

the values of thermal dissociation $\alpha_*(\text{Na}_3\text{FSO}_4) = 0.71$ and $\alpha_*(\text{K}_3\text{FSO}_4) = 0.76$, which are the same values as obtained in [7].

It may be therefore concluded that the proposed thermodynamic approach yields the same result as the formal approach applied by Grjotheim [3]. Moreover, introducing the temperature dependence of the dissociation constant into the calculation it is possible to obtain more information on the thermal stability of the additive compound, e.g. the enthalpy of dissociation. This information may be compared with the calorimetric data. This case will be discussed in detail in the next paper.

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Electrodeposition of Molybdenum from $\text{KF}-\text{K}_2\text{MoO}_4-\text{SiO}_2$ Melts

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Electrolytic preparation of molybdenum coatings has been investigated in the molten system $\text{KF}-\text{K}_2\text{MoO}_4-\text{SiO}_2$. It was found that from the above system coherent smooth and well adhesive Mo-layers on electrically conductive substrates can be prepared. The influence of composition, temperature, and cathodic current density j_c on the quality of Mo-coatings was studied. The best results were obtained with the electrolyte of the composition 85 mole % $\text{KF}-10$ mole % K_2MoO_4-5 mole % SiO_2 , temperatures 1173 K up to 1273 K, and j_c in the range 73–450 A m^{-2} .

Molybdenum has from the practical point of view many significant properties, which promotes the effort for its effective preparation.

Electrodeposition from molten salts appears to be a very progressive method for preparation of compact surface layers of molybdenum on different materials. The importance of this method is emphasized by the fact that it is not possible to deposit molybdenum from aqueous solutions.

Recently there were published intensive studies concerning the deposition of molybdenum from the systems $\text{KF}-\text{M}_x\text{MoO}_4$, $\text{M} = \text{Na}, \text{K}, \text{Ca}$ [1], $\text{KF}-\text{MoO}_3$ [2, 3], with addition of $\text{Li}_2\text{B}_4\text{O}_7$ [4], $\text{Na}_2\text{B}_4\text{O}_7$ [5], B_2O_3 [1, 6], and CaO [7].

In all the above listed literature the influence of the operational parameters of electrolysis (temperature, cathodic current density (j_c), electrolyte composition, etc.) on the character of the deposited product was studied. Most of the authors declared to obtain the best Mo coatings at temperatures 750–950 °C. The very important factor is j_c , the best results are reported for values 100–10000 A m^{-2} . It was found that the optimal value depends on both the temperature and concentration of the electroactive component in electrolyte.

In the present work, the electrodeposition of molybdenum from the molten ternary system $\text{KF}-\text{K}_2\text{MoO}_4-\text{SiO}_2$ was examined. In this work the limits

concerning the composition, j_c , and temperature were stated within which good quality coatings on different substrates were obtained.

EXPERIMENTAL

The experiments were performed in an electric furnace (Fig. 1) with resistive heating element. The furnace shaft consisted of a sintered alumina tube. Inner wall of the shaft was protected by lining made from the Ni-sheet. The shaft was closed by the water-cooled air tight head. The electrolytic cell consisted of graphite crucible (internal dimensions $\phi = 30$ mm, $h = 40$ mm), which served also as an anode. Copper, nickel, and steel strips 10 mm wide were used as a cathode. The strips were immersed into electrolyte so deep that the active surface was 3.4 cm². The electrolyses were carried out under galvanostatic condition. Time of the electrolysis was 2700 s. D.C. power supply TR-9177 was used as a source of the electrolytic current. All experiments were performed under an inert argon atmosphere with a small overpressure of 3 kPa.

