

ELECTROCHEMICAL SURFACE PLATING BASED ON TUNGSTEN CARBIDE AND ZIRCONIUM DIBORIDE

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The present study is dealing with electrodeposition of coatings of W_2C and ZrB_2 from electrolyte containing NaCl, KCl, NaF, K_2ZrF_6 , KBF_4 , Na_2WO_4 and Na_2CO_3 . The effect of electrolysis parameters on the coating composition and properties and the physicochemical properties of the coatings were studied. It was also tested the corrosion resistance of steel 3 type samples plated with W_2C and ZrB_2 .

INTRODUCTION

Deposition of coatings based on refractory compounds of metals belonging to Subgroup IVb-VIb with carbon, boron, and silicon is often the most effective and sometimes the single possible way of solving complex technological problems.¹⁻³ These coatings are characterized by yet another important feature, viz., they are economically profitable because in some cases their use allows simplifying the technology and replacing expensive and rare metals by more abundant metals without any sacrifice in the operation of parts, structures, and aggregates. The use of wear-resistant and heat-proof coating makes it possible to increase the service life and enhance the reliability of engines and tools.

The prospects of the use of deposits based on carbides and oxides of Group IVb-VIb metals in the catalysis as intermediates or active compounds and also catalytic layers as such were discussed.⁴

High-temperature electrochemical synthesis (HES) from ionic melts^{2,3} is one of the promising methods for the deposition of coatings based on refractory compounds. Earlier, we managed to deposit molybdenum carbide coatings by the

electrolysis of tungstate-molybdate-carbonate oxide melts⁵ and studied their physicochemical properties as layers on steels.⁶ Tungsten carbide W_2C and zirconium diboride ZrB_2 , surpass molybdenum carbide⁷ Mo_2C in microhardness compared values are 30 and 31.5 GPa and melting temperatures values of 3068 and 3313 K respectively, which allows to obtain enhanced physical, mechanical, and service characteristics for parts plated with these substances.

We developed methods for electrochemical deposition of W_2C and ZrB_2 coatings from ionic melts.^{8,9} Taking into account the peculiarities of the electrodeposition of tungsten, zirconium, carbon, and boron from melts, thermodynamic data on the decomposition potentials of the corresponding compounds, and technological characteristics of deposition of tungsten carbide coatings, we have chosen a halide-oxide melt $NaCl-LiF-Na_2WO_4-Na_2CO_3$. A halide melt $NaCl-KCl-NaF-K_2ZrF_6-KBF_4$ was selected for deposition of zirconium diboride coatings. The mechanism of high temperature electrochemical synthesis in these melts was previously studied by us in detail in.⁸⁻¹⁰

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RESULTS AND DISCUSSION

The Effect of Electrolysis Parameters on the Coating Composition and Properties

The potential ranges of the deposition of tungsten and tungsten carbide from a NaCl-LiCl (3:1 mass ratio) melt were discussed in another

paper.⁸ The reduction of tungstate ions to tungsten proceeds at electrode potentials by 100-150 mV more negative than the reduction of carbonate ions. At the concentrations corresponding to the composition of the melt used in the synthesis, the electroreduction of tungstate and carbonate ions is accomplished simultaneously in a sufficiently narrow potential range (Fig. 1).

