Surface modification for creation of functional materials in molten salts and their application from cryogenic to ultrahigh temperatures

S A Kuznetsov and A R Dubrovskiy
Tananaev Institute of chemistry and technology of rare elements and minerals of the Kola Science Centre of the Russian Academy of Sciences, 25a Akademgorodok st., 184209, Apatity, Murmansk region, Russia
E-mail: kuznet@chemy.kolasc.net.ru

Abstract. Nowadays coatings are produced mostly by CVD, PVD methods, plasma and detonation spraying. At the same time, utilization of molten salts for coatings electrodeposition is highly attractive. Creation of a rotor cryogenic gyroscope, a biomedical material nitinol-tantalum, highly active, stable catalysts of the new generation in the form of nanostructured Mo2C coatings on molybdenum, a composite material MoSi2-MoB4 for protection of molybdenum microreactors and ultrahigh temperature Nb-Hf coatings has been discussed.

1. Introduction

Extreme conditions of articles exploitation cause utilization of expensive refractory metals and their metal-like refractory compounds ensuring their adequate performance. The problem can be approached by depositing coatings on the surface of units and mechanisms, i.e. creating composite materials. In this case, the substrate material provides the strength and electric characteristics while the coatings realize the necessary surface properties.

Nowadays coatings of metal-like refractory compounds are used in aircraft, rocket space vehicle and mostly produced by CVD, PVD, SHS methods, plasma and detonation spraying. At the same time, using molten salts for deposition coatings is highly attractive. Molten salts provide the production of coatings by electrochemical synthesis, precise surface alloying, by employing the reaction of disproportionation and currentless transfer.

Electrochemical methods have the following advantages, as compared with other possible techniques of production of metal-like refractory compounds:

- smooth coatings can be deposited even at surfaces of complicated geometry;
- single crystals, polycrystalline coatings and even ultra-disperse powders can be deposited depending on the parameters of the process;
- the composition of the deposit can be precisely controlled through process parameters;
- relatively low temperature of synthesis (down to 600°C), cheap and simple technological background and the cheap raw materials required make the process attractive from the economic point of view.
2. Experimental and results

2.1. Superconductive coatings

Niobium in the form of thin films and coatings is used in high-tech cryogenic devices using the phenomenon of superconductivity. For their preparation, the niobium ability to form electrolytic structurally dense cathodic films in molten salts can be utilized. Electrolytic method does not require complex equipment and allows forming uniform coatings with the desired thickness on the inner and outer surfaces of articles with the complex configuration.

Electrodeposition of the niobium coatings on spheres 10 mm in diameter, manufactured from carbopyroceram, carried out at a temperature of 1023 K. The anodic current density was less than 1 mA·cm⁻² and the cathodic current density during electrolysis was chosen 15 mA·cm⁻². The NaCl-KCl-NaF(10 wt.%)-K₂NbF₇(8 wt.%) electrolyte [1] was employed for niobium coatings electrodeposition on carbopyroceram spheres. Due a spherical shape of substrates, a special form of the cathode should be used for plating of samples by niobium in molten salts. In the present study the construction of the cathode was developed. It consists of two parts: top part is fixed; bottom part is rotating by digital controlled stirrer. Construction of the cathode provides the electrical contact in a random point of the sample and such contact allowed obtaining uniform coatings. The stirrer rotation speed in all experiments was not changed and was chosen to be 30 rpm. Two-stage electrolysis (10 hours plus 10 hours) was applied to obtain smooth uniform niobium coatings with the thickness up to 140 µm (Figure 1).

Spectral quantitative analysis of niobium coatings detected the following contents of impurities (wt.%): Mn < 2·10⁻⁴; Mg < 3·10⁻⁴; Si < 1·10⁻³; Fe < 2·10⁻³; Ni < 5·10⁻⁴; Pb < 5·10⁻⁴; Sn < 5·10⁻⁴; Ti < 1·10⁻³; Al < 5·10⁻⁴; Co < 1·10⁻³; Mo < 1·10⁻³; Ca < 1·10⁻³; Zr < 2·10⁻³; V < 3·10⁻⁴; Cu ≤ 1·10⁻³; Cr < 5·10⁻⁴.

