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Electrochemical Methods for Obtaining Thin Films of the Refractory Metal Carbides in Molten Salts

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Synthesis of Cr_7C_3, NbC and TaC coatings on the surface of carbon steels and carbon fibers was carried out using currentless transfer. The corrosion resistance of the Cr_7C_3, NbC and TaC carbides coatings was studied in concentrated HCl, H_2SO_4 and H_3PO_4 acids. The wear resistance was evaluated by the sample mass loss. Due to the high wear and corrosion resistance Cr_7C_3, NbC and TaC coatings on carbon steels can be applied in aggressive medium with the abrasive wear. Coatings of NbC or TaC on carbon fibers make better the fiber's mechanical resistance. Mo_2C coatings were obtained on Mo substrate at the temperature 1123 K by electrochemical synthesis in NaCl-KCl-Li_2CO_3-Na_2MoO_4. The Mo_2C/Mo composition was tested as a catalyst for the water-gas shift reaction. The steady-state reaction rates for the Mo_2C/Mo composition were higher than those for the bulk Mo_2C and commercial Cu/ZnO/Al_2O_3 catalysts over in the temperature range explored.

Keywords: Molten salts; Coatings; Refractory metals carbides; Electrochemical synthesis; Currentless transfer; Corrosion and Wear Resistance; Catalytic activity

1. INTRODUCTION

At the present time, in industrially advanced countries, there is a trend to substitute inexpensive steels with coatings for expensive alloyed steels. These coatings based on refractory metals (Nb, Ta, Cr, Mo) or their compounds determine the surface properties of the total construction [1, 2].

Coatings based on refractory metal (Nb, Ta, Cr, Mo) carbides have high wear and corrosion resistance in various corrosive media. Because of the above-listed properties, the formation of protective coatings based on refractory metal carbides is a promising area in the field of material protection. Coatings of the refractory metal carbide also have been successfully applied in catalysis. For example, Mo_2C/Mo composition can be used as a catalyst for the water-gas shift reaction [3, 4].

Being important cermet materials, niobium and tantalum carbides are commercially utilized in tool bits for cutting applications, hard electrical contacts and are sometimes added to tungsten carbide alloys [5, 6]. Tantalum carbides are also used improving the vane tips, front sections of aircraft, gas turbine jet [7].

Coatings of the refractory metal carbides can be obtained by different methods: plasma and detonation sputtering and deposition from the gas phase. However, in case of using the detonation method, the coating porosity is 1-3%, in the case of the plasma methods; it is 5-15%. The method of chemical deposition is characterized by temperatures above 1273 K, which results in an active diffusion interaction with the substrate. Methods of physical deposition from vapor are promising, but they are complex in terms of instrumentation and rather expensive. The deposition from vapors is related to difficulties with coating uniform distribution over the article surface.

In [8-12] it was described the various methods of synthesis coating chromium carbide Cr_3C_2, such as chemical deposition from the vapor phase [7], aluminothermic reduction of mixture chromium and graphite [10], magnetron sputtering [12]. It was shown that the deposition of the coating Cr_3C_2 is demonstrated to result in an increase in hardness and wear resistance and in a decrease in the coefficient of friction. [11, 12]

NbC and TaC coatings have been obtained by sintering and laser cladding in [13, 14]. Some tribological properties of niobium and tantalum carbides were reported in these studies.

In monograph [15] various ways of depositing the protecting coatings are assessed on the basis of the following criteria: principal possibility of production and control; achieving adequate quality; technological and cost parameters. It was concluded [15] that one of the promising methods for obtaining coatings is the electrolysis of molten salts allowing to produce uniform coatings on complex configuration articles.

Adherent tantalum carbide coatings have been deposited on nickel substrates from a ternary LiF-NaF-KF eutectic melt containing a few percent each of K_2TaF_7 and K_2CO_3. [16]. The coatings were highly resistant to abrasion and thermally stable up to 873K. Experimental studies relevant to electrodeposition of refractory metal carbides including niobium from fluoride melts were summarized in [17]. The synthesis of TaC on carbon fibers in molten salts was reported in study [18].

