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Coatings by Refractory Metal Carbides: Deposition from Molten Salts, Properties, Application

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Abstract—High-temperature electrochemical synthesis and currentless transfer in molten salts were used to obtain coatings constituted by carbides of refractory metals (Mo_2C, Cr_7C_3, NbC, and TaC). It was found that the Mo_2C/Mo composite synthesized from a chloride-carbonate-molybdate melt has the highest catalytic activity. It was shown that the Mo_2C catalytic coating preserves its properties for at least 5000 h of tests. The protective properties of refractory metal carbides of composition Cr_7C_3, NbC, and TaC significantly improve the corrosion resistance of steel articles in concentrated solutions and raise their wear resistance by an order of magnitude.

At present, a tendency is observed in industrially developed countries toward replacement of expensive alloyed steels with inexpensive steels having coatings composed of refractory metals or compounds of these, which will determine the surface properties of the whole construction [1–3].

Carbides of refractory metals (Nb, Ta, Mo, Cr, etc.) have high hardness, wear resistance, and corrosion resistance, which enables their application as protective coatings on articles working in a corrosive medium with abrasive wear [4, 5].

Refractory metal carbides, including those in the form of coatings, are successively used in catalysis. For example, the Mo_2C/Mo composite can be used as a catalyst for the water-gas shift reaction (WGS) [6–8].

There exists a large number of ways to deposit coatings of refractory metal carbides [9]. In each particular case, the choice of the deposition method is to be made with consideration for the future working conditions. Among these methods, mention should be primarily made of the so-called CVD (chemical vapor deposition) techniques. These methods use intricate hardware, are expensive, and have characteristics temperatures higher than 1000°C, with the last circumstance resulting in an active diffusion interaction of coatings with a substrate. These techniques cannot be used to obtain coatings on large-area articles or produce even coatings on intricately shaped articles [10]. The process of joint plastic deformation involves intermittent annealings in a vacuum or inert atmosphere. The explosive cladding is not applicable, either, in the case of intricately shaped or very long articles. The standard methods with reduction of refractory metal oxides with graphite at 1673–2073 K are also rather cost intensive.

At the same time, refractory metal carbides can be produced by high-temperature electrochemical synthesis in molten salts. This method has the following advantages.

– The electrolysis of melts with pulse and reverse currents enables easy control over the structure of deposits; thickness, porosity, roughness, and texture of plated coatings; and grain size.

– The synthesis temperature is comparatively low: 973–1123 K.

– The electrodeposition parameters determined on laboratory setups can be transferred to large-scale installations.

– The coatings are highly pure even with poor-quality starting reagents because metals are refined in the course of electrolysis.

– The maintenance expenditure and the cost of the electrochemical apparatus are low.

Refractory metal carbides can also be synthesized by the method of currentless transfer [11, 12]. The currentless transfer method is an electrochemical technique and the processes occurring in this case obey laws of electrochemical thermodynamics, kinetics, and reactive diffusion in solids. With the currentless transfer method, a more electronegative metal is deposited onto the electropositive substrate, with the metal being deposited interacting with the substrate to give a surface diffusion alloy-coating. The driving force of this process is the alloying energy. This method can be successfully used to synthesize protective coatings well adhering to a substrate [12].

The Mo_2C coating has been produced by high-temperature electrochemical synthesis from a NaF–LiF–Na_2MoO_4–Na_2CO_3 salt melt at a temperature of 1173 K and cathodic current density of 80 mA cm^{-2} on a glassy-carbon cathode [13]. In [14], Mo_2C was synthesized from a Na_2WO_4–Li_2MoO_4–Li_2CO_3 electrolyte. It has been found that electrolytic Mo_2C coatings have a high microhardness and wear resistance. However, there are no data on the catalytic activity of the coatings in [13, 14]. We are not aware of any reports, except our own studies, concerned with the synthesis of thin-film coatings of chromium, niobium, and tantalum carbide produced on steels by the currentless transfer method and with the properties of these coatings.

The present report briefly reviews studies in which refractory metal carbides were produced for various functional purposes by the methods of high-temperature electrochemical synthesis and currentless transfer in molten salts.

EXPERIMENTAL

The procedure used to prepare salts of alkali metal chlorides was described in detail in [8].

