale resistance and corrosion resistance due to the formation of additional oxides of silicon and titanium.

MATERIAL AND EXPERIMENTAL PROCEDURES

The purpose of the work was an increase in the corrosion resistance of brass LC40Mc3J under SHS conditions. Chemical-thermal treatment was carried out in an open type reactor (P = 105 Pa) in the operating temperature range of 900…1100 °C.

The duration of isothermal exposure varied from 30 to 60 min. The surface preparation of the samples consisted of successive grinding, polishing, and degreasing in acetone. The initiation of the process of thermal self-ignition was carried out by preheating the resistance in the furnace to the temperature of the beginning of the exothermic reaction (t*) [12].

To analyze the phase composition of the coatings, a DRON-3M X-ray diffractometer was used. The study of the elemental composition of the coatings was carried out by X-ray microanalysis using a JEOL "Superprob-733" microprobe.

Corrosion resistance tests are carried out on cylindrical specimens with a diameter of 10 mm and a height of 20 mm. Samples of brass LC40Mc3J are examined in 30% aqueous solutions of hydrochloric, sulfuric and nitric acids at a temperature of 20 °C. Before and after testing, the samples were washed with acetone, dried, and dissolved on an analytical balance for 7 days. every 24 h with an accuracy of 1 mg and the mass loss per unit surface of the sample under the influence of corrosion is calculated [13–15].

EXPERIMENTAL RESULTS AND DISCUSSION

The composition of the considered brass LC40Mc3J consists of α+β-phase, where there is more β-phase. Brass has acquired corrosion resistance in normal atmospheres as well as in maritime climates. At the same time, brass containing less than 15% Zn is close to copper in terms of corrosion resistance.

The reaction rate of bronze under atmospheric conditions does not exceed 0.001 mm/year; in fresh water, the rate is insignificant and at a temperature of 20 °C is 0.0025...0.025 mm/year.

Brass corrodes intensively under a significant content of mineral acids (nitric, hydrochloric). Sulfuric acid is significantly slowed down by brass, but in an environment of oxidizing agents {$K_2Cr_2O_7$, $Fe_2(S0_4)_3$}, the reaction rate is two orders of magnitude. Bars are quite stable in alkali solutions (with the exception of ammonia) and in concentrated solutions of neutral salts.

Hydrogen sulfide is highly corrosive to brass. At the same time, brass with a high level of zinc (more than 30%) is more resistant to hydrogen sulfide than brass with a low level of zinc. To study corrosion resistance, corrosive materials are used that simulate the intended application:

– pumps for pumping acids in the production of titanium;

– bearing assemblies at the objects of special equipment of the rocket, space and defense industries;

– for the manufacture of parts of a simple design for responsible purposes and fittings for marine shipbuilding, production at temperatures up to 300 °C of massive parts, propeller rifles and their blades.

Mathematical modeling was performed to obtain optimal compositions of the saturating powder medium. Corrosion resistance tests were performed in concentrated HNO_3 at a temperature of 20 °C. Before and after the test, samples made of LC40Mc3Zh brass were washed with acetone, dried and weighed on an analytical balance. The characteristic of corrosion resistance was the change in the mass of the sample made of LC40Mc3Zh brass, on which the coating was obtained at: tp = 800 ºC and τd = 60 min. The mass loss per unit surface of the sample under the influence of corrosion was determined.

From the analysis of Fig. 1, it can be seen that the content of silicon and chromium components has the greatest effect on corrosion resistance. The optimal content of silicon is 15% by weight, the chromium component is 14…15% by weight. When studying the influence of the thermal self-ignition mode, it was established that the optimal temperature of the process is at the point of 800 °C, the duration of exposure at this temperature is 60 min.

