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ELECTRODEPOSITION OF METALLIC MOLYBDENUM FROM AQUEOUS ELECTROLYTES CONTAINING HYDROFLUORIC ACID

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The influence of hydrofluoric acid on the cathodic reduction of molybdate ions has been investigated. It is shown that the mechanism of the process is determined by the acid concentration: in the range of concentrations less than 25 $g{\cdot}l^{-1}$ *black or colored deposits are formed on the cathodic intermediate products of reduction of the molybdate ions the average valency of molybdenum in which is 3.6–4. At concentrations higher than 50* $g{\cdot}l^{-1}$ *molybdate ions are completely reduced, forming on the cathode dense lustrous metal coatings 3–5 μm of thickness with good adhesion to the substrate. Addition of hydrofluoric acid prevents polymerization of molybdate ions. On the basis of Arrhenius equations, the effective activation energy of electroreduction of molybdate ions is determined, the ion size predetermining diffusion limitations of the processes proceeding at the film formed on the electrode surface.*

Досліджено вплив фтороводневої кислоти на катодне відновлення молібдат-іонів. Показано, що механізм процесу визначається її концентрацією. При концентрації менше 25 г/л на катоді утворюються проміжні продукти відновлення молібдат-іонів — чорні або кольорові осади, середня валентність молібдену в яких становить 3,6–4. При концентрації понад 50 г/л молібдат-іони повністю відновлюються, утворюючи на катоді щільні світлі металеві покриття товщиною 3–5 мкм з доброю адгезією до основи. Додавання фтороводневої кислоти запобігає полімеризації молібдат-іонів. З використанням рівняння Арреніуса визначено ефективну енергію активації процесу електровідновлення молібдат-іонів, величина якої характеризує дифузійні обмеження процесів, які перебігають у плівці, що формується на поверхні електрода.

Introduction

Numerous attempts to deposit metallic molybdenum from aqueous solutions of molybdate ions have not led to positive results, for example [1–3], which was accounted for by a high overvoltage of molybdenum and a low overvoltage of hydrogen on it. Thus all authors of studies, summarized and analysed partly in [2], observed formation of oxide-containing compounds on the cathode, the deposits containing molybdenum in the lowest oxidation state, though they disagreed regarding the chemical and phase structure of these compounds.

The deposition kinetics, structure of the cathode deposits formed on reduction of MoO_4^{2-} ions, and also electroreduction kinetics of these ions are investigated in detail in [4–6].

A chemical analysis has revealed that the average valency of molybdenum in the compounds formed in electrolytes containing sulfuric acid is 4.96, and the formula $xMoO_{2,4+z}{\cdot}yH_2O$ [4] (where $x : y = 1$ and $z = 0{,}1$) has been assigned to the compound deposited on the cathode.

In [3] was found that the formation of a film of molybdenum oxide-containing compounds on the cathode is the first stage of the molybdate ion electroreduction process.

We have shown [7] that a precondition for transition metal electroplating is formation on the cathode of a bifunctional electrochemical system: electrode/film /electrolyte, the central part of which, a film, consists of low-valency compounds of a particular metal, having a mixed conductivity. At the bounddary electrolyte/film takes place film formation due to the reduction of discharged metal ions to an intermediate oxidation state, and at the interface electrode/film proceeds consumption of a film substance due to further reduction of its lower valency forms to metal. As a result of the simultaneous course of these processes, the film is constantly in a condition of dynamic balance. The electrode processes at interfaces of electrode/ film/electrolyte system are easily controlled in fluoride-containing aqueous solutions where it is possible to adjust the degree of reduction of ion contained in electrolyte to metal [8].

In our work, electrodeposition of molybdenum coatings from electrolytes containing hydrofluoric acid and the role of acid in the complex formation in electrolyte were investigated. For this purpose, the complex formation and electroreduction of ions MoO_4^{2-} were investigated at various ratios of initial concentrations of molybdate ions and hydrofluoric acid.

Experimental details

The main method used for studying ions electroreduction was potential scanning voltammetry.

Voltammograms were recorded in galvanodynamic mode with the help of a pulse potentiostat PI-50-1,1 and a laboratory compensating x-y recorder PDA-004 at a potential scan rate of 0,002–0,5 V·s^{-1} and IR-error compensation.