Uniform and porousless Mo_2C coatings on nickel or steel substrates were obtained by galvanostatic electrolysis in the LiF-NaF-KF-Na_2CO_3-K_2MoO_4 melt [19]. In studies [20, 21] Mo_2C coatings were produced by high temperature electrochemical synthesis in the NaF-LiF-Na_2MoO_4-Na_2CO_3 and Na_2WO_4-Li_2MoO_4-Li_2CO_3 melts on a glassy carbon substrate. It was determined that these coatings have high microhardness and wear resistance. However, there is no information on the catalytic activity of synthesized coatings in [19-21].

To our best knowledge, no studies, except our investigations, on the synthesis of thin film coatings of chromium, niobium and tantalum carbides on steels obtained by the currentless transfer method.

The aim of this work was obtaining of refractory metals carbide coatings on different substrates using electrochemical synthesis, currentless transfer method and determination their corrosion resistance, microhardness, wear resistance and catalytic activity.

2. EXPERIMENTAL

The technique of the salt preparation consists of the following. Sodium and potassium chlorides of analytical grade were subjected to recrystallization, calcined in a muffle furnace, mixed in an equimolar ratio, and placed into a quartz retort. The retort was evacuated to a vacuum of 0.66 Pa firstly at room temperature and next heated at gradually rising steps to 473, 673, 873K. After that, it was filled by argon and the electrolyte was melted.

The supporting molten salt was placed into a glassy carbon crucible of grade SU-2000 and charged into retort of an electrochemical cell, where the above-mentioned operations evacuation and melting were repeated.

K_2TaF_7, K_2NbF_7 and $CrCl_3$ were used without additional treatment. Li_2CO_3 and Na_2MoO_4 of pure grade dried in vacuum oven at473 K for 6 hours.

Electrochemical investigations were carried out by an AUTOLAB PGSTAT20 potentiostat with a GPES application software package (version 4.4). All experiments were carried out in argon of pure grade, which before the intake into the electrochemical cell was passed through a titanium sponge heated to a temperature of 1073K.

To study the chromium electrodeposition, chronopotentiometry was used. We used an equimolar mixture of NaCl-KCl with the content of 2.0-5.0 wt. % $CrCl_3$ being in equilibrium with metallic chromium. In such melt occurs a metal-salt reaction [22]:

$$2\mathrm{Cr(III)} + \mathrm{Cr} \rightarrow 3\mathrm{Cr(II)} \quad (1)$$

The reaction equilibrium is completely shifted to the right side, which is verified by increasing chromium concentration in the melt by a factor of 1.5. Working electrodes of ARMCO iron and steel grade St3 in 2 mm diameter were mirror-polished by diamond paste and degreased in ethyl alcohol with the use of ultrasound. A glassy carbon crucible was used as an auxiliary electrode. As a reference electrode, we used metallic chromium deposited by galvanostatic electrolysis (current density of 0.2 A cm^{-2}, temperature of 1023 K, electrolysis duration of 10 min) on a molybdenum bar.

Charging curves (cathodic chronopotentiograms) were recorded at a temperature of 1023 K and a current density of 5×10^{-3} A cm^{-2} until the potential difference of the cathode and the reference electrode of chromium became zero. After that, the electrolytic cell was switched off and the discharge curve (open-circuit chronopotentiogram) was recorded. The preference was given to recording the open-circuit chronopotentiograms because they had better reproducibility than cathodic chronopotentiograms.

Electrolysis products were identified by a DRON-2 diffractometer (Russia) and investigated by a SEMLEO – 420 scanning electron microscope (Germany).

The corrosion rate was determined by a gravimetric method. We used cylindrical samples 30 mm in length and 7 mm in diameter, which were degreased thoroughly in ethyl alcohol. Corrosion tests were performed in concentrated hydrochloric (38%), sulphuric (98%) and phosphoric (85.9%) acids at a temperature of 293±1 K, and the exposure was 48 h. Samples after the removal of corrosion products were weighed on an analytical balance with an accuracy of up to 1×10^{-5} g.

Wear resistance tests of the coatings of grade St3 steel were carried out by means of a SMTs-2 machine (Russia) at a specific load of 5 mPa in transformer oil, at a slip velocity of 1.2 m s^{-1}, and on a path segment of 2000 m. The sample of grade St3 hardened steel was used as a rider.