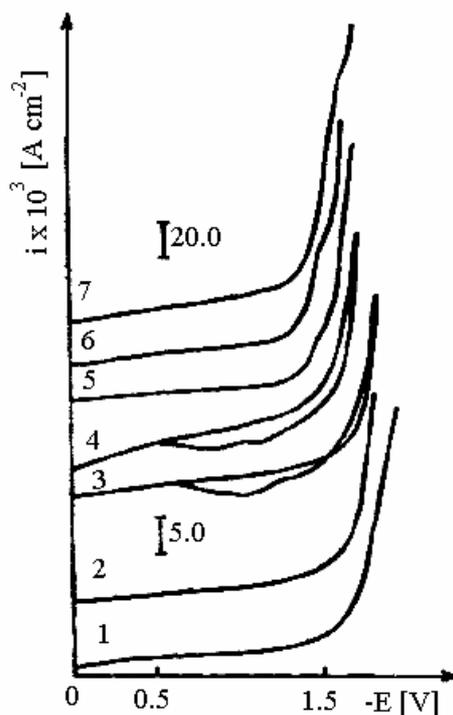


Fig. 1 – Voltamograms of (1) NaCl-KCl melt (3 : 1 wt %): of this supporting electrolyte (1) at the sequential addition of (2-4) Na_2WO_4 and (5-7) Na_2CO_3 , mol/cm³: (2) 1.1×10^{-4} , (3) 1.6×10^{-4} , (4) 2.75×10^{-4} , (5) 0.64×10^{-4} , (6) 1.28×10^{-4} , (7) 3.22×10^{-4} ; T = 1123 K, Pt cathode, polarization rate 0.1 V/s.

Tungsten and carbon can form two carbides, namely, WC and W_2C . It is impossible to crystallize WC as a continuous deposit, because this compound is formed at a certain excess of carbon, which is known to passivate the electrodeposited layer.^{11, 12}

Therefore the crystallization of tungsten carbide as a continuous deposit requires a finer control during the electrosynthesis process and should be carried out under conditions of W_2C formation. The experiments performed at 1173 K have shown that tungsten carbide coatings can be deposited from a melt containing 5 wt % Na_2WO_4 . If the Na_2CO_3 content does not exceed 0.2 wt %, a continuous deposit of W- W_2C alloys (the composition of which also depends on the carbonate concentration) is deposited on the

cathode. Continuous W_2C deposits appear at a concentration of 0.2-0.5 wt %, whereas continuous W_2C -WC deposits appear at 0.5-1.0 wt %; poorly adhered deposits W_2C -WC are formed at higher concentrations.

To study the effect of other electrolysis parameters on the properties and structure of W_2C coatings, we have selected as the optimal supporting electrolyte NaCl-LiCl, with: 0.5 wt %, Na_2WO_4 and 0.4 wt % Na_2CO_3 . Uniform deposits were obtained at 1073-1173 K. At lower temperatures, tungsten oxides are deposited together with metal and carbide. Well adhered, uniform, and nonporous coatings were obtained at a cathodic current density of 2-15 A/dm² and a deposition rate from 2 to 20 $\mu\text{m}/\text{h}$ (Fig. 2).

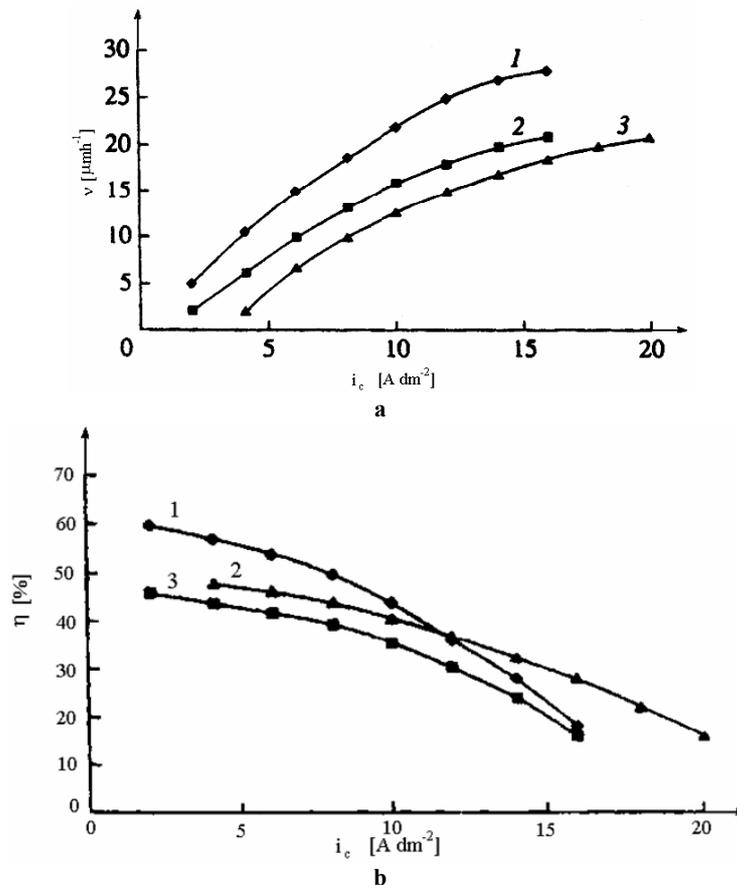


Fig. 2 – Dependence of (2a) the deposition rate of coatings and (2b) current efficiency using steel-3 type substrates on the current density. The coatings are: (1) Mo₂C [5], (2) W₂C, (3) ZrB₂.