The error of registration did not exceed ± 0,5 %. In experiments we used a three-electrode cell made of high pressure polythene, in which the auxiliary electrode was a platinum plate with a surface area of 4 cm^2, and an end of a molybdenum rod of the area 0,78 mm^2 inpressed in Teflon served as working microelectrode. Current density was related to the geometrical surface of electrode. Before every measurement the working electrode was cleansed with a fine emery paper, polished with a filter paper, degreased with Vienna lime and activated in dilute hydrochloric acid, which provided good reproducibility of the results. The Luggin capillary reference electrode had a diameter of 0.1 cm and was placed at a distance of 0.2 cm from the working electrode surface. Such arrangement of electrodes allowed us to minimize the ohmic loss [9]. A saturated calomel electrode was used as the reference electrode. The potential values are given against normal hydrogen electrode. All experiments were carried out at 20±0,1 °C.

Solutions containing 5–100 g·l^{-1} ammonium molybdate (on metal basic) and 1–100 g·l^{-1} hydrofluoric acid (or equimolar quantity of sulfuric acid) were used in the experiments. Ammonium molybdate was of reagent grade, hydrofluoric and sulfuric acids were obtained from "Sigma". Current density in electroplating varied from 0.5 to 500 A dm^{-2}, the electrodes were made of platinum.

The solid phase deposition rate (g·(A·h)$^{-1}$) on the cathode was determined by usual electrochemical method from deposit weight increase in electrolysis.

The chemical composition of the deposits obtained on the cathode in the electrolysis of the investigated solutions was determined with an atomic absorption spectrophotometer SP-9-80, and the average valency of molybdenum in the products of intermediate reduction was determined permanganatometrically [1].

The thermogravimetric analysis was carried out on a derivatograph "Orion" (Hungary) with heating in air to 900°C at a rate of 5 °C/minute, IR spectra were recorded on a spectrometer IRS-14 in the range of 4000–400 cm^{-1}.

Results and discussion

At the hydrofluoric acid concentrations of 1–25 g·l^{-1} in a current density range 0,05–50 A dm^{-2} , formation of oxide-containing compounds of intermediate reduction of ions MoO_4^{2-} was observed.

Thus at small current density (0,05–0,5 A·dm^{-2}), colored deposits and at a current density of 0,5–50 A·dm^{-2} black deposits were formed. The rate dependence of deposition of oxide-containing compounds resulting from MoO_4^{2-} ions intermediate reduction on hydrofluoric acid concentration in electrolyte is shown in fig. 1.

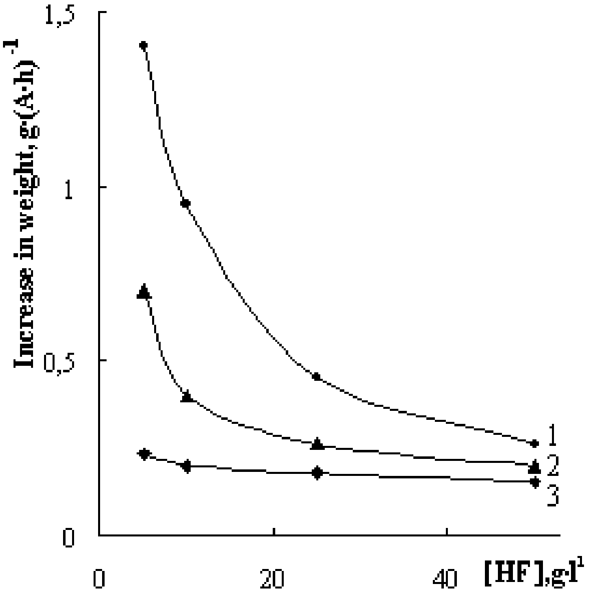


Fig. 1. Dependence of oxide-compounds of intermediate reduction of MoO_4^{2-} ions deposition rate from hydrofluoric acids concentration at the current density:
1 is 0,5;
2 is 1,0;
3 is 10

The rate of formation of these products on the cathode decreases with increasing hydrofluoric acid concentration in electrolyte.

The thermograms of the deposits of intermediate reduction oxide-containing compounds obtained are characterized by a number of endothermic effects, which are caused by loss of water and OH groups. So, in the temperature range 140–180°C, an endothermic effect is distinctly observed, caused by loss of water, the quantity of which was 5–9 %.

On further heating in a temperature range 350–380°C, removal of OH-groups was observed, thus the weight loss was 12–14 %.

The results obtained are in agreement with the analysis data [10] for the synthesized oxide-hydroxide compounds of molybdenum. In this case, the endothermic effect caused by removal of water is observed at 160°C, the weight loss was 12 %.