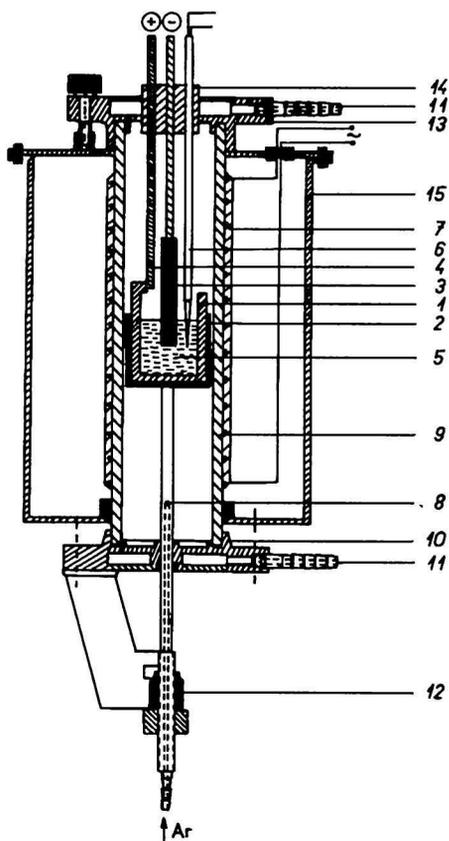


Fig. 1. Electrolytic container for electrodeposition of molybdenum coatings. 1. Graphite crucible (anode); 2. steel container; 3. cathode; 4. electric anode contact; 5. electrolyte; 6. thermocouple; 7. heating element; 8. Ar inlet; 9. sintered alumina tube; 10. water-cooled flange; 11. cooling water; 12. shift of crucible; 13. water-cooled flange; 14. teflon electric insulator; 15. furnace body.

Commercially available chemicals of anal. grade KF (Lachema), SiO₂ (Reakhim), and K₂MoO₄ (Fluka) were used for the preparation of electrolyte. All chemicals were dried before use at higher temperature, moreover, K₂MoO₄, KF, and SiO₂ were dried under vacuum in the presence of P₂O₅.

The deposited Mo-layers were identified by X-ray diffraction analysis (Philips) and by means of a Jeol JXA-840-A scanning electron microscope.

DISCUSSION

In the presented paper an influence of the operating parameters, *i.e.* electrolyte composition, cathodic current density, temperature, and different substrates, on the quality of the molybdenum deposits was studied.

Influence of the Electrolyte Composition

To find the region of the electrolyte composition, from which it is possible to obtain the visually smooth and well adhesive coatings, thirty different electrolytes (the composition of which is given in Table 1) were checked. Fig. 2 presents the results obtained by visual evaluation as well as by X-ray diffraction.

Table 1. Composition of Electrolytes

System	Series	x/mole %			
		KF	SiO ₂	K ₂ MoO ₄	
1	I	95	0	5	
2		90	5	5	
3		85	10	5	
4		80	15	5	
5		75	20	5	
6		70	25	5	
7	II	90	0	10	
8		85	5	10	
9		80	10	10	
10		75	15	10	
11		70	20	10	
12		65	25	10	
13	III	85	0	15	
14		80	5	15	
15		75	10	15	
16		70	15	15	
17		65	20	15	
18		60	25	15	
19	IV	80	0	20	
20		75	5	20	
21		70	10	20	
22		65	15	20	
23		60	20	20	
24		55	25	20	
25	V	75	0	25	
26		70	5	25	
27		65	10	25	
28		60	15	25	
29		VI	70	0	30
30			65	5	30

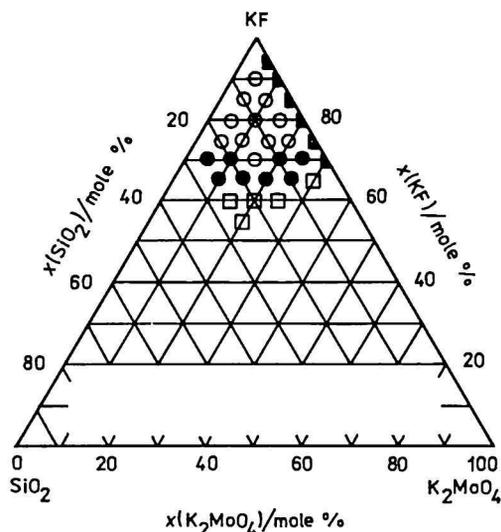


Fig. 2. Results of visual examination and X-ray diffraction analysis. Conditions of electrolysis: copper cathode, graphite anode, current density 156 A m^{-2} , temperature 1123 K , time 2700 s . ■ No deposits; □ black compounds; ○ smooth, adherent deposits; ● co-deposits of Mo and black compounds.

It was impossible to obtain any coherent molybdenum coatings from the binary electrolytes of the type $\text{KF}-\text{K}_2\text{MoO}_4$. The preliminary experiments have shown that the addition of minor amount of silica (1 mole %) to the above electrolyte enables the deposition of the metal-look molybdenum layers. Appearance of the coatings changed according to the silica amount in the electrolyte from silver-grey through dark grey up to black. Visually smooth and adhesive coatings without the dendrites on the edges were obtained from the electrolytes in a relatively narrow composition region. This region becomes even narrower in the melts with greater content of

