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Assessment of the nanocrystalline silicon carbide effectiveness in electroplating, ceramics, surface modification

V V Rudneva¹, G V Galevsky¹, S G Galevsky² and G N Chernovsky¹

¹Siberian State Industrial University, 42 Kirova street, Novokuznetsk, 654007, Russia

²St. Petersburg Mining University, V.O., 21 Line, 2, St. Petersburg, 199106, Russia

E-mail: kafcmet@sibsiu.ru

Abstract. Technological advantages and conditions for ensuring a new quality of coatings and products achieved with the use of silicon nanocarbide are established in the processes of composite electrodeposition of coatings, formation of structural ceramics, surface hardening of steels with electric explosive alloying. Nanocarbide of silicon is recommended for use in wear-resistant and corrosion-resistant chromium-carbide electrodepositable coatings operating at elevated temperatures, for hardening tools and rigging, including with especially difficult microrelief of working surfaces. Nanocarbide of silicon in the compositions “silicon carbide – boron – carbon” can be used for the production of ceramic billets by solid-phase sintering in argon with pressure 0.1 MPa and temperature 2273 K. The use of silicon nanocarbide in the technology of surface hardening of tool steels by electric explosive alloying provides a protective layer of high microhardness, wear resistance and heat resistance with depth about 20 μm .

1. Introduction

The production of silicon carbide is the most important in the structure of modern metallurgy. The combination of exceptional thermal and physical, mechanical and physical-chemical properties of silicon carbide makes it a unique material for many branches of technology and predetermines such basic applications as bonded materials, ceramics, composite materials and coatings.

The purpose of this work was to evaluate the effectiveness of silicon nanocarbide in composite electrodeposited coating (EC) technology, structural ceramics, electric explosive alloying (EEA) of steels. In carrying out experimental studies silicon nanocarbide and its compositions were used, obtained on the basis of the innovative technology proposed by the authors [1].

2. Application of silicon nanocarbide in composite electrochemical coating technology

Nanocarbide of silicon was used as a strengthening phase in the processes of electrochemical deposition of coatings from chromium electrolytes. To solve the problems of composite hardening, nanocarbide obtained by the carbidization of silicon micropowder with methane – SiC (1) and plasma modification of micropowder – SiC (2) was used. The characteristics of nanopowders (NP) of silicon carbide SiC (1) and SiC (2) and their physical and chemical properties are described in detail in [1 - 3].

For the electrodeposition of EC chrome – nanocarbide, a chrome solution containing silicon carbide SiC (1) or SiC (2) NP was used of the following composition, kg/m³: chrome anhydride 250, sulfuric acid 3, chromium trivalent 8. To prepare the electrolyte – suspension a small amount of pure electrolyte was added the the weight powder, the components were mixed until the powder was



completely wetted, transferred to the cell, and diluted to the desired concentration. PH adjustment was performed using solutions of NaOH or H₂SO₄.

Analysis of the research results and industrial application of silicon nanocarbide SiC (1) and SiC (2) confirmed the parametric, concentration, structural and technological effects established earlier for nanocarbitides and nanoborides and described in [4 - 6]. Thus, the chromium electrolyte used was characterized, depending on the dispersity of the filler, by the following change in the cathode current density (MP – micropowder of silicon carbide with particle size less than 5 μm):

Without filler (5 kA/m²) → MP SiC (5.5-6.0) → NP SiC (2), SiC (4) (8-10).

The increase in the permissible cathode current density is apparently due to the stabilization of the pH values in the near-cathode layer when introduced into the electrolyte of the second phase. The saturation of the coating with carbide nanoparticles occurs with a smaller mass content in the coating and concentration in the electrolyte (table 1), which is caused by an increase in the number of nanoparticles per unit volume, contributing to the dispersion hardening of the metal matrix. The microhardness of composite coatings with chromium-based nanocomponents is 1.80-1.90 times higher than in chromium, and in 1.10-1.20 higher in comparison with composite coatings with micropowders (table 1), in all cases the microhardness value increases with the content of particles in the composite material. The increase in hardness is due to the high efficiency of nanoparticles as barriers to the propagation of dislocations. The inclusion of nanoparticles in the chromium matrix reduces the intensity of its wear when the content of nanosized powder varies from 0.15 to 0.45 wt% by 1.25-2.5 times. A significant increase in the wear resistance of Cr – NP SiC material is associated with the elimination of causes of local stress concentration – microcracks in the structure of the layer present in significant amounts in chromium layers. Determination of the corrosion resistance of EC Cr – NP SiC in liquid media shows that the ECs exceed the conventional chromium-based coatings by 1.3-1.5 times (corrosion frequency rate 0.3%) and can be classified as resistant.