Li_2CO_3 and Na_2MoO_4 were dried in a vacuum box at 473 K for 6 h.

Li_2C_2 was synthesized in situ from a melt of the $LiCl$–KCl eutectic via discharge of Li^+ cations on a graphite cathode with cathode current density of 2 A cm^{-2}.

Chromium chloride $CrCl_3$ of chemically pure grade was used without additional purification.

Potassium heptafluorotantalate (K_2TaF_7) and potassium heptafluoroniobate (K_2NbF_7) produced at the pilot shop of the Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Kola Scientific Center, Russian Academy of Sciences, were recrystallized in a hydrofluoric acid solution, washed with ethanol, and dried in a vacuum box at 383–393 K [11, 15, 16]. The electrochemical synthesis of molybdenum carbide coatings on a molybdenum substrate was performed by galvanostatic electrolysis with the following molten salt systems: $NaCl$–KCl–Li_2CO_3, $NaCl$–KCl–Li_2CO_3–Na_2MoO_4, and $LiCl$–KCl-Li_2C_2 at a temperature of 1123 K in the course of 7 h at a cathodic current density of 5 mA cm^{-2}.

Electrochemical studies were carried out with an AUTOLAB PGSTAT 20 potentiostat with a GPES (version 4.4) applied software package. All the experiments were performed in the atmosphere of argon of pure grade, which passed, before being delivered into the electrochemical cell, through a titanium sponge heated to a temperature of 1073 K. The working electrodes with diameter of 2 mm, made of molybdenum, ARMKO iron, and carbon steels, were polished to mirror shine with diamond pastes and degreased in ethanol with the use of an ultrasonic treatment. A glassy carbon crucible served as the auxiliary electrode. Cyclic voltammetric curves were recorded on a molybdenum cathode relative to a platinum reference quasi-electrode [8]. In chronopotentiometric studies, the role of an electrode was played by metallic chromium deposited by galvanostatic electrolysis (current density 0.2 A cm^{-2}, temperature 1023 K, electrolysis duration 10 min) on a molybdenum bar [17].

The cathodic products were identified with a DRON-2 X-ray diffractometer with monochromatic CuK_α radiation at a scanning rate of 0.25 deg min^{-1}. The microstructure of the coatings was examined with an SEM LEO-420 digital scanning electron microscope.

The specific surface area of the Mo_2C/Mo composite was measured by the BET method with a Micromeritics ASAP 2010 V4.00 C surface analyzer.

The corrosion rate was determined gravimetrically with cylindrical samples 30 mm long and 7 mm in diameter, preliminarily thoroughly degreased in ethanol. Corrosion tests were made at a temperature of 293 ± 1 K and exposure duration of 48 h. After the corrosion
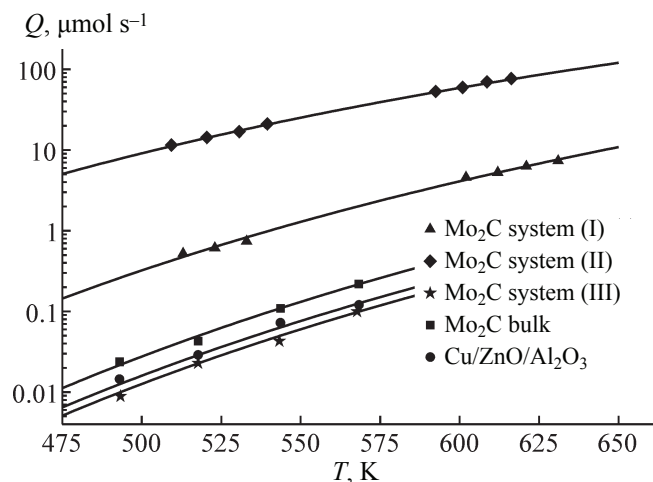
Fig. 1. VCR rate as a function of temperature T on varius catalysts. Reaction conditions: pCO = 300 Pa, pH$_2$O = 760 Pa, pCO$_2$ = 1.2 kPa, pH$_2$ = 40 kPa, He for balance, gas flow rate 50 cm^3 min^{-1} (s.c.) (Q) CO expenditure.

products were mechanically removed, the samples were weighed on an analytical balance with accuracy as good as 1×10^{-5} g.

