Electrodeposition of Molybdenum from Molten Salts

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Electrolytic preparation of molybdenum coatings has been investigated in molten NaCl—KCl, KF, and KF—B_2O_3 electrolytes containing Na_2MoO_4 as the electrochemically active component. Molybdenum can be successfully electrodeposited from the molten mixture KF—B_2O_3—Na_2MoO_4 in the form of coherent layers on different electrically conductive substrates. The thickness of the layer depends on the temperature and current density used for deposition.

Electrodeposition from molten salts appears to be a progressive method for creation of compact surface layers of metals on electrically conductive substrates. The importance of this method increases, when the coatings cannot be prepared by electrolysis of aqueous solutions, for example in the case of refractory metals.

Electrodeposition of molybdenum from molten salts has been extensively studied over the last period. From an analysis of the literature data it follows that several types of molten systems were tested as electrolytes. On the basis of the electroactive species used they can be divided into two main groups:

– systems containing either K_3MoCl_6 [1—5], or K_3MoF_6 [6] which were dissolved in alkali metal halides, mainly chlorides and fluorides;

– systems containing oxide compounds of molybdenum, such as molybdenum oxide MoO_3 [7, 8], alkali metal molybdates [7, 9—12], and $CaMoO_4$ [13]. As a basic electrolyte LiCl—KCl [8], sodium and lithium metaborates [7], KF—$Na_2B_4O_7$ [9], KF—$Li_2B_4O_7$ [12], KF—B_2O_3 [10], and $CaCl_2$—CaO [13] molten mixtures were used.

In all the above-mentioned literature the influence of the operating parameters of electrolysis (temperature, current density) and the electrolyte composition on the character of the electrodeposited product was studied. The temperature employed ranges from 600 °C [2—4] to 1000 °C [13] depending on the electrolyte used. Most of the authors declared the best molybdenum coatings were obtained at temperatures from 750 °C to 900 °C. The quality of Mo-coatings is also influenced by cathode current density. The tested values were in the range from 10 to 500 mA cm^{-2}. It was found that the optimal value depends both on the working temperature and the concentration of the electroactive component of the electrolyte.

In the present work, the electrodeposition of molybdenum coatings on steel (CSN 11373), nickel, and graphite was studied. The molten NaCl—KCl—Na_2MoO_4, KF—Na_2MoO_4, and KF—B_2O_3—Na_2MoO_4 electrolytes at different operating parameters of the process were used. To explain processes taking place at the cathode the voltammetric measurements in electrolytes containing potassium fluoride were performed.

EXPERIMENTAL

The experiments have been carried out in an electric resistance shaft furnace. The shaft consisted of a sintered corundum tube with an internal nickel anticorrosive lining. On both ends, the shaft was closed by air-tight water-cooled heads. The electrolytic cell for electrochemical measurements consisted of a platinum crucible which was used at the same time as an auxiliary electrode. As the working and reference electrodes, the platinum wires with diameter 1 mm were used. The electrodes were immersed into the electrolyte by means of a micrometer screw through specially adapted top-head. In the molybdenum electrodeposition experiments, a graphite crucible (d = 30 mm, h = 40 mm) served as a cell container and as an anode simultaneously. As a basic material for molybdenum coatings, low-alloy steel, nickel, and graphite were used. Electrolyses were done in both galvanostatic and potentiostatic conditions. In all experiments, the inert working atmosphere has been preserved by an overpressure of about 3 kPa of argon.

For the electrolyte preparation, the commercially available reagents of anal. grade were used. Before using, all the chemicals were dried at higher temperature, moreover, Na_2MoO_4, KF, and B_2O_3 were dried in vacuum in the presence of P_2O_5.

A potentiostat (Tacussel PRT 20-2) externally controlled by a generator of triangular pulses [14] was used as a source of potential and current.