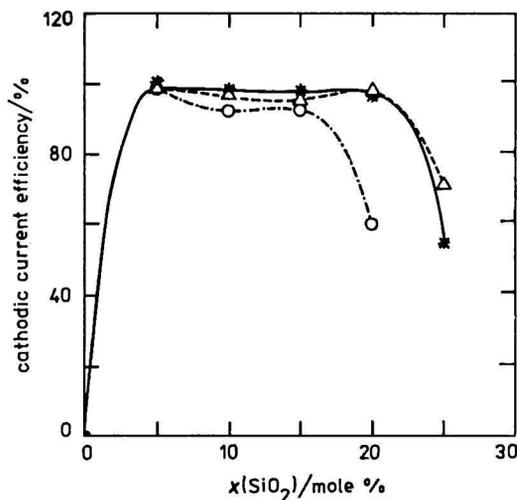
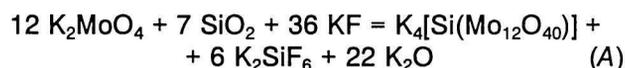


Fig. 3. Variations of cathodic current efficiency with SiO_2 and K_2MoO_4 concentrations. Conditions of electrolysis are the same as in Fig. 2. * 5 mole % K_2MoO_4 ; Δ 10 mole % K_2MoO_4 ; \circ 20 mole % K_2MoO_4 .

K_2MoO_4 . X-Ray diffraction analysis of the deposited layers showed that the black material contains mainly MoO_2 .

In Fig. 3 the relationship between the cathodic current efficiency (c.c.e.) and the silica content in the electrolyte is given. The determination of the current efficiency was performed using the gravimetric method. Current efficiency of the process varied between 90–100 %. The higher concentrations of the silica and K_2MoO_4 have a negative influence on the current efficiency, while the dark coatings were obtained. This can be explained by the fact that the current efficiency was calculated on the assumption of the six-electron cathodic reaction which is not the case when MoO_2 is deposited.

In Fig. 4 is shown the voltage across the electrolyzer vs. silica content. After addition of 5 mole % of silica to the electrolyte the substantial drop of the voltage was observed. The further increase of the silica content has only the minor effect on the voltage. The voltage drop is possible to explain by the fact that the silica changes the structure of the melt considerably. From the literature data [8, 9] we assume that the following reaction scheme can take place



When the complex heteropolyanion $[\text{Si}(\text{Mo}_{12}\text{O}_{40})]^{4-}$ is formed, the coordination number of molybdenum increases from 4 to 6. The central silicon heteroatom is surrounded by twelve MoO_6 octahedral groups with common oxygen atoms. Such heteropolyanion is rather voluminous and thus much more polarizable. In the vicinity of the cathode in electric double-layer this anion is strongly polarized and finally destructed to the smaller species, from which consecutive mo-

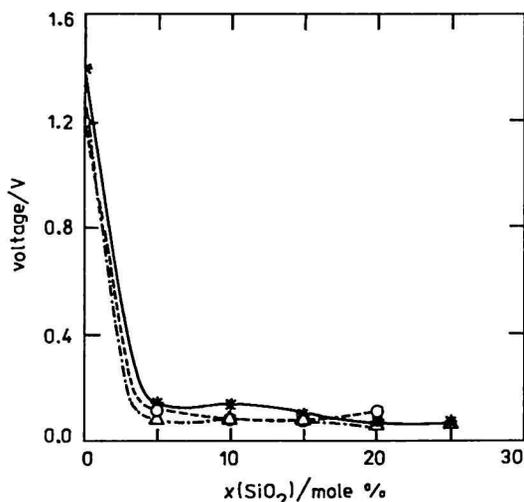


Fig. 4. Variations of cell voltage with SiO_2 and K_2MoO_4 concentrations. Conditions of electrolysis as in Fig. 2.

lybdenum deposition takes place.

In the course of the electrolysis, solid deposits on the top closure and furnace wall were observed. By X-ray diffraction analysis it was proved that the deposit consists of pure K_2SiF_6 , which supports the assumption concerning the reaction (A). Since no relevant thermodynamic data were found in the literature, it was impossible to calculate the thermodynamic parameters of the above reaction.

Influence of the Cathodic Current Density

For the determination of the influence of the cathodic current density (j_c) on the quality of the deposited coatings, electrolyte with the composition KF (85 mole %)— K_2MoO_4 (10 mole %)— SiO_2 (5 mole %) was used. This composition was selected, because from this electrolyte the best quality coatings were obtained. As it follows from Table 2, a good quality coating on the copper substrate can be obtained up to $j_c = 450 A m^{-2}$. At higher j_c the coatings are of lower quality with co-deposition of MoO_2 and traces of Mo_2C , which originates from graphite anode as a result of the reaction between anodic product CO_2 and deposited Mo. This assumption is supported also by the literature data [1].