Wear-resistance tests of coatings on St.3 steel were made with an SMTs-2 machine under a specific load of 5 MPa in transformer oil at a sliding rate of 1.2 m s^{-1} on a route length of 2000 m. A sample of St.3 steel served as a counter body.

RESULTS AND DISCUSSION

Catalytic coatings. The processes in which Mo$_2$C catalytic coatings were synthesized on a molybdenum substrate were studied by cyclic voltammetry.

It was found by using the diagnostic criteria of the method of cyclic voltammetry that molybdenum semicarbide is formed in a chloride-carbonate melt [system (I)] by the following electrochemical reactions [18]:

$$CO_2 + 4e + 2Mo \rightarrow Mo_2C + 2O^{2-}, \quad (1)$$

$$CO_3^{2-} + 4e + 2Mo \rightarrow Mo_2C + 3O^{2-}. \quad (2)$$

The electrochemical reaction (1) is preceded by the chemical reaction

$$CO_3^{2-} \rightleftarrows CO_2 + O^{2-}. \quad (3)$$
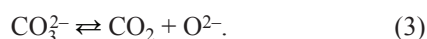
In the NaCl–KCl–Li$_2$CO$_3$–Na$_2$MoO$_4$ melt [system (II)], molybdenum semicarbide is formed in the joint electroreduction of CO_3^{2-} and MoO_4^{2-}, together with the electrochemical processes (1) and (2), by the reaction [19]:

$$2MoO_4^{2-} + CO_3^{2-} + 16e \rightarrow Mo_2C + 11O^{2-}. \quad (4)$$
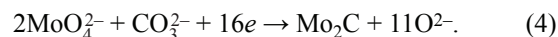
In the LiCl–KCl–Li$_2$C$_2$ chloride-carbide melt [system (III)], the synthesis of Mo$_2$C is possible in the case of an anodic polarization of the molybdenum substrate. The dissociation of lithium carbide in the LiCl–KCl–Li$_2$C$_2$ melt yields electrochemically active C$_2^{2-}$ species, which are oxidized on molybdenum [8]:

$$C_2^{2-} - 2e + 4Mo \rightarrow 2Mo_2C. \quad (5)$$

The X-ray diffraction patterns of Mo$_2$C coatings obtained on a molybdenum substrate for systems (I) and (III) contain lines of metallic molybdenum, these lines being absent for system (III). This indicates that the thickness of coatings produced from melts (I) and (III) markedly differs from that of the Mo$_2$C coating synthesized in system (II).

The thicknesses of Mo$_2$C coatings produced from systems (I) and (III) were about 0.5–2.0 and 0.3–0.5 μm, respectively, because refractory metal carbides form excellent barrier layers and the mutual diffusion coefficients of molybdenum and carbon decrease by several orders of magnitude. The specific surface area of the coatings was 18 m^2 g^{-1} for synthesis in melt (I) and 11 m^2 g^{-1} for that in electrolyte (III). The joint electroreduction of MoO_4^{2-} and CO_3^{2-} ions [system (II)] yielded Mo$_2$C coatings with thickness of about 25–50 μm and specific surface area of 38 m^2 g^{-1} [19].

In all cases, molybdenum semicarbide with a hexagonal crystalline lattice was obtained. Mo$_2$C with a hexagonal lattice is formed in the course of electrochemical synthesis due to the specific conditions of the electrocrystallization process, such as the action of an electric field and a high temperature and the existence of a double layer.