The observed I—E and E—t curves were recorded by means of an X-Y recorder HP 7004 B. The electrodeposited Mo-layers were identified on polished cross-section by means of a scanning microscope JXA-840-A (Jeol).

RESULTS AND DISCUSSION

The analysis of the literature data did not answer unambiguously the question of the most convenient electrolyte composition for the electrodeposition of molybdenum coatings. To choose the suitable electrolyte one has to take into account not only the electrochemical behaviour of the electrolyte, but also the physicochemical properties (viscosity, electric conductivity, vapour pressure) of the melt and the availability (price) of the reagents as well. On the basis of the above considerations the following molten mixtures, containing sodium molybdate as an electroactive component, have been chosen as an electrolyte: NaCl—KCl—Na_2MoO_4, KF—Na_2MoO_4, and KF—B_2O_3—Na_2MoO_4.

The first two series of experiments have been done in the molten equimolar NaCl—KCl mixture containing 5 and 10 mole % Na_2MoO_4, respectively. The temperature was maintained at 800 °C. Cathode current density j varied from 10 to 300 mA cm^{-2}. Graphite rods with the diameter of 4 mm served as a cathode.

At these conditions of electrolysis no molybdenum coatings were identified on the cathode. X-Ray analysis of the powdery product of electrolysis confirmed, in accordance with [1], that it consisted of the mixture of molybdenum oxides Mo_2O_3 and MoO_2.

With regard to the unsatisfactory results gained in the chloride melt containing Na_2MoO_4, the in-

vestigations in the molten systems containing potassium fluoride have been carried out. The electrolysis (temperature 850 °C, j 10—300 mA cm^{-2}, content 7 mole % Na_2MoO_4) in the binary system KF—Na_2MoO_4 did not provide good results. No deposit was observed at the cathode after the experiment. However, only small addition of B_2O_3 (1 mole %) to the electrolyte causes that the compact molybdenum coatings appear at the cathode after the electrolysis. These results are in a good agreement with [10], and indicate an important influence of boron oxide on the mechanism of cathodic reaction in electrodeposition of molybdenum.

To obtain more information about the cathodic reaction, the voltammetric measurements have been performed in both KF—Na_2MoO_4 and KF—B_2O_3—Na_2MoO_4 systems. The scan rate varied from 0.1 to 1 V s^{-1}. Fig. 1 shows the voltammetric curve recorded in the molten mixture consisting of 93 mole % KF and 7 mole % Na_2MoO_4 at 850 °C and speed of polarization 1 V s^{-1}. Curves recorded at various scan rates exhibited the same character. Peaks a and b represent electrodeposition of potassium and oxygen, respectively. Despite the high molybdenum concentration in the melt, no peaks representing reduction of molybdenum cations are observed on the curve. Moreover, after the electrolysis at -0.5 V and -0.7 V no deposits have been found on the cathode.

In Fig. 2 the voltammetric curve recorded in the molten mixture consisting of 92 mole % KF, 1 mole % B_2O_3, and 7 mole % Na_2MoO_4 is shown. Here again all curves recorded at various scan rates exhibited the same shape. As can be seen from the figure, the small addition of B_2O_3 to the binary KF—Na_2MoO_4 system evokes remarkable changes in the shape of the curve. The high peaks appeared
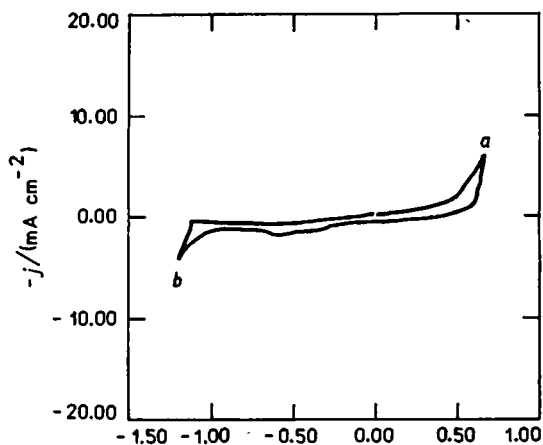