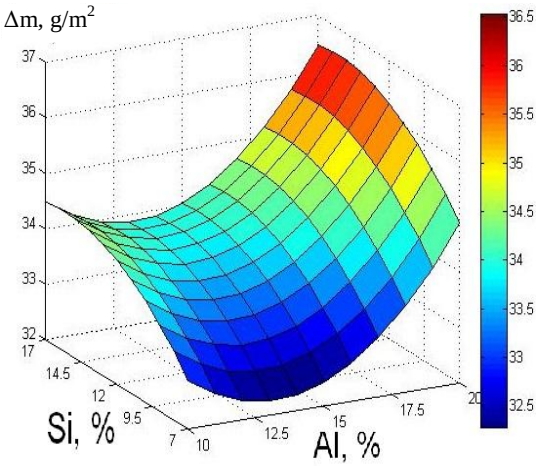


Fig. 1. Optimizing the corrosion resistance of alloyed protective coatings for the Cr-Al-Si system: the effect of aluminum and silicon content on corrosion resistance

The corrosion resistance of LC40Mc3J brass requires a protective coating containing passive film forming elements. In this case, with different ionic passivation, oxide compositions of the film are formed: Cr_2O_3, Al_2O_3, TiO_2, SiO_2, which protect the metal from destruction.

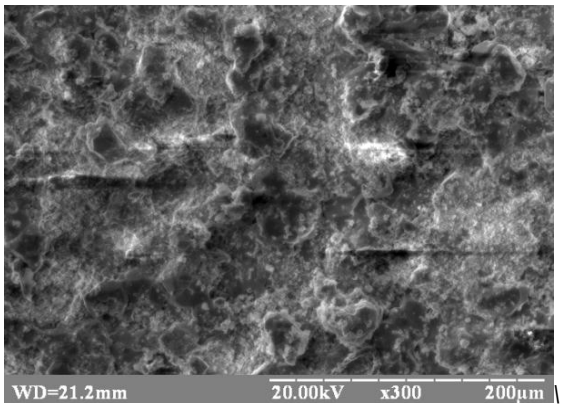
The results obtained can be explained by the formation of doped phases on the surface, which leads to surface passivation in aggressive media. It can also be assumed that the effect of electrochemical retardation of anodic dissolution of metals at a higher concentration of alloying elements compared to coatings obtained in isothermal alloyed hard coatings (Fig. 2), which indicates the absence of microcracking. Alloyed coatings have phases CuSi, CuAl, $CuAl_2$, CuTi, Ti_2Cu_3, CuCr, Cu_3Al, Cu_2Al, Al_3Si, and α-phase doped with Cr, Al, Si, B, Ti.

When tested in a 30% aqueous solution of hydrochloric acid, coatings alloyed with silicon and titanium have the best resistance, having the following weight loss indicators: 13.8 and 16.7 g/m^2. Metallographic analysis shows that the protective coatings on all samples were uniformly corroded to a shallow depth, so it is advisable to use a silicon-doped coating in a 30% hydrochloric acid solution, which, in addition to good corrosion resistance, also has high wear resistance.

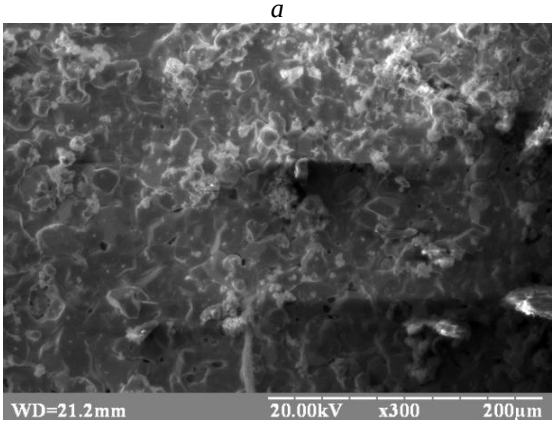
When tested in a 30% aqueous solution of nitric acid, a coating alloyed with titanium and silicon shows good stability, having the following weight loss coefficients, respectively: 32 and 37 g/m^2.