Testing of the samples on the superconducting properties showed the same results as the samples of high purity bulk niobium [2].

2.2. Protective coatings

2.2.1. Biocompatible coatings

The Ni-Ti shape memory alloys are currently a topic of notable interest in medicine. They provide a unique opportunity to make novel surgical implants and instruments for vascular and orthopedic surgery. However, high nickel content in these alloys could cause the problem of biocompatibility because of nickel toxic effect. In turn, a tantalum is successfully used in medicine as a wire or sheet. It does not irritate the living tissue and does not harm the functioning of the organism, but it has a high specific weight. So using of tantalum coatings on various materials is more appropriate than utilization of a bulk metal. Thus, it is necessary to improve the corrosion resistance of nickel-titanium alloys (nitinol) that can be achieved with applying of protective porousless tantalum coating.

For obtaining of tantalum coatings the NaCl-KCl-NaF(10 wt.%)-K₂TaF₇(10 wt.%) melt was used at the temperature 1023 K. Direct (DC) and pulsed current (PC) was supplied for electrodeposition. A cathodic current density was changed from 5 to 100 mA·cm⁻² at the galvanostatic mode. The same cathodic current density and the time of electrolysis (tₑ = 0.5-5.0 s) with pauses (tₚ = 1-2 s) were used...
Electroreduction of tantalum complexes in chloride-fluoride melt on nitinol electrode was investigated. A voltammetric curve registered on nitinol electrode except of the electroreduction peak of tantalum fluoride complexes to tantalum has several peaks corresponding to formation of intermetallic compounds of nickel and tantalum.

In the case of formation of intermetallic compounds between the substrate and the coating is an important aspect of the coating adhesion to the substrate. The adhesion was measured by cross-sections method using a tester of adhesion Elcometer 107. The measurements showed that the coatings obtained using DC can be classified as adhesion to international standards ISO (1) and ASTM (4B). At the same time, the coatings deposited on nitinol by PC have a maximum class of adhesion ISO (0) and ASTM (5B) [3]. This result is probably due to the greater thickness of the intermediate layers at constant current, as for tantalum coatings of the same thickness during electrolysis at constant current requires a longer time.

The porosity of tantalum coatings was determined by Erhard’ technique based on measuring the current dissolution at a certain potential, in which dissolves the substrate material and the coating remains passive.

Corrosion resistance of the composition nitinol-tantalum coating was studied in dilute mineral acids: HCl (5%), H2SO4 (5%), H3PO4 (5%) and 0.9% solution of NaCl. In the case of nonporous tantalum coatings, corrosion in all test media was negligible [3].

2.2.2. Coatings for microreactors from molybdenum
Molybdenum can be used as a basic reactor material. However, molybdenum corrodes in contact with aggressive and water vapors at elevated temperatures. Therefore, low temperature oxidative stability of molybdenum substrates can be improved by siliciding in molten salts to produce a MoSi2 layer followed by boronizing of the MoSi2 phase.

Boronizing treatments were conducted in molten salts under inert gas atmosphere in the 973-1273 K temperature range for 3-7 hours. The oxidation resistance of the films was investigated by the weight change in an air-water (2.3 vol.%) mixture at a temperature of 723 K for a period up to 700 hours [4].

In non-current boronizing the MoSi2 phase was transformed to the Mo5Si3 phase, which became a major (content 10-30 wt.%) phase after boronizing step performed in the 1023-1173 K range and the matrix phase (>60 wt.%) above 1223 K. The MoSi2 phase was always present in the films in the temperature range of 1073-1223 K after electrochemical synthesis. The main boride phases were MoB2 and Mo2B3. The formation of the Mo5(BSi)3 phase was only observed in electrochemical synthesis at 1033 K. Pure MoB4 was formed in the bulk MoSi2 phase after electrochemical boronizing in the range of 1033-1113 K with a maximum content of ca.15 wt.% at 1073 K. The presence of small amounts (12-15 wt.%) of the MoB4 phase formed during boronizing of MoSi2/Mo films greatly improved the oxidation resistance of the molybdenum substrates. The weight gain observed was \(6.5 \times 10^{-4} \text{mg cm}^{-2} \text{h}^{-1}\) [4]. To provide the maximum protection, the duration of the boronizing step was adjusted to boronize an external MoSi2 layer without boronizing the molybdenum substrate. No pest disintegration of the molybdenum substrate was observed in an air-water mixture at 773 K after 700 hours.