Fig. 1. Voltammetric curve recorded in the electrolyte 93 mole % KF and 7 mole % Na_2MoO_4 at 850 °C; $v = 1$ V s^{-1}.
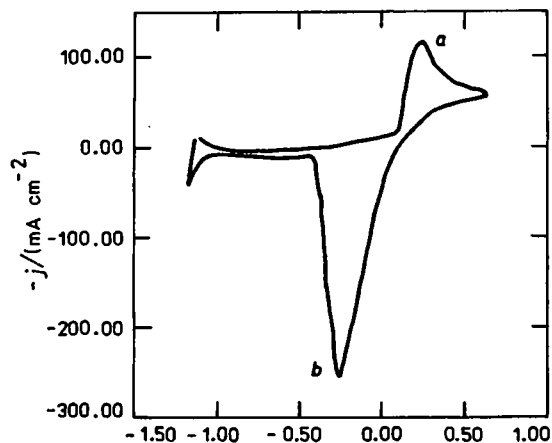
Fig. 2. Voltammetric curve recorded in the electrolyte 92 mole % KF, 1 mole % B_2O_3, and 7 mole % Na_2MoO_4 at 850 °C; $v = 1$ V s^{-1}.

on the cathodic *a* and anodic *b* parts of the curve. Electrolysis at − 0.5 V proved that the peak *a* represents the reduction of molybdenum cations to molybdenum metal. The anodic peak *b* represents the dissolution of the electrodeposited molybdenum. From an analysis of both cathodic and anodic parts of the voltammetric curve it follows that the electrodeposition of molybdenum from the tested system takes place under the full reversible electrochemical reaction.

On the basis of the presented voltammetric measurements we can conclude that in the binary molten system KF—Na_2MoO_4 molybdenum is bonded strongly in complex oxide or oxide-fluoride anions. The structure and the bond strength do not allow the reduction of molybdenum cations at more positive potentials than the reduction of K^+ occurs. The addition of B_2O_3 to the KF—Na_2MoO_4 system causes the changes in the structure of the melt and, consequently, changes in the electrochemical behaviour of the melt. *Rawson* [15] described the heteropolyacid ions present in the melt of MoO_3-based glasses. These ions consist of MoO_6 groups and contain boron as a central atom. The more detailed investigation of the mechanisms of electrode processes will be presented in the next paper.

As it follows from the presented electrochemical measurements and from the literature data [9—12], the electrodeposition of molybdenum coatings in the melt consisting of 75 mole % KF, 15 mole % B_2O_3, and 10 mole % Na_2MoO_4 at temperatures 750, 800, and 850 °C has been tested. The current densities employed varied from 10 to 140 mA cm^{-2}. As a substrate material a low-alloy steel was used. The results of electrolysis are summarized in Table 1. Theoretical mass of the molybdenum deposit was calculated on the basis of the Faraday law. The assumption of the six-electron cathodic process was accepted.

The operating parameters of electrolysis have an important influence on both the cathode current efficiency (CCE) and the character of deposited molybdenum. The results show that the temperature does not influence current efficiency significantly. In the tested temperature range the CCE decreases slowly with decreasing temperature probably due to the increase of the viscosity of the melt. This statement is confirmed by an increase of the cell voltage for all current densities with the temperature decrease.