When tested in 30% aqueous sulfuric acid, good resistance to all protective coatings. Thus, when alloyed with boron, the mass loss is 11.7 g/m^2, when alloyed with silicon, it is 10.8 g/m^2, and when titanium alloy is used, it is 12.4 g/m^2. A comparative analysis of the

corrosion resistance of protective coatings obtained under isothermal conditions shows that they have a weight loss 1.7–2.1 times less.



a



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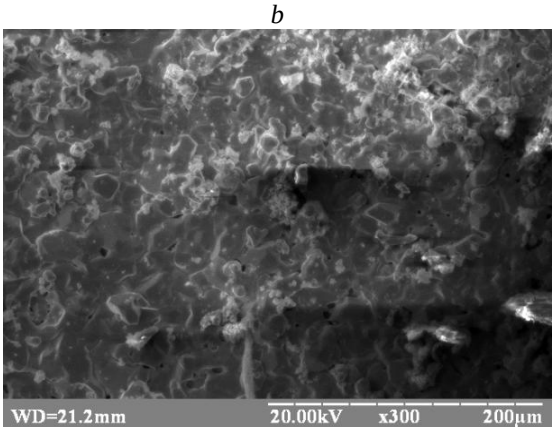

c

Fig. 2. Surface morphology of LC40Mc3J brass specimens after testing in 30% aqueous HNO_3 solution with different doping, processing mode t = 800 °C, τ = 60 min; a – boron alloying; b – silicon alloying; c – titanium alloying

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

The obtained results can be explained by the formation of doped phases on the surface, which leads to the passivation of the surface in aggressive environments. It is also possible to assume the operation of electrochemical inhibition of anodic dissolution of metals at higher concentrations of alloying elements. Thus, the concentration of alloying elements is 4.7…5.2% higher for the coatings obtained under the conditions of SHS, compared to the coatings obtained under isothermal conditions.

It has been established that mechanical stresses (in our case, compressive residuals) affect the corrosion behavior of metals, as a result of additional energy being obtained by the structural material due to the fact that the level of residual stresses in the coatings obtained under the conditions of thermal self-ignition of SHS-charges is higher. As a result, the probability of microcracking of passive oxide membranes, decreases, which leads to an increase in corrosion resistance.

CONCLUSIONS

Anti-corrosion protective coatings doped with silicon and titanium were obtained to improve the operational characteristics of machine parts and mechanisms. It is proven that after the test:

– in a 30% aqueous solution of hydrochloric acid, protective coatings doped with silicon and titanium, with mass loss indicators of 13.8 and 16.7 g/m^2, showed the best resistance;

– in a 30% aqueous solution of nitric acid, protective coatings alloyed with titanium and silicon showed good resistance, with weight loss indicators of 32 and 37 g/m^2, respectively;

– all protective coatings have good stability in a 30% aqueous solution of sulfuric acid. Thus, with boron doping, the mass loss was 11.7 g/m^2, with silicon doping 10.8 g/m^2, and with titanium doping – 12.4 g/m^2.

Doping with silicon and titanium contributes to the formation of passive oxide membranes Al_2O_3, Cr_2O_3, TiO_2, SiO_2. A comparative analysis of the corrosion resistance of the protective coatings obtained in isothermal conditions and SHS showed that they have a mass loss 1.7–2.1 times greater.

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МОДИФІКАЦІЯ ПОВЕРХНІ МІДНИХ СПЛАВІВ АЛЮМІНІЄМ В УМОВАХ САМОРОЗПОВСЮДЖУВАЛЬНОГО ВИСОКОТЕМПЕРАТУРНОГО СИНТЕЗУ

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Досліджено вплив технологічних параметрів СВС-процесу (температури, часу витримки та легування B, Cr, Ti) на корозійну стійкість латуні з поверхневим алітованим шаром, який ефективно протистоїть β-випромінюванню. Дослідження проводили в 30% водяних розчинах HNO_3, HCl, H_2SO_4. Алітовані покриття, леговані кремнієм, які отримані при оптимальних параметрах, мають у 1,7–2,1 рази вищу корозійну стійкість, ніж леговані B та Ti. Алітовані покриття мають фази: CuSi, CuAl, $CuAl_2$, CuTi, Ti_2Cu_3, CuCr, Cu_3Al, Cu_2Al, Al_3Si та α-фазу, леговану Cr, Al, Si, B, Ti. При випробуванні у 30% водному розчині HNO_3 покриття, леговані титаном та кремнієм, мають втрату ваги відповідно 32 та 37 г/м^2.