Table 1. Dependence of the content of the hardening phase (a) and microhardness (H) of EC^a on the concentration of NP and MP in the electrolyte.

Concentration of NP, MP in electrolyte, kg/m ³	a, wt%. / H, GPa		
	Cr – NP SiC (1)	Cr – NP SiC (2)	Cr – MP SiC
1.0	0.20/9.0	0.24/9.1	0.47/8.4
3.0	0.41/9.3	0.43/9.2	0.72/8.6
10.0	0.59/9.7	0.58/9.4	0.89/8.9
20.0	0.82/10.1	0.84/10.1	1.1/9.0

^aConditions of electrodeposition: EC Cr – NP, MP SiC – cathode current density 8.0 kA/m², pH 2.0, T = 323 K.

It can be seen that chromium-carbide coatings have comparable to chromium-diamond wear resistance, microhardness, corrosion resistance, higher service life in operation at temperatures above 473-573 K, achieved at lower concentrations of carbide nanopowder in the electrolyte and a significant reduction in the cost of 1 m³ of electrolyte – suspension.

Table 2. Comparative characteristics of chromium-based coatings with nanopowders of silicon carbide SiC (1) and diamond.

Conditions of electrodeposition and the results achieved		Technological options					
		1	2	3	4	5	6
Electrolyte composition, kg/m ³	Chromic anhydride	250	250	250	250	250	260
	Sulfuric acid	3	3	3	3	3	0.34
	Trivalent chromium	8	8	8	8	8	–
	Potassium silicofluoride	–	–	–	–	–	19

	Barium sulphate	–	–	–	–	–	7
	NP of silicon carbide	4	6	7	8	10	–
	NP of diamond	–	–	–	–	–	20
Mode of deposition	Temperature, K	328	328	328	328	328	331
	Current density, A/dm ²	55	55	55	55	55	55
Results	Wear resistance ^a	0.96	1.0	1.05	1.07	1.08	1.0
	Microhardness, GPa	8.9	9.0	9.1	9.15	9.15	9.0
	Corrosion resistance ^a	0.96	1.05	1.07	1.10	1.10	1.0
	Service life at temperature above 473-573 K ^a	1.1	1.50	1.70	2.00	2.06	1.0
	Cost of 1 m ³ of electrolyte suspension	0.13	0.16	0.18	0.20	0.23	1.0

^aDurability, corrosion resistance, service life at a temperature above 473-573 K, cost of 1 m³ of electrolyte suspension are given in relation to option 6, for which the values of these indicators are taken as 1.0.

According to the research results, the method for obtaining composite electrochemical coatings based on chromium and technological processes of composite hardening with silicon nanocarbide have been developed. EC based on Cr – NP SiC are recommended for the protection of parts and equipment that are subject to wear (for example, threadlike sensor of torsion machines, shock absorber rods, etc.), simultaneous wear and corrosion (for example, molds for molding products from thermoplastics, parts of oil and gas field equipment, etc.). But economically and technologically it is most expedient to use them instead of chrome-diamond ECs for surface hardening of tools, rigging, parts of machines and mechanisms operating at elevated temperatures (above 473-573 K): press tools for powder metallurgy, tool production details - punches, stamps, molds, punch holders, etc., parts of the piston group of internal combustion engines, etc.

3. Application of silicon nanocarbide in the technology of structural ceramics

For the technology of structural ceramics, silicon nanocarbide was used obtained by the carbidization of silicon micropowder with methane-SiC (1) and modification of microcarbon powder in the plasma nitrogen flow – SiC (2) followed by refining.

Silicon nanocarbide according to the main characteristics (level of dispersion, phase and chemical compositions) is not inferior to silicon carbide powders of constructional designation produced by foreign firms. The technological advantage of the material is the possibility of its provision the form of a composition containing additives (reactive boron and carbon) that activate the sintering process.