2.3. Catalytic coatings
A new generation of highly active and stable catalytic films for the water-gas shift reaction by high-temperature electrochemical synthesis in molten salts has been developed.

Electrochemical synthesis of molybdenum carbide films on molybdenum substrate was performed by potentiostatic and galvanostatic electrolysis with utilization of the next molten salts systems: NaCl-KCl-Li2CO3 (1); NaCl-KCl-NaF-Na2MoO4-Li2CO3(2); LiCl-KCl-Li2C2 (3). In all cases Mo2C films with the hexagonal lattice were obtained. At the same time a bulk Mo2C usually has a cubic lattice.
The formation of Mo$_2$C with the hexagonal structure in the processes of electrochemical synthesis is due to specific conditions (electrical field, double layer, high temperature) of electrocrystallization. It was noted in our studies the similarities of the effects of electrochemical crystallization and the external high pressure.

The steady-state reaction rates for the Mo$_2$C/Mo films were higher than those for the bulk Mo$_2$C and commercial Cu-Zn-Al catalysts over in the temperature range explored (Figure 2). The catalytic activity is enhanced by at least an order of magnitude comparing to that of the pure Mo$_2$C phase [5, 6]. The methanation reaction was completely suppressed in the whole temperature range studied on the Mo$_2$C/Mo films. The catalytic activity remained constant during 5000 hours on-stream. The films were also stable during the thermal cycling, while the activity of commercial catalysts tends to decrease with time.

Figure 2. Temperature dependence of the WGS reaction rate on the catalyst: 1 — Mo$_2$C/Mo; 2 — Mo$_2$C/Mo; 3 — Mo$_2$C/Mo; 4 — bulk Mo$_2$C; 5 — Cu-ZnO-Al$_2$O$_3$.

2.4. Ultrahigh-temperature Nb-Hf coatings

Articles based on graphite are widely used presently in aerospace techniques because of the unique properties of graphite. However, a drawback of graphite-based compositions is a low heat resistance in oxidizing atmosphere. It was shown that Nb-Hf coatings of $\alpha+\beta$-composition with a planar growing front and thickness of 20-40 $\mu$m can be obtained from the NaCl-KCl-NaF (5 wt.%)-K$_2$NbF$_7$ (1 wt.%)–K$_2$HfF$_6$ (10 wt.%) electrolyte. It was found that niobium stabilized the low temperature monoclinic modification of HfO$_2$, which was formed during oxidation. The temperature of exploitation graphite articles can be increased up to 2373 K if to use niobium-hafnium protective coatings [7, 8].

References
[1] Kuznetsov S A, Marenkova E A and Kalinnikov V T 2015 Doklady Chemistry 463 1
[2] Dubrovskiy A R, Okunev M A, Makarova O V and Kuznetsov S A 2018 Coatings 8 213
[3] Marenkova E A, Shamshurin A I and Kuznetsov S A 2015 Russ. J. Appl. Chem. 88 3
[4] Kuznetsov S A, Dubrovskiy A R, Kuznetsova S V, Rebrov E V, Mies M J M, De Croon M H J M and Schouten J C 2009 Molten Salts and Ionic: Never the Twain? (John Wiley & Sons) pp 193-217
[5] Dubrovskiy A R, Makarova O V and Kuznetsov S A 2018 Coatings 8 442
[6] Stulov Yu V, Dolmatov V S, Dubrovskiy A R and Kuznetsov S A 2017 Int. J. Electrochem. Sci. 12 5174
[7] Kuznetsov S A 2009 Pure Appl. Chem. 81 8
[8] Kuznetsov S A 2012 Chemical Papers 66 5