The electrochemical synthesis of molybdenum carbide coatings on a molybdenum substrate was performed by electroplating with the use of the NaCl-KCl-Li_2CO_3-Na_2MoO_4 melt. Molybdenum plates (99.99 wt. % Mo) 100 mm long, 10 mm wide, and 0.1 mm thick were used. The synthesis of Mo_2C on molybdenum plates was carried out at 1123 K for 7 h at cathodic current density (*i*) of 5 mA cm^{-2}. A glassy carbon (SU-2000) ampoule was used as the anode.

The roughness of the original substrates and coatings was measured on a PROFI-130 profilometer.

The procedure of the determination catalytic activity for the composition Mo_2C/Mo was described in [4].

3. RESULT AND DISCUSSION

3.1 Protective coatings

The open-circuit chronopotentiogram obtained on the electrode of grade ARMCO iron (Fig. 1) has no sites of a potential delay. This means that chromium and iron do not form intermetallic compounds, and solid solutions are monophasic. This conclusion agrees with the equilibrium state diagram of Fe-Cr [23].

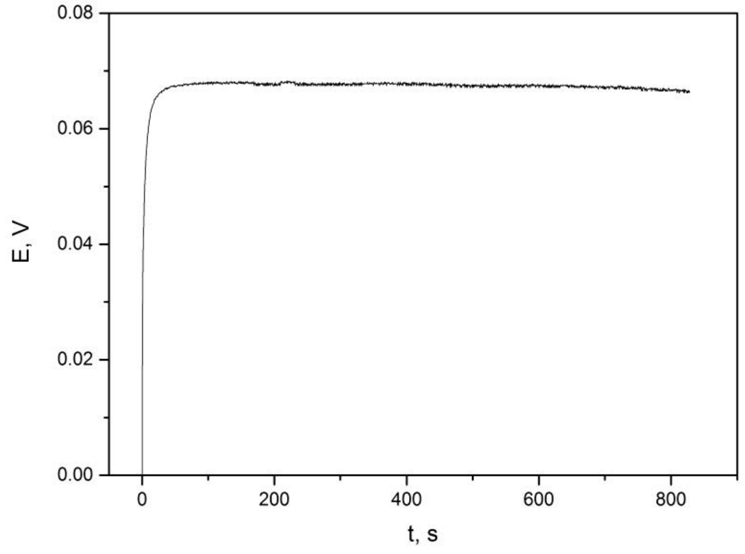

Figure 1. Open-circuit chronopotentiogram of the NaCl-KCl-$CrCl_2$(4.5 wt.%) melt, working electrode is iron (ARMCO), reference electrode is chromium. Temperature 1023 K.

At the same time, the chronopotentiogram recorded on the electrode of grade St3 steel (Fig.2) shows three plateaus of the potential delay (*a*, *b*, and *c*) which, according to the equilibrium state diagram of Cr-C [23], correspond to the formation of $Cr_{23}C_6$ + Cr_7C_3, Cr_7C_3 + Cr_3C_2, and Cr_3C_2 + C two-phase areas in the surface layer. Potentiostatic electrolysis at plateau potentials (Fig. 2) resulted in the formation of cathodic deposits with the following composition: $Cr_{23}C_6$ + Cr_7C_3 carbides at the potential corresponding to plateau *a*, two-phase product of Cr_7C_3 + Cr_3C_2 carbides at the potential of plateau *b*, and Cr_3C_2 + C at the potential of plateau *c*.

Similar discharge curves (Fig. 2) were obtained in chloride-fluoride melts with different cations compositions.

The chromium carbide coatings were also synthesized by the currentless transfer method. It is necessary to note that the currentless transfer method is an electrochemical method, and processes in this method are subject to the laws of electrochemical thermodynamics, kinetics and reaction diffusion in solids.