Table 2. Effect of Current Density j_c on the Deposition of Molybdenum from KF (85 mole %)— K_2MoO_4 (10 mole %)— SiO_2 (5 mole %) Electrolytes

Current density $A m^{-2}$	X-Ray analysis	Cathodic current efficiency %	Cell voltage V	Visual evaluation
73	Mo	98.2	0.05	Smooth deposit
156	Mo	98.5	0.09	Smooth deposit
293	Mo	92.5	0.23	Smooth deposit
440	Mo	90.6	0.29	Smooth deposit, dendrites
633	Mo	77.0	0.30	Smooth deposit Black powder
879	Mo, MoO_2	24.8	0.31	Black powder
1466	Mo, MoO_2 , Mo_2C	24.5	0.52	Black powder

Conditions of electrolysis: copper cathode, graphite anode, temperature 1123 K, time 2700 s.

Influence of the Operating Temperature

For the study of the influence of the temperature on the deposition process, electrolyte of the same composition as in the previous paragraph and $j_c \approx 300 A m^{-2}$ was used. From Table 3 it follows that the good quality coating is possible to prepare at temperatures higher than 1073 K. At lower temperatures lower cathodic current efficiency and higher voltage across the electrolyzer is observed, probably due to higher viscosity of the electrolyte and to some problems connected with electrocrystallization. Tem-

Table 3. Effect of Temperature on Deposition of Molybdenum from KF (85 mole %)— K_2MoO_4 (10 mole %)— SiO_2 (5 mole %) Electrolytes

T K	X-Ray analysis	Cathodic current efficiency %	Cell voltage V	Visual evaluation
1073	Mo	81.2	0.25	Smooth deposit
1123	Mo	92.5	0.09	Smooth deposit
1173	Mo	95.6	0.13	Smooth deposit
1223	Mo	95.6	0.11	Smooth deposit
1273	Mo	97.6	0.07	Smooth deposit

Conditions of electrolysis: copper cathode, graphite anode, cathodic current density $293 A m^{-2}$, time 2700 s.

peratures above 1073 K do not have any significant influence on the cathodic current efficiency, the value of which is approximately 95 %. Influence of temperature was observed up to the temperatures 1273 K, which was limited by the construction of the furnace.

Influence of the Substrate

To find the influence of the cathodic material on the quality of the coatings, copper, nickel, graphite, and steel were tested (Table 4). The same electrolyte composition as used previously was used at temperature 1173 K and $j_c \approx 300 A m^{-2}$. Coatings on all used substrates were smooth and well adhesive, without dendrites on the edges. Cathodic current efficiency and voltage across the electrolyzer did not change substantially for the used substrates. C.c.e. was high (90—97 %). When graphite was used as the cathodic material, c.c.e. achieved 104 %. The value higher than 100 % can be explained by penetrating the electrolyte into the graphite, which was also confirmed by X-ray analysis, where potassium was detected in the bulk of the cathode.

Microphotographs (Figs. 5—8) show metallographic cuts of Mo-layers on different substrates. Layers on copper, nickel and graphite are well adhesive. On the steel substrate it was possible to observe the cracking of the Mo-layers under mechanical strain. This

Table 4. Deposition of Molybdenum on Different Substrates from KF (85 mole %)— K_2MoO_4 (10 mole %)— SiO_2 (5 mole %) Electrolytes

Substrate	X-Ray analysis	Cathodic current efficiency %	Cell voltage V	Visual evaluation
Copper	Mo	97.3	0.09	Smooth deposit
Graphite	Mo	103.9	0.10	Smooth deposit
Nickel	Mo	92.1	0.07	Smooth deposit
Steel CSN 11 373	Mo	95.6	0.14	Smooth deposit

Conditions of electrolysis: copper cathode, graphite anode, current density $293 A m^{-2}$, temperature 1123 K, time 2700 s.

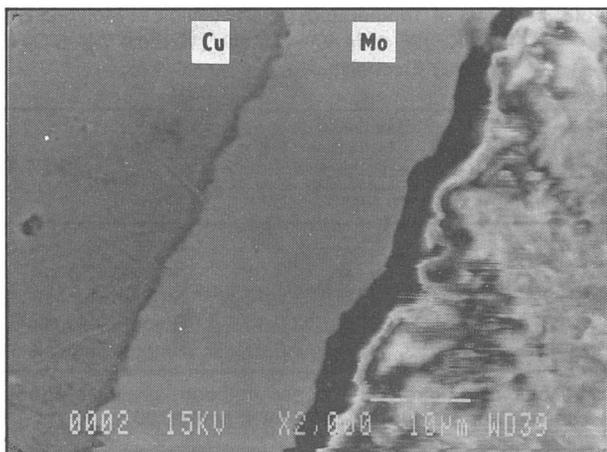


Fig. 5. Molybdenum layer on copper substrate. Conditions of electrolysis: graphite anode, current density 293 A m^{-2} , temperature 1123 K , time 2700 s .