The current efficiency for W₂C deposition approached 40-50%, and the deposit thickness reached 50 μm . The low current efficiency of coatings is associated with the growth disturbance of the deposit as a result of its passivation by lithium oxide formed in the electrode reaction.

Further deposition largely produces a carbide powder in addition to the coating, and the thickness of the latter does not exceed 50 μm . The grain size of coatings could be reduced when reversal pulse electrolysis was used (Fig. 3).

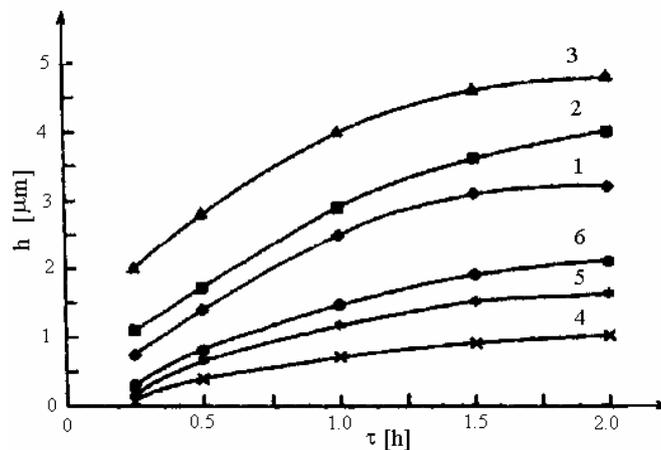


Fig. 3 – Dependence of the roughness amplitude of the coatings on steel-3 type substrates on the electrolysis time: (1-3) cathodic current $i_c = 6 \text{ A}/\text{dm}^2$, (4-6) reversal mode of deposition. The coatings are: (1, 4) Mo₂C [5], (2, 5) W₂C, (3, 6) ZrB₂.

The cathodic to anodic pulse duration ratio τ_c/τ_a was changed within 30-60, the anodic pulse time was 0.5-1.5 s at a current density of 15-50 A/dm². This allowed us to increase the total carbide coating thickness to 100 μm . The optimal parameters of the reversal mode were $\tau_c=45$ s, $\tau_a=1.5$ s, $i_c=8-10$ A/dm², $i_a=20-30$ A/dm².

The voltammetric studies⁹ have shown that stable discharge of combined complexes of

zirconium and boron can be achieved by maintaining the molar ratio at a certain level $[\text{Zr(IV)} + \text{B(III)}]:[\text{F}^-] > 1:4$ (at a ratio $[\text{Zr(IV)}]:[\text{B(III)}]=1:2$) in the KCl-NaCl melt. Under these conditions, the voltammograms demonstrate a wave of electroreduction of chloride-fluoride heterocenter complexes of zirconium and boron in place of the waves of partial electroreduction of zirconium and boron (Fig. 4).