As the melt, we used an equimolar NaCl-KCl mixture with the addition of 10 wt. % $CrCl_3$ and the excess of metallic chromium. The melt was held for 2 h before the synthesis. The synthesis carried out at a temperature of 1123 K for 8 h. Because the equilibrium of reaction (1) is practically shifted completely to the right [22], chromium in the melt is present only in the form of Cr(II) complexes. These complexes diffuse to the steel substrate and, on its surface, are disproportionate with the chromium carbide formation and Cr(III) complexes [24]:

$$21Cr(II) + 3C(\text{steel surface}) \rightarrow Cr_7C_3 + 14Cr(III) \qquad (2)$$

The driving force of reaction (2) is the carbide formation energy $\Delta G(Cr_7C_3)$. The Cr(III) complexes formed by reaction (2) diffuse to metallic chromium and, interact with it by reaction (1), form Cr(II) complexes of the reduction form. Thus, chromium transfer on the carbon steel surface is closed in the cycle.

The obtained coatings were analyzed by the XRD method, which showed the formation of Cr_7C_3 chromium carbide (Fig. 3), both on grade St3 steel (carbon content of 0.14-0.22 wt.%) and on grade U9 steel (carbon content of 0.9-1.0 wt.%). The peaks of the diffraction pattern corresponding to the substrate are conditioned by the insignificant thickness of the synthesized coating.

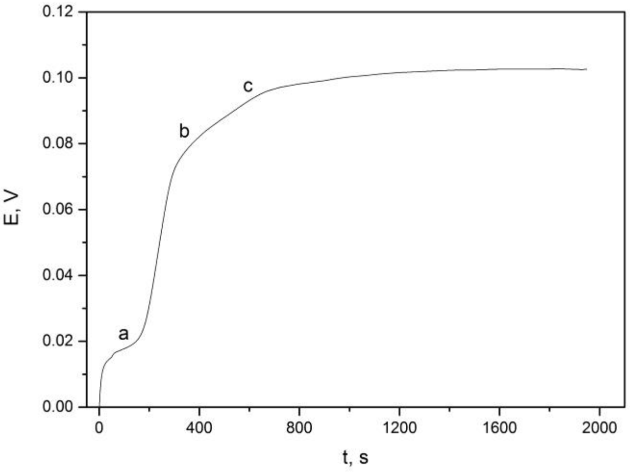

Figure 2. Open-circuit chronopotentiogram of the NaCl-KCl-$CrCl_2$(4.5 wt.%) melt, working electrode is steel (grade St3), reference electrode is chromium. Temperature – 1023 K.

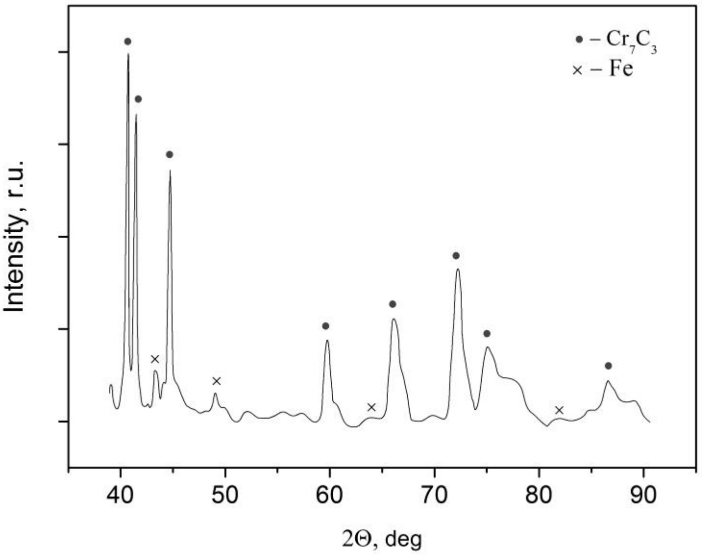

Figure 3. XRD pattern of the Cr_7Cl_3 coating on the St3 steel substrate.