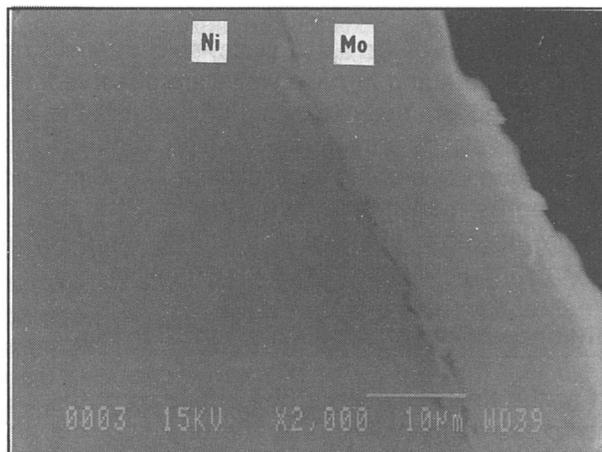


Fig. 7. Molybdenum layer on nickel substrate. Conditions of electrolysis as in Fig. 5.

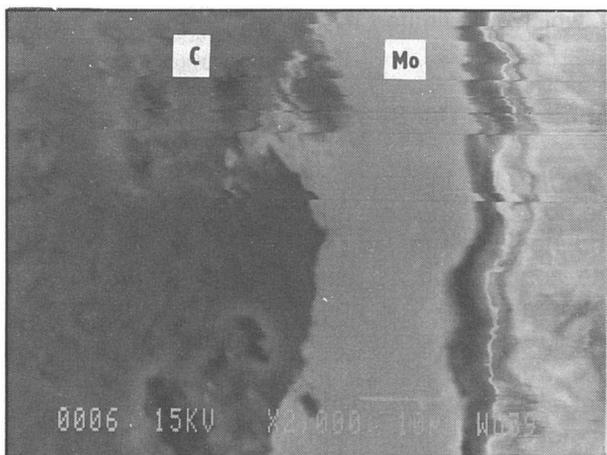


Fig. 6. Molybdenum layer on graphite substrate. Conditions of electrolysis as in Fig. 5.

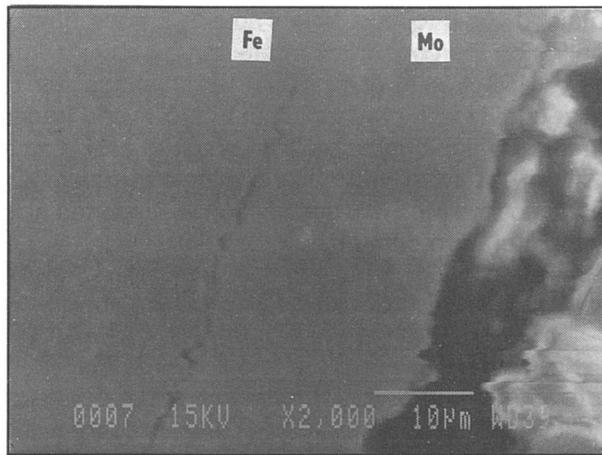


Fig. 8. Molybdenum layer on steel substrate. Conditions of electrolysis as in Fig. 5.

effect was suppressed by cleaning well the surface of the substrate, or by depositing of an interlayer of copper (or nickel) prior to the deposition of Mo.

CONCLUSION

The system $\text{KF-K}_2\text{MoO}_4\text{-SiO}_2$ was examined as the one of the potential electrolytes for preparation of Mo coatings. It was found that the binary system $\text{KF-K}_2\text{MoO}_4$ is not suitable for obtaining the Mo coatings. On the other hand, the addition of silica to the electrolyte is changing substantially the structure of the electrolyte and thus enabling the deposition of metallic molybdenum on electrically conductive substrates.

As it follows from the experiments, visually nice, smooth, and well adhesive Mo coatings were obtained from the relatively narrow composition region. The best results were obtained with electrolyte of the composition 85 mole % KF —10 mole % K_2MoO_4 —5 mole % SiO_2 , temperatures 1173 K up to 1273 K , and j_c in the range $73\text{--}450 \text{ A m}^{-2}$. Formation of the MoO_2 and Mo_2C was observed at higher j_c . There

was not found any substantial effect of the material of the substrate on the quality of the coatings.

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