The IR-spectroscopic data confirm the presence of water and OH-groups in oxide-containing compounds regneting from molybdate ions intermediate reduction. Absorption is observed in the region of O–H stretches at 3707 cm^{-1} and deformation vibrations near 969 and 938 cm^{-1} for the samples obtained in a current density range 0.05–50 $A{\cdot}dm^{-2}$ at various concentrations of hydrofluoric acid. Molecular (crystallization) water absorbs at 3268–3258 cm^{-1} (stretching vibration) and 1643 cm^{-1} (deformation vibration).

The results of determination of the average valency of molybdenum in the intermediate products of MoO_4^{2-} ion reduction are presented in table.

Dependence of average valency of molybdenum in intermediate reduction products of MoO_4^{2-} ions on hydrofluoric acids concentration in electrolyte

Kind of a deposit	Hydrofluoric acids concentration, g/l	Average valency
Color	5	4,0
	10	3,9
Black	5	3,4
	10	3,6

In the black deposits the average valency of molybdenum is lower, and the degree of MoO_4^{2-} ion electroreduction, accordingly, is higher in comparison with the colored deposits. Thus, the general rule for these two cases is decrease in the average valency of molybdenum in the products of intermediate reduction with increasing hydrofluoric acid concentration in electrolyte in the range specified.

When the hydrofluoric acid concentration in electrolyte was increased above 50 $g{\cdot}l^{-1}$ and at a higher current density of 70–400 $A{\cdot}dm^{-2}$, no products of intermediate reduction of molybdate ions were deposited on the cathode. Thus, there takes place deposition of metallic - molybdenum coatings, i.e. complete electroreduction of Thus, increase in the number of ligands in the structure of an uncharged particle in molybdenum fluoride complex formation along with prevention of polymerization of metal ions in solution (a phenomenon known not only for molybdenum, but also for the ions of such metals as tungsten, titanium and niobium) causes a decrease in the activation energy of charge transfer to this particle.

An increase in polarization leads to acceleration of electrode processes as a result of an increase dissociation rate of complex compounds.

Voltammograms of MoO_4^{2-} electroreduction processes in the presence of hydrofluoric and sulphuric acids are shown in fig. 3 ion, which is confirmed by the percentage of molybdenum in the deposits obtained on the cathode as function of hydrofluoric acid concentration (fig. 2).

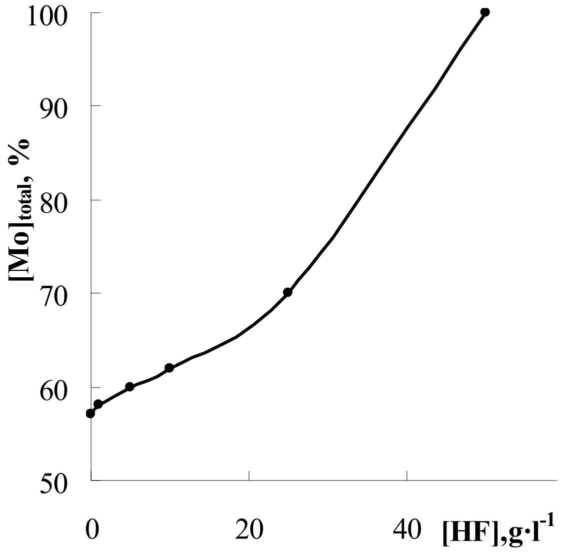


Fig. 2. Dependence of the content of molybdenum in deposits as function of hydrofluoric acid concentration

The results observed can be explained basing on the concepts of the bifunctional electrochemical system electrode/film/electrolyte, suggested in [7].

The rate of the electrochemical reaction of intermediate reduction product formation at the electrolyte/film interface exceeds the rate of molybdenum reduction to metallic state from the solid-phase products of the cathode film at the film/electrode interface, which takes place in the range of low fluoride-ion concentrations in the electrolyte at low current density.

A similar phenomenon was observed in the case of electroreduction of chromium [11, 12], manganese [13], nickel, copper [11], rhenium [14] ions.

Complete electroreduction of metal ions occurs in the case where equality of reaction rates for the formation of intermediate reduction products and their subsequent discharge to metals are ensured, the process taking place at the interface of the electrode/film/electrolyte system.

The data obtained correspond to the results of the study of the composition and structure of the complexes formed in the electrolytes investigated.

It is known that anions MoO_4^{2-} has strong tendency to polymerize [15], especially in acidic media, where according to [16] an equilibrium is established:

$$MoO_4^{2-} + 8H^+ \qquad Mo_7O_{24}^{6-} + 4H_2O.$$

This balance in acidic media is practically quantitatively shifted to the formation of a heptamolybdate ion since it is characterized by a very high value of equilibrium constant, which is $5{,}5\cdot10^{57}$ [17].