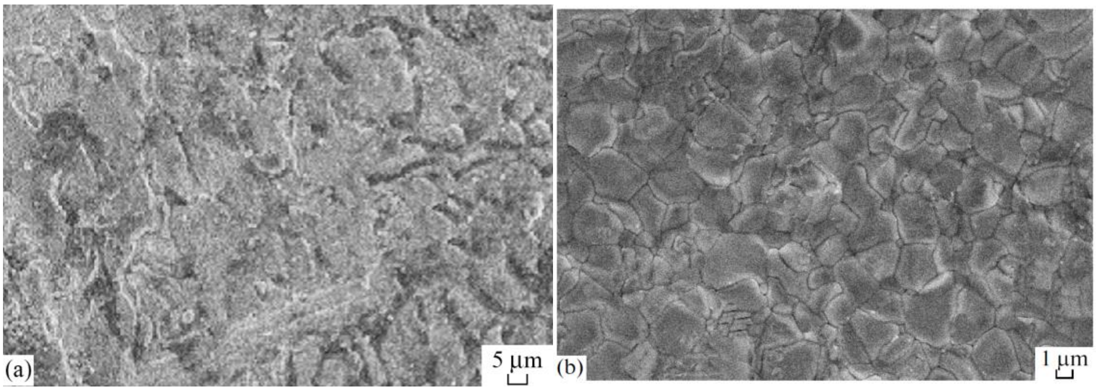

Figure 4. Surface morphology: (a) original St3 steel substrate, (b) after deposition of the Cr_7C_3 coating.

The morphology of the substrate surface and chromium carbide on the surface of grade St3 steel is represented in Fig. 4. As is evident from the microphotograph (Fig. 4a), the origin substrate has no texture of rolled metal. The carbide layer is characterized by the presence of grains (Fig. 4b), whose size along the diagonal is 1-6 µm, and one can observe the sharp interface between the grains. It should be noted that the morphology of the chromium carbide surface on grade U9 steel is no different from that on grade St3 steel. The thickness of the chromium carbide coatings was determined on the cross section. The thickness of the chromium carbide coatings was 1-2 µm for grade St3 steel and 4-6 µm for grade U9 steel, which is associated with the higher carbon content in the latter. The roughness of the original substrates was 0.15-0.17 µm (parameter R_a is the arithmetic mean deviation of the profile) both for grade St3 steel and grade U9 steel; and the roughness of the Cr_7C_3 coating on the same substrates was 0.23-0.27 µm.

Coatings of TaC and NbC on steel substrates and carbon fibers (Carbopon B-22) were synthesized also by currentless transfer in NaCl-KCl-K_2MeF_7(30 wt.%) melts in contact with Me (Me – Ta, Nb) at temperature 1073-1123 K, and time of process from 6 up to 24 hours. The mechanism of formation, for example, for niobium carbide by currentless transfer can be described by the following reactions [25-27]:

$$4Nb(V) + Nb \rightarrow 5Nb(IV), \tag{3}$$

$$5Nb(IV) + C(\text{steel surface}) \rightarrow NbC + 4Nb(V) \tag{4}$$

$$Nb + C \rightarrow NbC \tag{5}$$

Synthesized coatings were subjected to tests on corrosion resistance to the concentrated mineral acids. To determine the corrosion rate, samples with the known surface area were submerged in concentrated sulfuric, orthophosphoric, and hydrochloric acids. The data of the corrosion tests are represented in Fig. 5.

As can be seen from Fig. 5, that refractory metal carbides coatings significantly decrease the corrosion rate of steel substrates in concentrated acids, especially in the case of sulfuric and hydrochloric acids. Of course, the quality of obtained coatings (porosity) affects the results to a certain degree.

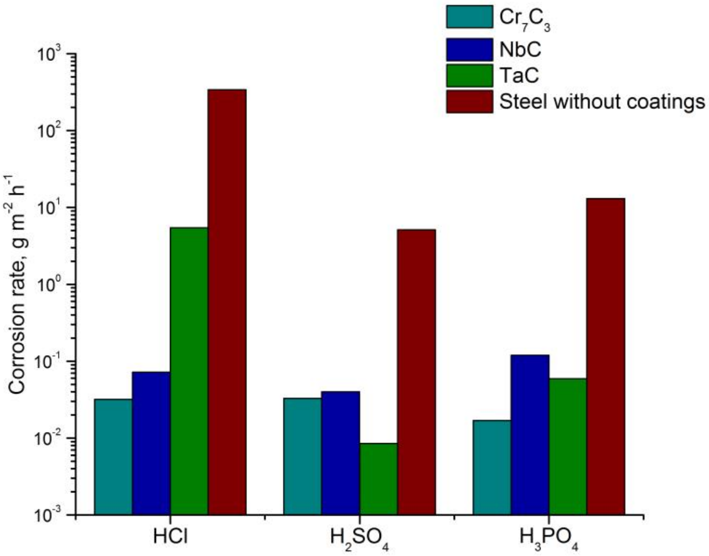

Figure 5. Corrosion rates of compositions “steel/refractory metal carbide coating” in the concentrated mineral acids.