We examined the catalytic activity of the Mo$_2$C/MO composites synthesized in the study by measuring the steady-state rates of WGS reaction [8]. The steady-state rates for the Mo$_2$C/Mo composite synthesized in melts (I) and (II) were, respectively, one and three orders of magnitude higher than that for the bulk Mo$_2$C phase with specific surface area of 61 m^2 g^{-1} [20], obtained by
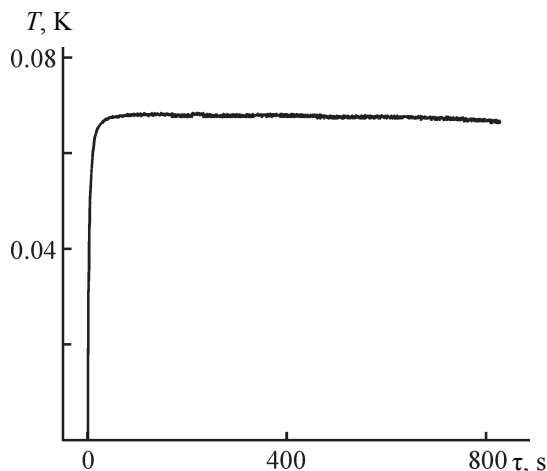
Fig. 2. Chronopotentiogram of the NaCl–KCl–CrCl$_2$ (4.5 wt %) melt. Working electrode, ARMKO iron; reference electrode, chromium; temperature 1023 K. (E) Potential and (τ) time; the same for Fig. 3.
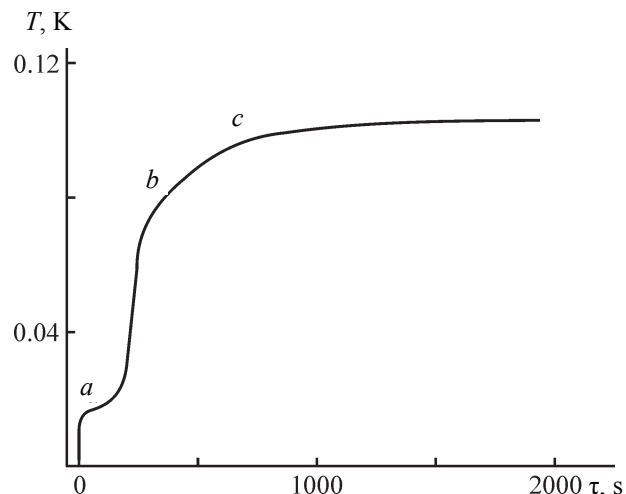

Fig. 3. Chronopotentiogram of the NaCl–KCl–CrCl$_2$ (4.5 wt %) melt. Working electrode, St.3 steel; reference electrode, chromium; temperature 1023 K.

using a temperature-programmed reaction and Cu/ZnO/Al$_2$O$_3$ industrial catalyst (Fig. 1). The steady-state rate of the water-gas shift reaction for the Mo$_2$C/Mo composite produced from the molten system (III) was somewhat lower than that for the industrial Cu/ZnO/Al$_2$O$_3$ catalyst (Fig. 1) because of the insignificant thickness of a coating and its small specific surface area. The high catalytic activity of Mo$_2$C coatings deposited from systems (I) and (II) is accounted for, despite their substantially smaller specific surface area as compared with the bulk Mo$_2$C phase, by the presence in the latter of 5–7 wt % Mo$_2$C with cubic lattice, which leads to a significant decrease in the activity and stability of the catalyst.

No methane was formed in the whole temperature range in which Mo$_2$C/Mo coatings were tested. The catalytic activity remained constant during 5000 h of tests. The coatings also remained stable in cyclic temperature tests, whereas the activity of industrial catalysts decreased.

A highly active and stable Mo$_2$C/Mo catalytic system was used to design and fabricate a microstructured reactor–heat exchanger for the water-gas shift reaction [8, 21].

Protective coatings. Chromium was electrodeposited from an equimolar NaCl–KCl mixture with 2.0–5.0 wt % CrCl$_3$, which is in equilibrium with metallic chromium. In a melt of this kind, the following metal–salt reaction occurs [22]:

$$2Cr^{3+} + Cr \rightleftarrows 3Cr^{2+}, \qquad (6)$$
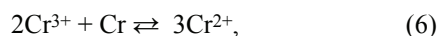
with the equilibrium of this reaction being fully shifted to the right, which is confirmed by the 1.5-fold increase in the chromium concentration in the melt.

The charging curves (cathodic chronopotentiograms) on electrodes made of ARMKO iron and St.3 steel were recorded at a temperature of 1023 K and current density of 5×10^{-3} A cm^{-2} until the potential difference between the cathode and chromium reference electrode became zero. After that the electrolytic cell was disconnected and the switch-off curve (anodic chronopotentiogram) was recorded. Preference was given to measuring the switch-off curves because of their better reproducibility, compared with charging curves.

The switch-off curve obtained on the electrode made of ARMKO iron (Fig. 2) has no potential delay plateaus. This means that chromium and iron form no intermetallic compounds and solid solutions have no two-phase regions. This conclusion agrees with the equilibrium constitution diagram of Fe–Cr [23].