Accordingly in acidic media molybdenum ions exist in polymeric forms, whose presence, as is known, hinders electrodeposition of metals.

At the same time it has been found, that fluoride ion in aqueous solutions destroys polymers even at a greater concentration of hydrogen ions [18]. Hydrofluoric acid concentration and hydrogen ions in electrolyte determine the structure and stability of the complexes formed [19].

In the range of small hydrofluoric acid concentrations (up to 10 $g\cdot l^{-1}$), a rather stable complex is formed, containing three fluoride ions, the conditional constant stability constant of which is $\lg \beta_3 = 3{,}8 \pm 0{,}6$.

In the range of greater concentrations of ligands (more than 50 $g\cdot l^{-1}$), a complex ion with four ions HF_2^- is formed, the conditional stability constant of which is $\lg \beta_4 = 3{,}0 \pm 0{,}5$.

Thus, increase in the number of ligands in the structure of an uncharged particle in molybdenum fluoride complex formation along with prevention of polymerization of metal ions in solution (a phenomenon known not only for molybdenum, but also for the ions of such metals as tungsten, titanium and niobium) causes a decrease in the activation energy of charge transfer to this particle. An increase in polarization leads to acceleration of electrode processes as a result of an increase dissociation rate of complex compounds.

Voltammograms of MoO_4^{2-} electroreduction processes in the presence of hydrofluoric and sulphuric acids are shown in fig. 3.

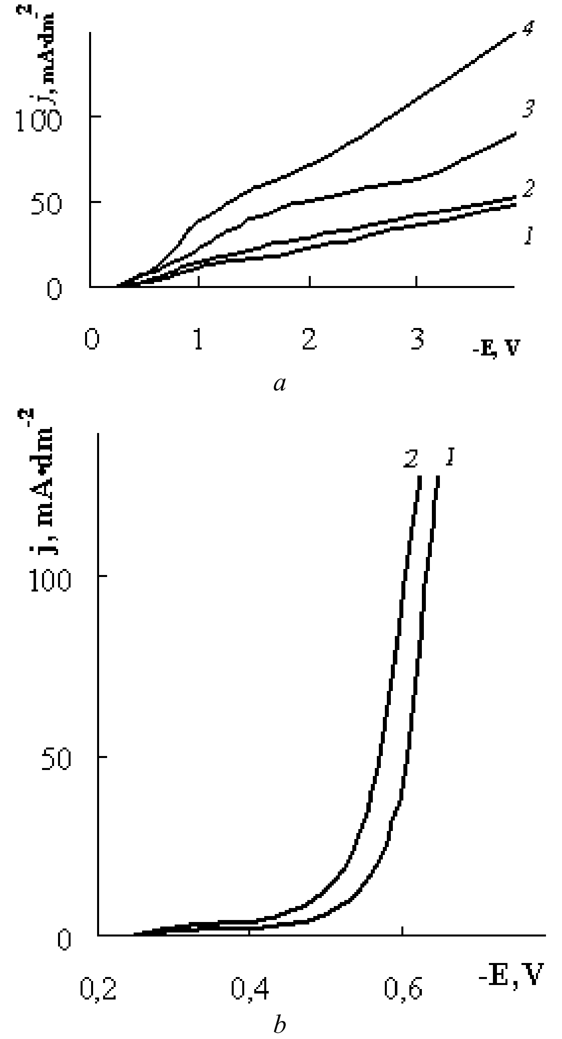
More electronegative values of cathode potential in the electrolytes that contain hydrofluoric acid are caused by a stronger complexing action of F^- ion and, accordingly, formation of stronger, in comparison with sulphate, complex compounds.

Studying polarization in molybdate ion electroreduction has shown that its character is determined by hydrofluoric acid concentration (fig. 3, *a*).

At low acid concentration (less than 5 $g\cdot l^{-1}$), the total rate of electroreduction process is low, which is evidenced by the small slope angle in the initial part of the voltammograms (curves *1*, *2*, fig. 3, *a*). The electrode potential is considerably shifted towards more electronegative values. Increase in hydrofluoric acid concentration in the electrolyte contributes to significant acceleration of the overall process of MoO_4^{2-} ion reduction (curves *3*, *4* fig. 3, *a*).

When the hydrofluoric acid concentration is increased to 50 $g\cdot l^{-1}$, the catode potential at the current density of 25 $A\cdot dm^{-2}$ shifts towards electropositive values by 2–2,5 V. It will be noted that rise in temperature also shifts the cathode potential towards more electropositive values, however the magitude of this shift is much smaller than that observed on hydrofluoric acid concentration change.