The microhardness of refractory metal carbides on grade U9 steel, which is measured on the cross section, had the values 21 GPa, 29 GPa, 31 GPa for Cr_7C_3, NbC, TaC, respectively. The wear resistance was evaluated by the sample mass loss with the accuracy of 0.1 mg. The mass loss of a sample from hardened St.3 was 35.2 mg cm^{-2} and that of a coated with a chromium carbide – 4.7 mg cm^{-2}, niobium carbide – 2.9 mg cm^{-2} and tantalum carbide – 2.2 mg cm^{-2}.

The values of microhardness are higher and wear resistance characteristics much better comparing carbides obtaining by other methods [6, 13, 14, 16] because coherent and porousless coatings are produced by the currentless transfer method.

Due to the high wear and corrosion resistance NbC, TaC and Cr_7C_3 coatings on carbon steels can be applied in aggressive medium with the abrasive wear. Deposition of NbC coatings on parts of oil pumps increased their lifetime in several times. Tests carried out by LLC "Ecotech" showed that the coatings of Cr_7C_3 or TaC on the knifes for cutting rubber, made of St3, can improve their wear resistance and increase a tool lifetime in 2.0 (for Cr_7C_3) and 2.5 (for TaC) times.

Fig. 6 shows micrographs of the surface of the separate fiber and group of fibers. It was not observed the splicing of fibers with each other; coatings were uniform in a cross section as well as along the fiber. As can be seen from the micrograph of the cross-section of separate fiber, presented on Fig. 6, the thickness of tantalum carbide coating is approximately 200 nm.

Thickness of tantalum and niobium carbides coating on carbon fiber varied of 50-250 nm. Clear boundary without transition zone between the carbon fiber and coating was observed. Coatings of NbC or TaC on carbon fibers make better a fiber’s mechanical resistance and they are compatible with fibers up to 1473 K in an aggressive atmosphere.

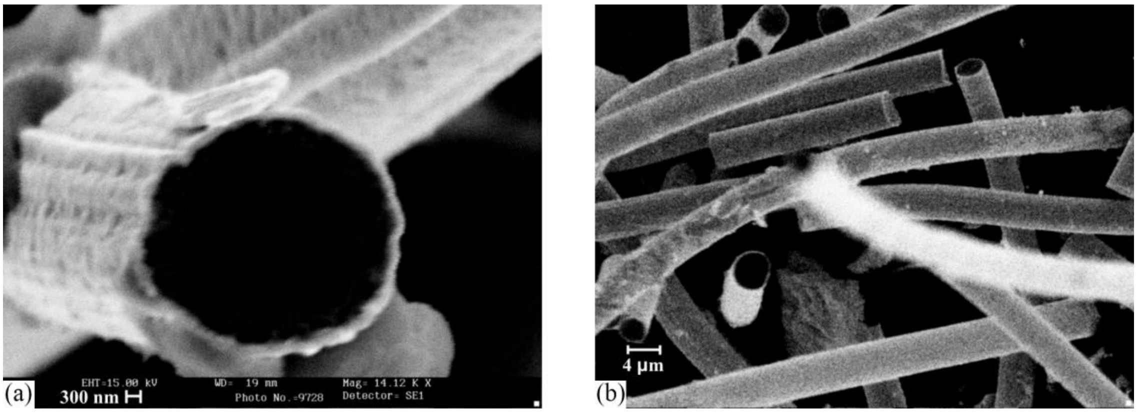

Figure 6. Micrographs of carbon fibers with TaC coating, obtained in the NaCl-KCl-K_2TaF_7 melt in contact with tantalum metal. Temperature = 1123 K, time = 24 h.