The chronopotentiogram obtained on a St.3 electrode (Fig. 3) shows three potential-delay plateaus (a, b, c), which correspond, according to the equilibrium constitution diagram of chromium–carbon [23], to the formation of, respectively, two-phase regions Cr$_{23}$C$_6$ + Cr$_7$C$_3$, Cr$_7$C$_3$ + Cr$_3$C$_2$, and Cr$_3$C$_2$ + C. A potentiostatic electrolysis at the plateau potentials (Fig. 3) resulted in that cathodic deposits of the following compositions were formed: carbides of composition Cr$_{23}$C$_6$ + Cr$_7$C$_3$ at the
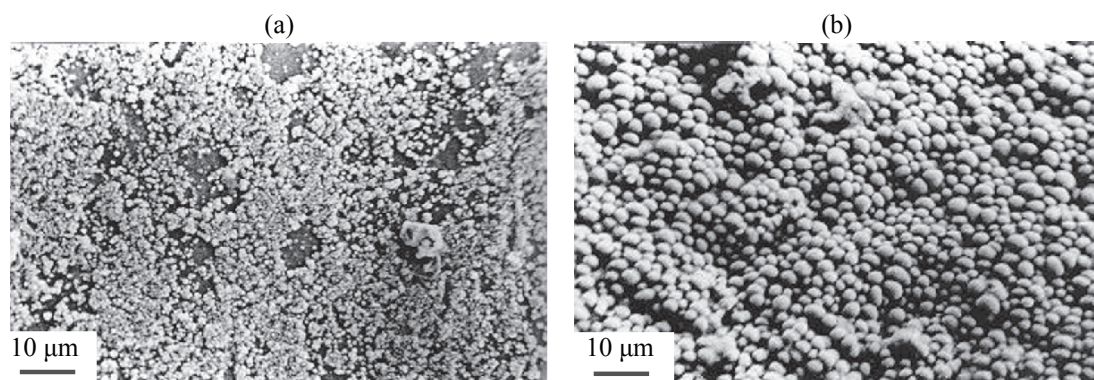
Fig. 4. Morphology of a steel substrate upon (a) 3 h keeping in a NaCl–KCl–K_2NbF_7 (10 wt %)–Nb melt and (b) 6 h keeping in a NaCl–KCl–K_2NbF_7 (30 wt %)–Nb melt. Synthesis temperature 1073 K.

potential corresponding to plateau a, two-phase carbide product $Cr_7C_3 + Cr_3C_2$ at the potential of plateau b, and carbide $Cr_3C_2 + C$ at potential c.

Because the cathodic deposit was two-phase as a result of the electrodeposition of refractory metal carbides, chromium carbides coatings were synthesized by the currentless transfer method. A NaCl–KCl equimolar mixture with addition of 10 wt % $CrCl_3$ and excess amount of metallic chromium served as the melt. Prior

to the beginning of a synthesis, the melt was kept for 2 h. The synthesis was performed at a temperature of 1123 K in the course of 8 h. Because the equilibrium of reaction (6) is nearly fully shifted to the right [22], chromium is present in the melt only as Cr^{2+} cations. The Cr^{2+} cations in the lowest oxidation state diffuse to the steel substrate and are disproportionated on its surface to give chromium carbide [11, 17]:

$$21Cr^{2+} + 3C(\text{steel surface}) \rightarrow Cr_7C_3 + 14Cr^{3+}. \quad (7)$$
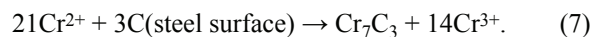
The driving force of reaction (7) is the carbide-formation energy $\Delta G_{Cr_7C_3}$, Cr^{3+} cations formed by reaction (7) diffuse toward metallic chromium and, entering into an interaction with it by reaction (6), formed reduced cations Cr^{2+}. Thus, the process in which chromium is transferred to the surface of carbon steels forms a cycle. The carbides NbC and TaC were also synthesized by currentless transfer in NaCl–KCl–K_2MeF_7 (30 wt %) molten salts brought in contact with their metals (M = Nb, Ta). The mechanism by which niobium and tantalum carbides are formed is similar to that considered above, and can be described, e.g., for niobium carbide by the following reaction [24, 25]:
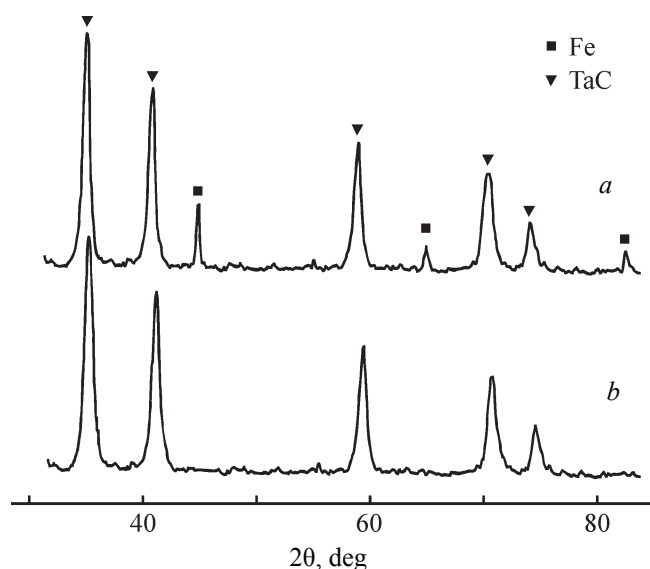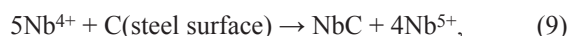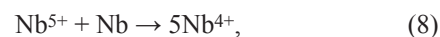
$$Nb^{5+} + Nb \rightarrow 5Nb^{4+}, \quad (8)$$

$$5Nb^{4+} + C(\text{steel surface}) \rightarrow NbC + 4Nb^{5+}, \quad (9)$$

$$Nb + C \rightarrow NbC. \quad (10)$$

Fig. 5. Diffraction pattern of tantalum carbide coatings produced on a St.3 substrate by currentless transfer in a NaCl–KCl–K_2TaF_7 (30 wt %)–Ta melt at 1123 K in the course of (a) 6 and (b) 12 h. (2θ) Bragg angle.

Micrographs of NbC coatings formed at various synthesis durations on St.3 steel are shown in Fig. 4. The
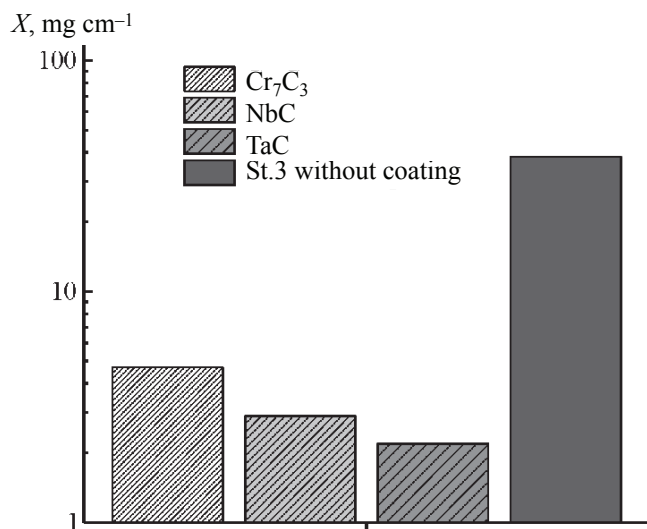
X, mg cm^{-1}

Fig. 6. Wear resistance X of a composite constituted by steel and refractory metal carbide coating.

coatings were constituted by close-packed spheroidal crystals. At a keeping in the melt for 3 h (Fig. 4a), the NbC coating on the steel substrate was not continuous. The coating became continuous as the exposure duration was raised to 6 h (Fig. 4b). Figure 5 shows diffraction patterns of tantalum carbide on a steel substrate. A tantalum carbide coating is formed on steel after a 6-h experiment,

but its diffraction pattern shows peaks associated with the steel substrate. These peaks are not recorded after a 12-h experiment, which indicates that a thicker tantalum carbide coating is formed (Fig. 5b).

The thickness of Cr_7C_3, NbC, and TaC coatings, found from their cross-sections was 1–2 μm for St.3 steel and 4–6 μm for U9 steel, which is due to the larger content of carbon in the steel of U9 brand.