The voltammograms recorded for the electrolytes containing sulfuric acid (fig. 3, *a*) differ from those recorded for the electrolytes containing hydrofluoric acid in shape and potential value. On these voltammograms there are no extreme points, and the voltammograms themselves are located in the region of more electropositive potentials, not exceeding – 0,8 V.



a

b

Fig. 3. Polarizing curves for MoO_4^{2-} ions reduction in the electrolytes containing:
a is [Mo] = 10, HF: 5 (*1*), 10 (*2*), 25 (*3*), 50 (*4*);
b is [Mo] = 10, H_2SO_4: 49 (*1*), 123 (*2*)

The electrode process at the beginning slightly depends on the change of potential sweep rate; all voltammograms exhibit a characteristic delay up to a potential of approximately –0.5 to. –0.55 V, where the current density is extremely low, and on further polarization increase there is a sharp increase in current density. Thus, on the cathode are formed only carbonaceous deposits, the structure of which differs greatly from that of black deposits obtained from electrolytes containing hydrofluoric acid. Metallic molybdenum does not deposit in the entire range of current density and sulfuric acid concentration in electrolyte.

On hydrofluoric acid concentration increase, the rate of the electroreduction process sharply increases, which indicates reduction of nonelectroactive polymolybdate ions in the electrolyte and an increase in the number of fluorine-containing electroactive complexes which are formed as a result of complexation of polymolybdate ions complexation with fluoride ions [19]. The electrode potential thus shifts towards more electropositive values. The increase in polarization results in electrode process acceleration owing to an increase in the dissociation rate complex compounds.

Several regions on the voltammograms recorded for the solutions containing hydrofluoric acid gives evidence of various processes occurring at the cathode.

The analysis of polarization curves and examining under a microscope (x500) molybdenum oxide-containing films deposited on the cathode surface allow to draw the conclusion that each of the voltammogram regions characterizes processes of formation of oxide-containing compounds of molybdenum resalting from intermediate reduction, the average valency of molybdenum in which decreases with increasing current density.

The increase in the degree of MoO_4^{2-} reduction on increase of hydrofluoric acid electrolyte concentration, reflected by the initial parts of the voltammograms, were confirmed by a chemical analysis (see table).

At a current density of 0,25–2,5 $A{\cdot}dm^{-2}$, colored films are formed on the cathode: in a current density range of 2,5–15 $A{\cdot}dm^{-2}$, dark deposits and at a current density of more than 25 $A{\cdot}dm^{-2}$ black deposits.

Metallic molybdenum is deposited as semibright deposits at a hydrofluoric acid concentration above 25 $g{\cdot}l^{-1}$ and a current density of more than 70 $A{\cdot}dm^{-2}$. Under these conditions, it is possible to obtain lustrous, dense molybdenum coating up to 5 microns thick, though the current yield is insignificant and is only 0,6–1,7% in terms of current density.

Thus the critical current density of metallic molybdenum deposition increases with hydrofluoric acid concentration in the electrolyte (fig. 4), which opens up great possibilities for electrodeposition process intensification.

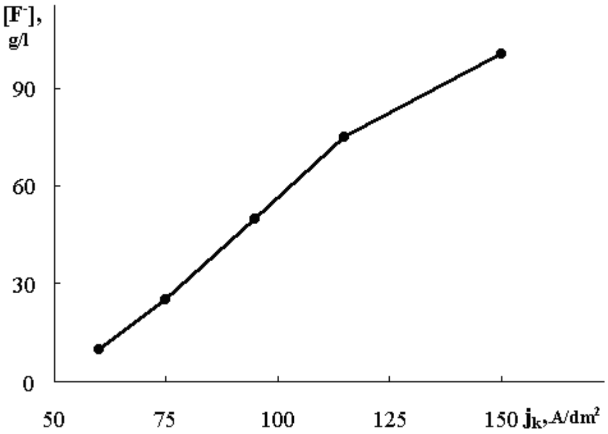


Fig. 4. Dependence of critical current density on deposition of metallic molybdenum on concentration in electrolyte hydrofluoric acids

Molybdenum coating has a good adhesion to the surface of not only platinum, but also mild steel and low-alloy steel, therefore it can find application as an anticorrosive coating, for example, for the protection of welding wire against corrosion [20]. During tests it was found that such wire with molybdenum coating considerably improves formation of weld seams.

Alloying a seam with molybdenum improves its mechanical properties, in particular, the resistance of seams to crystallization cracks increases, and metal spray in welding decreases.

Figure 5 shows voltammograms of molybdate ions reduction at various potential scan rates in a solution containing hydrofluoric acid.