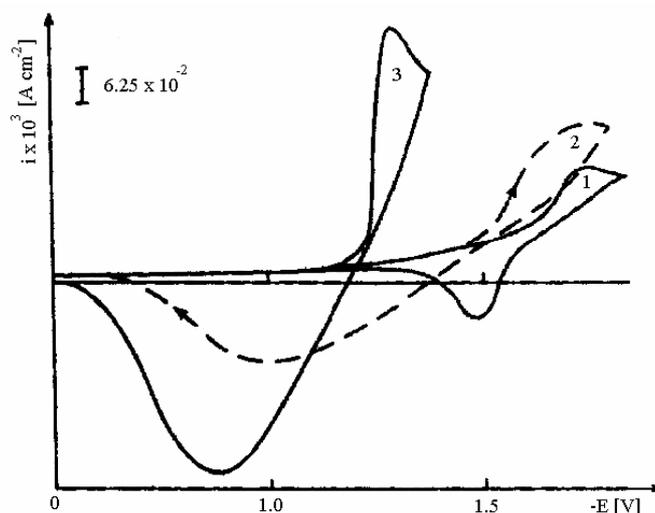


Fig. 4 – Cyclic voltammograms for the following electrode processes:
 (1) electroreduction of zirconium complexes in KCl-NaCl-NaF-K₂ZrF₆ melt ($C_{\text{Zr}} = 5 \times 10^{-5}$ mol/cm³, $[\text{Zr(IV)}]:[\text{F}^-] = 1:15$),
 (2) electroreduction of boron complexes in KCl-NaCl-KBF₄ melt ($C_{\text{B}} = 1 \times 10^{-4}$ mol/cm³, $[\text{B(III)}]:[\text{F}^-] = 1:15$),
 (3) synthesis of zirconium diboride in KCl-NaCl-NaF-K₂ZrF₆-KBF₄ melt ($[\text{Zr(IV)} + \text{B(III)}]:[\text{F}^-] = 1:15$).

In this case, the uniform phase of zirconium diboride is formed in a wide current density range. The absolute magnitude of the overall concentration of Zr(IV) and B(III) in the electrolyte (in a range of 0.6-30 wt %) has no significant effect on the product composition, as well as technological and economic parameters of the process. As was shown experimentally, the temperature threshold of synthesis in the melt studied lies in the interval of 923-943 K. The temperature interval of 1073-1173 K is optimum at a cathodic current density of 5-20 A/dm².

Physicochemical and Operational Properties of Coatings

The aspect of coatings is represented as dark gray fine-grain deposits with a columnar structure (Fig. 5).

According to X-ray spectral microanalysis, the concentration of metal admixtures including Al,

Cr, Ni, and Fe was of an order of magnitude from 2×10^{-2} to 5×10^{-4} wt %. At such a level, the admixtures do not affect strongly the coating structure. The absence of exfoliation of coatings at different test conditions indirectly confirms their strong adhesion. The porosity of coatings was determined by placing filter paper impregnated with a potassium ferricyanide solution on the surfaces of the electroplated coated samples of steel 3 and steel 45. The average number of pores per 100 cm² did not exceed 4-7 for optimum conditions, which was equivalent to the virtual absence of pores.

The microhardness of coatings was 18-19 GPa for molybdenum carbide⁶, 29-31 GPa for tungsten carbide, and 31-32 GPa for zirconium diboride, respectively. The presence of a diffusion zone that ensured the adhesion of coatings to the substrate was confirmed by qualitative and semiquantitative X-ray spectral microanalyses of microsections which were performed with a MS-46 Cameca

electronic probe. The continuity of the coating-substrate transition was confirmed by stereoscopic

images of the cross-sections of the electroplated samples.

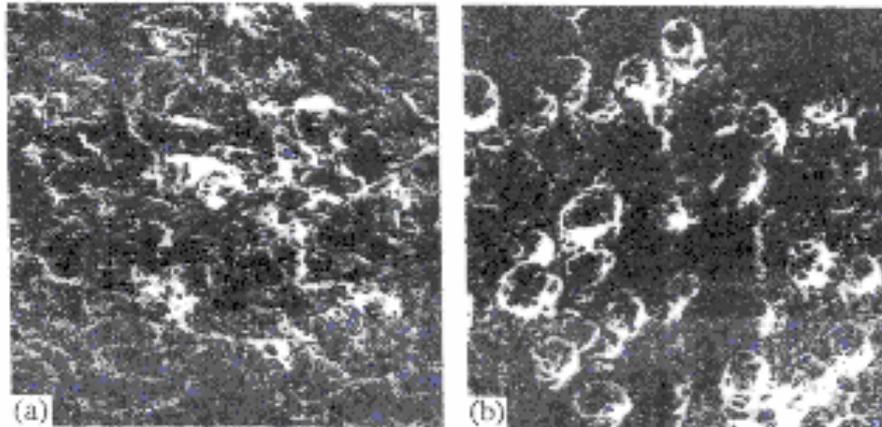


Fig. 5 – Surface microstructure of (a) tungsten carbide and (b) zirconium diboride deposited on steel samples.