3.2 Catalytic coatings

Electrochemical synthesis of Mo_2C on the molybdenum substrates was performed at 1123 K for 7 h with a cathodic current density of 5 mA cm^{-2} in the NaCl-KCl- Li_2CO_3-Na_2MoO_4 melt. Formation of monophasic molybdenum semicarbide with hexagonal lattice was found, which is confirmed by XRD analysis (Fig. 7).

Joint electroreduction of MoO_4^{2-} and CO_3^{2-} ions resulted by the formation of Mo_2C coatings 50 μm thicknesses. The morphology of Mo_2C coating is presented in Fig. 8. The specific surface area (SSA) was determined by the BET method and was found to be 36 $m^2\,g^{-1}$.

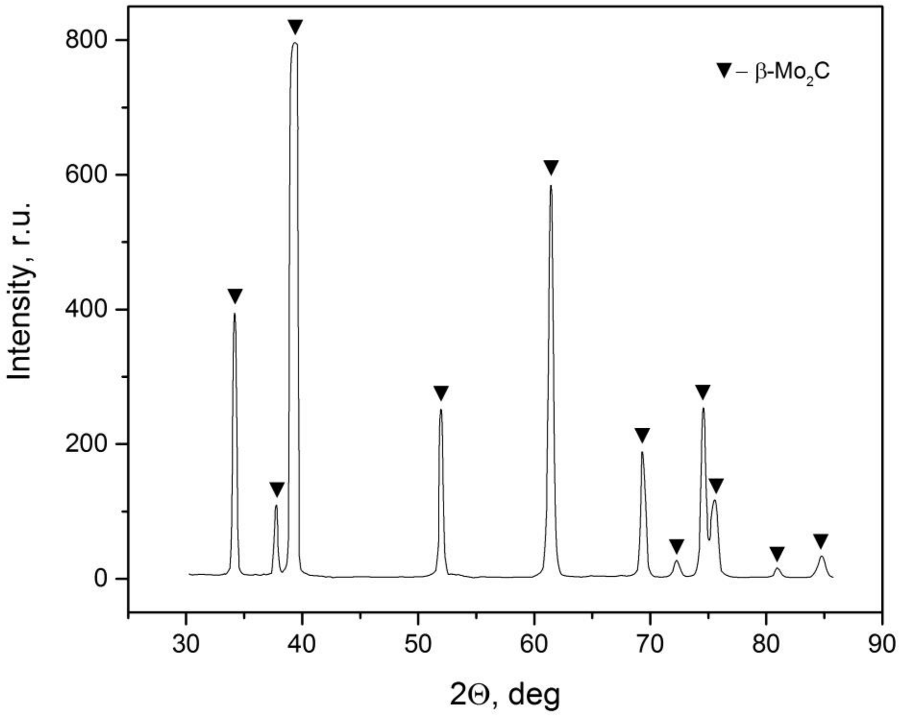

Figure 7. XRD pattern of molybdenum carbide coating on a molybdenum substrate. Temperature 1123 K, *i* = 5 mA cm^{-2}, melt – NaCl-KCl-Li_2CO_3 (1.5 wt %)-Na_2MoO_4 (8.0 wt %).