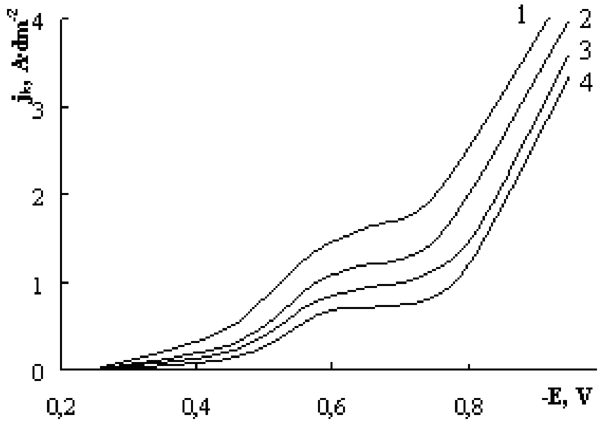


Fig. 5. Voltammogramms of cathodic reduction of MoO_4^{2-} ions in electrolyte of composition: [Mo] = 10, HF – 10, at the potential scanning rate, $мВ{\cdot}с^{-1}$: 100 (*4*); 50 (*3*); 20 (*2*); 10 (*1*)

The electrode process in the range of potentials preceding the limiting current depends weakly on the potential sweep rate.

Microscopic examination allows one to ascertain that formation on the electrode of a film of oxide-containing compounds of molybdenum resulting from intermediate reduction is observed. The plateau for this limiting current is reduced with increasing rate of polarization change, and at a rate of more than 0,2 $V \cdot s^{-1}$ the limiting current on voltammograms is not found at all.

At the maximal change in polarization rate, $|dE/d\tau|$, the ascending branch of the curve, corresponding to the reduction of molybdate ions, begins from less electronegative potentials. Along the decrease in the potential sweep rate, the voltammograms shift towards more negative potential values with simultaneous reduction of limiting current. The dependences of the limiting current ($i_{\lim}$) magnitude on potential scan rate V, in the coordinates $i_{\lim} - V^{1/2}$ are approximated by straight lines (fig. 6), thus evidencing diffusion kinetics of the processes which proceed in the range of potentials that characterize these regions of voltammograms.

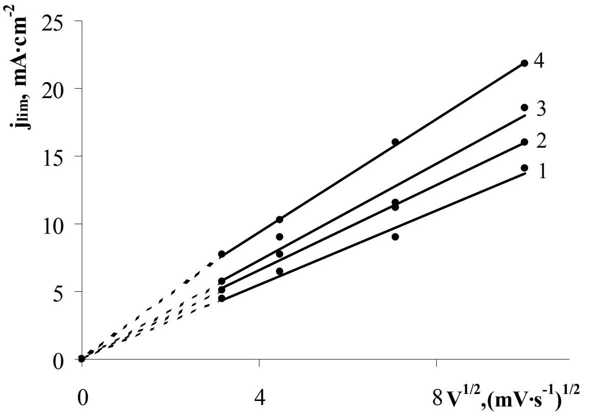


Fig. 6. Dependence of a limiting current voltammogramms in the electrolytes containing: [Mo] = 10, HF: 5 (*1*), 10 (*2*), 25 (*3*), 50 (*4*), on the potential scanning rate

The electrochemical parameters of molybdenum of electrodeposition are determined from the current yield of molybdenum and hydrogen during electrolysis.

Figure 7 shows a partial polarization curve of electroreduction of MoO_4^{2-} ions in an electrolyte with a hydrofluoric acid concentration of 50 $g \cdot l^{-1}$.

The factor *b* of Tafel equations is 0,47 V. Such magnitude of this factor allows one to make the conclusion that the metal deposition process on the cathode occurs starting from the oxide film substance, the statement which, in turn, confirms the results presented in [7].

The exchange current magnitude, determined by the straight line portion of the partial cathodic polarization curve extrapolated to zero overvoltage, was $i_o = 3{,}16 \cdot 10^{-7}$ A cm^{-2}. When the hydrofluoric acid concentration is increased, the exchange current magnitude increases, thus testifying an increase in the rate of the electrochemical process in these conditions. Thus, different cathodic reaction rates and the completeness of electroreduction of MoO_4^{2-} ions are determined by the nature of ligand and its concentration.

In the range of small and higher fluoride ion concentrations, as has been shown, complex compounds of various structures are formed, which along with the prevention of the polymerization process determines the kinetics of the cathodic process and provides such magnitude of cathodic polarization at which electrodeposition of metallic molybdenum on the cathode becomes possible.