The resistance to wear and abrasion was tested on steel-45 samples with different coatings. The second body in these tests was made of quenched steel 45. The wear resistance of samples increased by a factor of 5-7 for molybdenum carbide coatings⁵, 6-9 for tungsten carbide coatings, and 8-11 for zirconium diboride coatings.

The abrasive resistance of steel-45 samples with tungsten carbide coatings increased by a factor of 4 to 6.⁵ For tungsten carbide and zirconium dicarbide coatings, the abrasive resistance increased by factors of 7 to 8 and 8 to 10, respectively (Fig. 6).

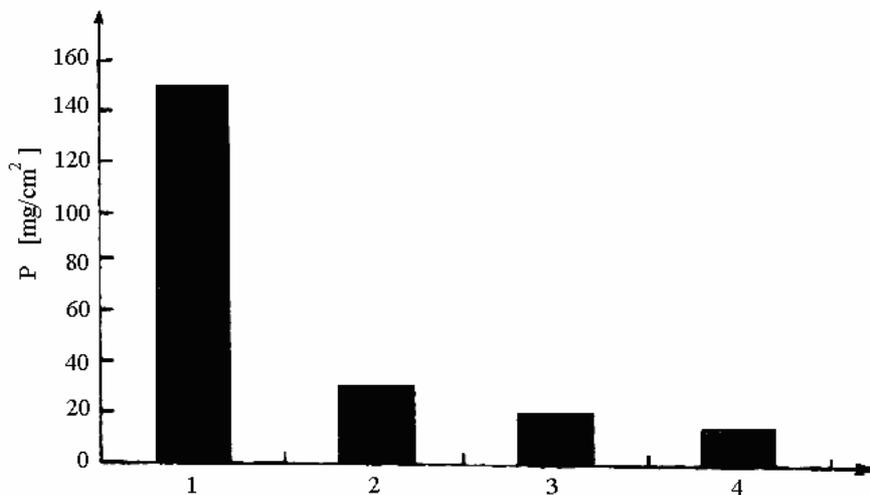


Fig. 6 – Histogram of abrasive stability of samples;
1 - steel 45, as substrate; 2 - Mo₂C electroplate [5], 3 - W₂C electroplate, 4 - ZrB₂ electroplate.

Corrosion resistance of steel 3 samples plated with W₂C and ZrB₂, was tested as follows: in a 3% sodium chloride solution for 96 h, in concentrated solutions of HCl (38 wt %), H₂SO₄ (95.1 wt %), and H₃PO₄ (85.9 wt %) at room temperature for 20 h; in solutions of these acids heated to 353 K; and diluted to 9.5 wt % for 8.5h.

The corrosion rate was determined by the weight loss. Tables 1 and 2 show the results of corrosion tests for the corresponding groups with the corrosion resistance assessed in points. The corrosion resistance of samples increases by a factor of 10-3000 compared with the naked substrate; in some cases, the coated samples were virtually insusceptible to corrosion.

Table 1

Negative weight change (K'_m) and average corrosion rate (K'_v) for the naked steel-3 type substrate and for samples electroplated with tungsten carbide (K''_m, K''_v), in various aggressive media

Nr.	Corrosion medium	K'_m	K'_v	K''_m	K''_v	K''_m / K''_v	Stability in the corrosion classification, points
		g [m ² h]		[mm/h]			
1.	3% NaCl solution	0.58-0.66	0.047-0.056	0.65-0.75	0.045-0.054	12-16	Stable, 4
2.	HCl solution (mf = 9.5), T=343–353 K	599-689	0.78-1.15	571-657	0.74-1.09	520-882	Reduced stability, class 4
3.	H ₂ SO ₄ solution (mf = 9.5), T=343–353 K	265-282	0.25-0.27	297-317	0.24-0.25	1018-1128	Stable, class 5
4.	H ₃ PO ₄ solution, T=343–353 K	530-571	0.25-0.27	542-594	0.24-0.26	1960-2290	Stable, class 5
5.	Concentrated HCl (38wt%)	332-370	1.04-2.29	373-415	0.99-2.18	143-360	Low stability, class 8
6.	Concentrated H ₂ SO ₄ (95.1wt%)	5.26-6.04	0.02-0.03	5.91-6.78	0.02-0.03	146-232	Stable, class 5
7.	Concentrated H ₃ PO ₄ (85.0wt%)	13-15	0.10	15-17	0.09-0.15	85-150	Stable, class 5