For the above coatings of refractory metal carbides, we determined the microhardness, wear resistance, and corrosion resistance against concentrated mineral acids. The microhardness of the coatings, found from their cross-sections was 21, 29, and 31 GPa for Cr_7C_3, NbC, and TaC, respectively. The results obtained in a study of the wear resistance are presented in Fig. 6. It can be seen that the wear resistance of steel substrates increased by an order of magnitude upon deposition of coatings of refractory metal carbides and a correlation is observed between the wear resistance and microhardness of the coatings.

The coatings were subjected to corrosion resistance tests against concentrated mineral acids. To determine the corrosion rate, the samples with a known surface are were submerged in concentrated sulfuric, orthophosphoric and hydrochloric acids. The results of these corrosion tests are
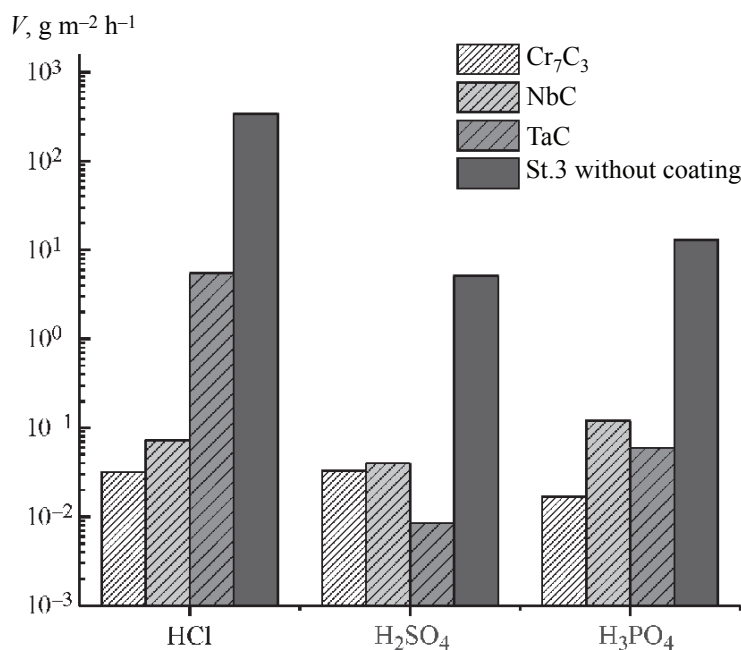
V, g m^{-2} h^{-1}

Fig. 7. Corrosion resistance of a composite constituted by steel and refractory metal carbide coating in concentrated mineral acids. (V) Corrosion rate.

presented in Fig. 7. Deposition of coatings composed of refractory metal carbides reduces their corrosion rate in concentrated mineral acids by 3–4 orders of magnitude. The corrosion resistance of refractory metal carbides against concentrated mineral acids varied in the following order: $Cr_7C_3 > NbC > TaC$ in HCl; $TaC > Cr_7C_3 > NbC$ in H_2SO_4; and $Cr_7C_3 > TaC > NbC$ in H_3PO_4. It should be noted that the corrosion rate depends not only on the composition, but also on the quality (porosity) of the coatings.

Tests made at New Technologies OOO demonstrated that the deposition of NbC and TaC coatings on steel members of pumps for transfer of corrosive fluids made it possible to make their service life twice longer. The synthesis of Cr_7C_3 and TaC on rubber-cutting knives made their service life 2.0 and 2.5 times longer, respectively (Ekotek OOO).

CONCLUSIONS

The catalytic activity of molybdenum carbide coatings was studied, and it was found that the highest activity is observed for Mo_2C synthesized with the NaCl–KCl–Li_2CO_3–Na_2MoO_4 system. It was shown that the Mo_2C catalytic coating remains active during at least 5000 h of tests.

The chronopotentiometric method was used to examine the process of chromium electrodeposition from a NaCl–KCl–$CrCl_2$ melt onto carbon steel substrates and determine the potentiostatic electrolysis parameters at which chromium carbides of different compositions are formed on the surface of steel.

The currentless transfer method was used to synthesize coatings of refractory metal carbides of composition Ct_7C_3, NbC, and TaC on steels. It was found that these coatings have a high microhardness, substantially improve the corrosion resistance of steel articles in concentrated acids, and raise by an order of magnitude their wear resistance.

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