Increase of temperature considerably increases the rate of the electrochemical process concerned.

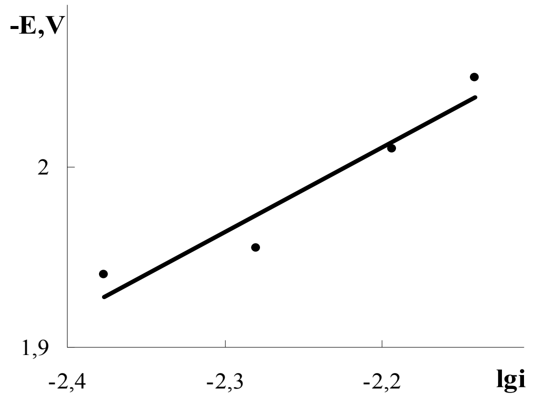
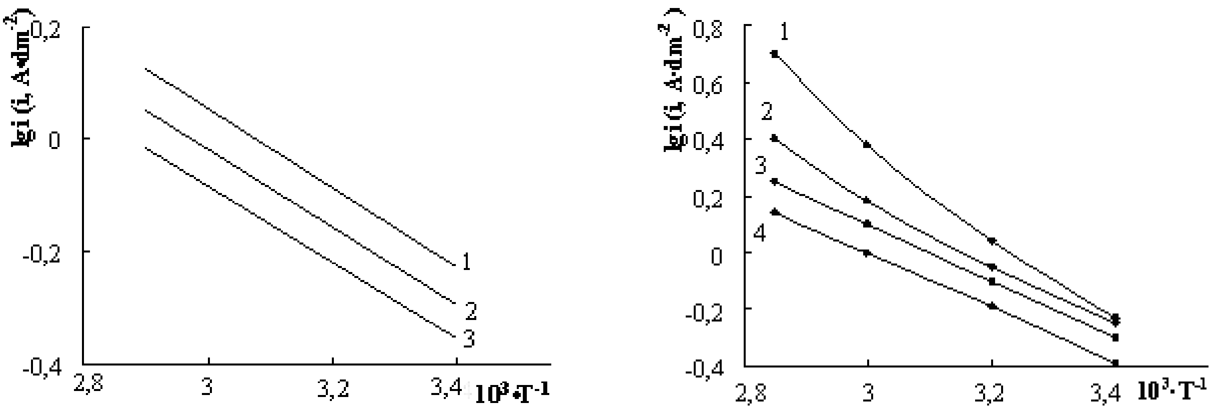


Fig. 7. Partial polarizing curve of reduction of ions in the electrolyte containing 10 $g \cdot l^{-1}$ of molybdenum (on metal) and 50 $g \cdot l^{-1}$ hydrofluoric acids

The linearity of $lgi - 1 \cdot T^{-1}$ plots (fig. 4) at a constant value of potential in a broad range of temperatures, i.e. formal similarity to Arrhenius equation, allows one to determine on its basis the value of effective activation energy.

Thus the trend of $lgi - 1 \cdot T^{-1}$ plots, obtained for the electrolytes containing more than 25 $g \cdot l^{-1}$ hydrofluoric acid, indicates that the process of molybdate ion reduction on metal is accompanied by diffusion limitations (fig. 8, *a*).

At the same time, in the range of small hydrofluoric acid concentrations, when formation of oxide-containing compounds by MoO_4^{2-} intermediate reduction takes place, the process is limited by activation polarization (fig. 8, *b*), the reason of which is cathode film formation [21].