* mf=molar fraction for the mixtures of acid with H₂O =mol (acid/H₂O)

Table 2

Negative weight change (K'_m) and average corrosion rate (K'_v) of naked steel-3 type substrate and for samples electroplated with zirconium diboride (K''_m, K''_v), in various aggressive media

Nr.	Corrosion medium	K'_m	K'_v	K''_m	K''_v	K''_m / K''_v	Stability in the corrosion classification, points
		g [m ² h]		[mm/h]			
1.	3% NaCl solution	0.58-0.66	0.031-0.043	0.65-0.75	0.041-0.048	13-21	Stable, 4
2.	HCl solution (mf = 9.5), T = 343–353 K	599-689	0.063-0.081	571-657	0.061-0.082	7395-10936	Stable, class 4
3.	H ₂ SO ₄ solution (mf = 9.5), T = 343–353 K	265-282	0.19-0.23	297-317	0.21-0.22	1152-1484	Stable, class5
4.	H ₃ PO ₄ solution, T = 343–353 K	530-571	0.15-0.19	542-594	0.19-0.21	2789-3806	Stable, class 5
5.	Concentrated HCl (38wt%)	332-370	0.96-1.56	373-415	0.83-1.56	213-385	Reduced stability, class 7
6.	Concentrated H ₂ SO ₄ (95.1wt%)	5.26-6.04	0.01-0.03	5.91-6.78	0.01-0.02	175-604	Stable, class 5
7.	Concentrated H ₃ PO ₄ (85.9wt%)	13-15	0.06-0.09	15-17	0.08-0.11	144-250	Stable, class5

* mf=molar fraction for the mixtures of acid with H₂O =mol (acid/H₂O)

EXPERIMENTAL

The electrolysis of melts was performed in graphite containers MPG-7 which simultaneously served as the anodes. Melts were prepared from preliminary dried chemicals NaCl, KCl, and NaF of the reagent grade and also K_2ZrF_6 , KBF_4 , Na_2WO_4 , and Na_2CO_3 of the analytical grade. The molten electrolyte was purified by its electrolysis at a cathodic current density of 10-15 A/dm² until it could provide stable deposition of continuous coatings. The cathodes represented by steel plates of 1 x 2 cm with nickel terminals. The deposits were subjected to X-ray diffraction and metallographic analyses. The coating thickness and the deposition rate were assessed by a gravimetric method, as well as by a VTO-25 micrometer and a 2 IGM detector on plane-parallel plates. Microhardness on microsections was determined by a PTM-3 device at a load of 100 G; the unit cell parameters were estimated using a DRON-4 X-rays diffractometer with $CuK\alpha$ radiation; the coating thickness was assessed by a 2 IGM detector and, in certain cases, by metallographic methods. Steady-state and transient current electrochemical experiments were controlled by a PI-50.1 potentiostat. Analysis of microsections was carried out with optical metallographic microscopes MIM-8M and Epiquant. The distribution of elements in the coating and in the substrate was revealed by the X-ray spectral microanalysis on a MS-46 Cameca analyzer.

Determining the porosity of coatings deposited on a steel surface involved the using a solution of potassium ferricyanide (10 g/L $K_3(Fe(CN)_6$ and 20 g/L NaCl). The test time was 5 min. The adhesion of deposits to the substrate was assessed qualitatively. Wear-resistance tests were performed on a CMTs-2 set-up at a specific load of 5 MPa in a medium of transformer oil. Tests for the abrasive stability of the electroplated steel-45 samples were carried out according to the GOST (National Standard) 23208-89 in a medium of electrocorundum of 150- μ m fraction at a load of 45 N. The total corrosion resistance was studied by complete immersion in above presented media. The procedures of tests, their citations in the literature, and physicochemical properties of Mo_2C electroplates (to compare with the coatings obtained in this study) are shown in another paper.⁶

CONCLUSIONS

Tungsten carbide and zirconium diboride electroplates deposited from ionic melts by the

high-temperature electrochemical synthesis can be recommended for the increase in the surface hardness, as well as for improving wear, abrasive, and corrosion resistance of steel materials.

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