In order to substitute the import of a non-grinding powder of silicon carbide of furnace synthesis by company “Hermann Starck Co.” grades A-10 and B-10, the testing of silicon nanocarbide was carried out in the solid-phase sintering processes of blanks for the manufacturing ceramic sealing rings series 156.017 and 156.073 (outer diameter from 16 to 30 mm, height from 18 to 30 mm) for pumps and submersible motors that pump oil, oil products, liquefied hydrocarbon gases. The technological advantages of silicon nanocarbide are confirmed and the following results are obtained. The use of silicon nanocarbide makes it possible to exclude the introduction of organic compounds into it during preparation of the charge and their carbonization to obtain uniformly distributed reactive carbon and to restore the silica film on the carbide nanoparticles, stirring on rolls, which simplifies and reduces the cost of the technology and allows it to be realized in the following industrially acceptable variant: heat treatment of the powder in vacuum at 1073 K, the introduction of a plasticizer, mixing and pressing at a pressure of 50 MPa, firing for 2 hours in argon at a pressure of 0.1 MPa at a temperature of 2273 K. Compliance technology provides a relative density after molding 0.62-0.63, 0.95-0.96 after sintering and stable shrinkage 26-29%.

4. Application of silicon nanocarbide in the technology of surface hardening of steels by EEA

In the technology of surface hardening of steels by EEA, silicon nanocarbide SiC (1) containing 99.21 wt% β -SiC with a specific surface area of 38000 m²/kg was tested for the first time as a powder additive. The formation of composite surface layers on samples of tool steel Kh12 during electric explosion of aluminum foil with introduction of silicon nanocarbide into the explosion zone was investigated using the technology described in [8].

The choice of this steel is due to the fact that it is widely used for the manufacture of tools designed for the processing of materials by pressure (dies, punches, etc.), thus, the increased resistance against abrasion is important for it. This circumstance made the researchers to focus on silicon nanocarbide. The phase composition of the surface layers of steel after processing was determined, as well as their properties – microhardness, wear and heat resistance.

As an exploding conductor, an aluminum foil with the mass weighing 30 mg was used, onto which a sample of silicon nanocarbide with a mass of 7.5 mg was placed. The steel samples with dimensions 25 x 20 x 5 mm were subjected to treatment. The time of surface exposure was 100 μ s, the effective value of the absorbed power density was 6.0 GW/m², the dynamic pressure of the jet on the surface reached 14.2 MPa. In this mode of action the depth of the alloying zone was about 20 μ m.

EEA in a high-intensity regime of plasma impact on the surface led, along with fusion, to saturation of the steel surface layers with the products of aluminum foil explosion and silicon carbide nanoparticles followed by self-heating and formation of austenitic structure. The microhardness of the samples surface without treatment proved to be equal to 2513 \pm 205 MPa, and after treatment it increased by 2.8 times in average. The loss of mass of the steel samples in the state of delivery during the wear tests was 27.4 \pm 7.3 mg, and after electric explosion treatment – 3.3 \pm 2.5 mg, i.e. wear resistance increased by 8 times. Heat resistance tests showed that the values of the mass corrosion index of samples in the initial state were 2.7; 5.2 and 10.6 g/(m²·h) at temperatures 800, 850 and 900 °C, respectively. After the protective treatment, the values of 0.3; 1.5 and 5.3 g / (m²·h) were obtained. The increase in the heat resistance at the indicated test temperatures was by 9; 3.5 and 2 times, which on average is 2 times greater than the corresponding heat resistance of this steel after a two-component EEA, for example, boron and gadolinium.

Thus, the alloying has a high microhardness and resistance against abrasive wear and high-temperature oxidation in the air.

5. Conclusion

The high efficiency of silicon nanocarbide application in the technology of composite chrome plating, structural ceramics, and surface modification of steels by electric explosive alloying was confirmed. Chrome-carbide coatings have comparable to chromium-diamond wear resistance, microhardness, corrosion resistance, higher service life. Sintered silicon carbide ceramic billets are characterized by high density and stable shrinkage. The alloying zone containing silicon nanocarbide possesses high microhardness, resistance against abrasive wear, thermal and oxidative stability.

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