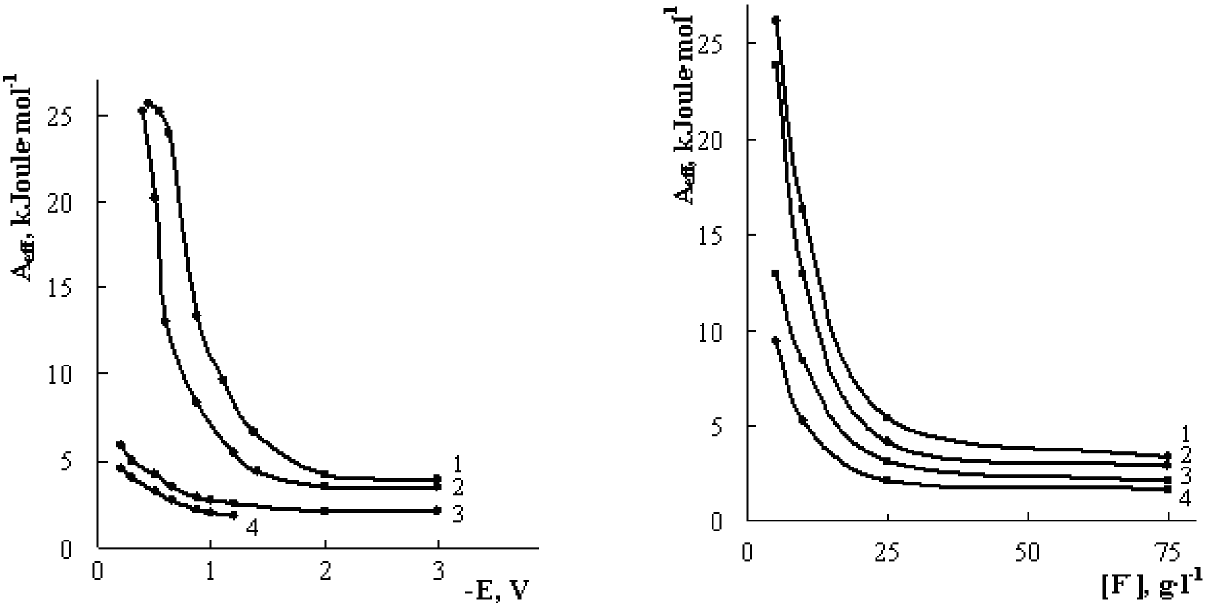
a *b*

Fig. 8. Temperature dependences of rate of ions cathodic reduction in the electrolytes containing [Mo] = 10 g·l^{-1}:
a is 25 g·l^{-1} hydrofluoric acids at potentials, V: 2,0 (*4*); 2,2 (*3*); 2,4 (*2*);
b is 5 g·l^{-1} hydrofluoric acids at potentials, V: 0,75 (*4*); 1,0 (*3*); 2,0 (*2*); 3,0 (*1*)

The apparent discrepancy between these results can be avoided by the assumption that the value of effective activation energy characterizes the diffusion limitations of the processes proceeding in a film formed on the electrode surface since at the film/electrolyte interface the polarization is of activation character [22].

The effective activation energy of electroreduction of molybdate ions in the presence of hydrofluoric acid depends strongly essentially not only on the electrode potential (fig. 9, *a*), but also on the hydrofluoric acid concentration in the electrolyte (fig. 9, *b*), which determines the metal surface condition in various regions of polarization curve; in this case, a redistribution process rates takes place within the electrochemical system electrode/film/electrolyte at the interfaces [14].

The magnitude of the effective activation energy of MoO_4^{2-} electroreduction decreases proportionally to the increase of potential, which lowers the reaction potential barrier electrostatically (fig. 9, *a*), the fact is especially clearly shown in the range of low hydrofluoric acid concentrations.



a *b*

Fig. 9. Dependence of effective activation energy of cathodic reduction of ions in the electrolytes containing [Mo] = 10 g·l^{-1}:
a – on potential of an electrode at hydrofluoric acid concentration, g·l^{-1}: 5 (*1*); 10 (*2*); 25 (*3*); 50 (*4*);
b – on hydrofluoric acid concentration at potential of an electrode, V: 0,5 (*1*); 0,6 (*2*); 0,9 (*3*); 1,2 (*4*)

Thus, as the polarization potential and the rate of electrode reaction increase there takes place a gradual decrease in the contribution of activation polarization and the role of diffusion limitations increases.

Thus, the effective activation energy gradually decreases to about 5 kJ mol^{-1}. The practically constant value of effective activation energy in the case of electrode potential variation a potential range of 2–3 V at low hydrofluoric acid concentrations in electrolyte (fig. 8, *a*) and in a hydrofluoric acid concentration range of 25–50 g l^{-1} at potentials of 0,5–1,2 V (fig. 9, *b*) is noteworthy.

It may indicate not only diffusion limitations of the electrode process [21], but also mutual compensation of simultaneous decrease in activation energy on electrode potential increase and its on incrrease in the derivative of current with respect to temperature in the Arrhenius equation due to an increase in the diffusion permeability of the cathode film, which acts as negative feedback. A similar fact of absence of dependence of effective activation energy in the case of potential variation was also noted in the anodic dissolution of nickel [23; 24].

On the whole, as the hydrofluoric acid concentration in the electrolyte increases the activation energy of electroreduction of molybdate ion being discharged decreases greatly; this was also observed when studying activation energy variation by varying the ligand concentration variation, and also when studying the structure of compounds deposited on the cathode CrO_4^{2-} electroreduction in the presence of at hydrofluoric acid.

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