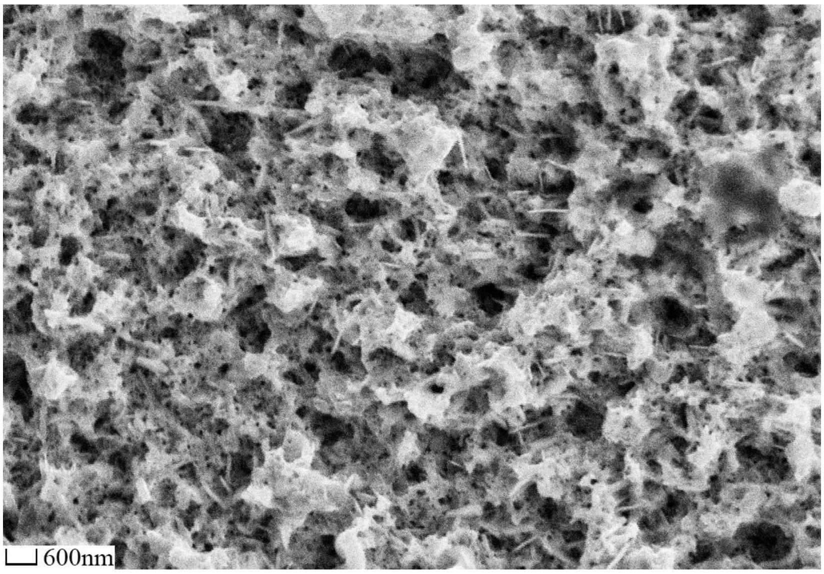

Figure 8. Morphology of molybdenum carbide coating on a molybdenum substrate. Temperature = 1123 K, *i* = 5 mA cm^{-2}, melt – NaCl-KCl-Li_2CO_3 (1.5 wt %)-Na_2MoO_4 (8.0 wt %).

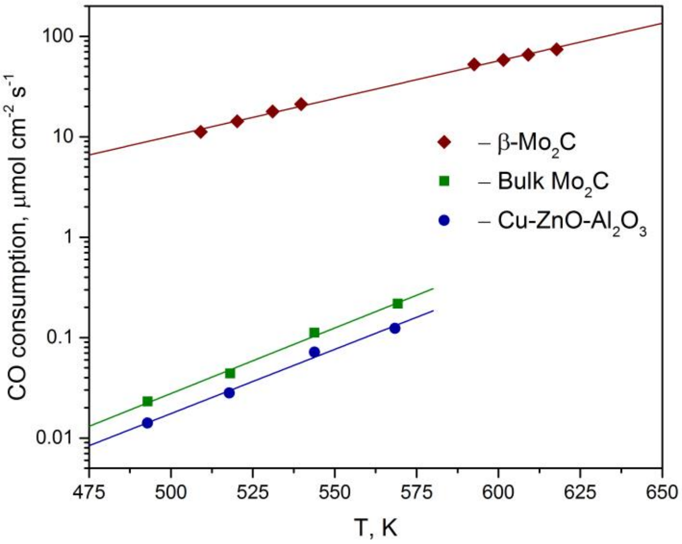

Figure 9. Temperature dependence of the water-gas shift reaction rate over different catalysts. Reaction conditions: p(CO) = 300 Pa, p(H_2O) = 760 Pa, p(CO_2) = 1.2 kPa, p(H_2) = 40 kPa, and balance helium. The gas flow rate is 50 cm^3 min^{-1}.

The steady-state reaction rates for the Mo_2C/Mo coatings were higher than those for the bulk Mo_2C and commercial Cu/ZnO/Al_2O_3 catalysts over in the temperature range explored (Fig. 9). The SSA of bulk Mo_2C was considerably higher (61 m^2 g^{-1}) [28]. The catalytic activity is enhanced by at least three orders of magnitude comparing to that of the pure Mo_2C phase, because the bulk Mo_2C contains at least a few weight percent of cubic molybdenum carbide. It sharply decreases catalytic activity and the rate of the water-gas shift reaction.

A detailed kinetic study was carried out on the Mo_2C/Mo coatings [29]. Based on the result of the kinetic study a novel microstructured reactor/heat-exchanger (MRHE) has been designed and constructed [29].

4. CONCLUSIONS

Chromium electrodeposition from the NaCl-KCl-$CrCl_2$ melt on the substrates of carbon steels was studied by chronopotentiometry, and the potential electrolysis parameters resulting in the chromium carbide formation with various compositions on the steel surface were found. Refractory metal carbide coatings (NbC, TaC and Cr_7C_3) on carbon steels and fibers were synthesized by the currentless transfer method, their microhardness, corrosion resistance and wear resistance were determined. Deposition of NbC coatings on parts of oil pumps and coatings of Cr_7C_3 or TaC on the knifes for cutting rubber increased their lifetime in several times. The Mo_2C/Mo composition was tested as a catalyst for the water-gas shift reaction. The steady-state reaction rates for the Mo_2C/Mo composition were higher than those for the bulk Mo_2C and commercial Cu/ZnO/Al_2O_3 catalysts over in the temperature range explored.

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