On the other hand, the influence of the cathode current density on the efficiency of the process was observed at all temperatures. The decrease of CCE at higher current densities was caused by the formation of dendrites. These were mostly formed at the edges of the steel cathode, appar-

Table 1. Results of the Electrodeposition of Molybdenum Coatings in the Melt 75 mole % KF, 15 mole % B_2O_3, and 10 mole % Na_2MoO_4 at Different Temperatures and Cathode Current Densities (Deposition Time 1 h)

$\theta/°C$	E/V	$j/(mA\ cm^{-2})$	$h/\mu m$	CCE/%
850	0.11	35	10	98.4
	0.18	70	18	88.9
	0.23	105	22	72.5
	0.32	140	25	61.9
800	0.17	35	9	86.6
	0.26	70	14	62.7
	0.35	105	21	69.2
	0.48	140	25	61.9
750	0.33	35	8	77.0
	0.43	70	14	67.6
	0.49	105	20	65.9
	0.67	140	24	58.8
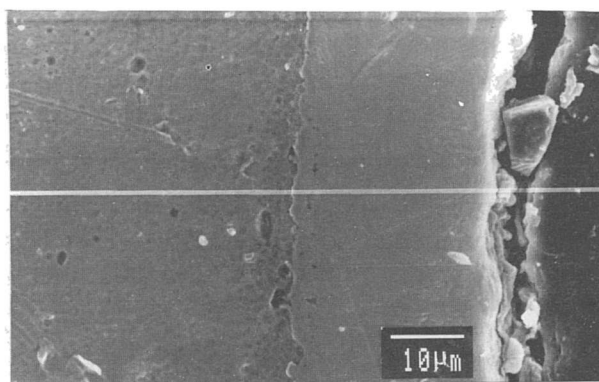
Fig. 3. Cross-section of a molybdenum-coated steel cathode; temperature 800 °C, current density 140 mA cm^{-2}.

ently due to the irregular distribution of the current.

Fig. 3 shows the cross-section of a Mo-coated steel cathode. The thickness of the deposit is about 20 μm, consisting of a homogeneous uniform layer of molybdenum with good adherence to the substrate. There was no difference in quality of the deposits prepared on various substrates used in this work.

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Mercury Traces Determination by Voltammetry on Gold Fibre Microelectrode in Some Food Samples

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Gold fibre microelectrode was applied for mercury traces determination by differential pulse anodic stripping voltammetry in mushrooms. The food sample decomposition procedure with concentrated HNO_3 under elevated pressure and temperature in a digestion device is described. The method was tested on synthetic samples spiked with $Hg(ClO_4)_2$. Sufficient decomposition of the organic matrix was reached during the sample pretreatment and no significant loss of mercury was observed.

Differential pulse anodic stripping voltammetry (DPASV) is a powerful electroanalytical technique for trace analysis of many toxic metals [1—3]. Three types of working electrodes are generally used for mercury determination by DPASV: platinum, glassy carbon, and gold. Multiple anodic peaks assigned to intermetallic compounds formation [4] are considered as main disadvantage of Pt electrodes. Glassy carbon is considered to be more advantageous material because the formation of mercury intermetallic compounds with electrode is excluded [5]. On the other hand, droplets of mercury can be lost especially in the case when the method of exchanged solution is applied [6]. Improving of accumulation of mercury on glassy carbon requires addition of another codepositing metal, *e.g.* Cu(II) or Cd(II) which represents further complication of analysis [7]. This also holds for preplating or *in situ* deposition of Au films on a glassy carbon electrode [8]. The lowest detection limit was reported for rotating compact gold disk electrode [9].

The combination of unique microelectrode properties (especially the possibility of deposition in a quiescent solution) with the most advantageous electrode material – pure gold, led us to propose the application of gold fibre microelectrode [10]. This electrode besides the possibility to omit stirring during accumulation from low-volume sample also enables a considerable reduction of Au consumption for working electrode construction (to less than 0.1 g) thus lowering its cost which can be of importance in practical application.

Mercury is a pollutant the occurrence of which represents a considerable health hazard even in trace amounts. One of the food products through which mercury can be brought to human body are mushrooms. These are often raised in deserted ore mine premises, where the probability of mercury uptake from the ore dust is much higher in comparison with the mushrooms growing in forests. Mushroom producers are therefore required to certify that Hg amount does not exceed legal