

Texture of electrolytic Mo deposition from molten alkali halide

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The electrocrystallization and texture of electrodeposited molybdenum in molten electrolytes has been investigated. Nucleation and growth of molybdenum electrodeposition on nickel electrode in NaCl-KCl-NaF molten electrolyte containing K_2MoO_4 under potentiostatic and galvanostatic conditions at 1123 K were focused on the influence of electrodeposition conditions on the nucleation phenomena and growth kinetics. Molybdenum initially nucleated and grew according to a three-dimensional diffusion controlled progressive nucleation process and later according to an instantaneous nucleation process. The nucleation density of molybdenum was high on the initial stage of electrolysis producing a fine and uniform electro-deposition. At long time of electrolysis, the nucleation density significantly reduced to about one hundredth of the initial stage and then decreased slightly with increasing electroplating molybdenum time. These investigations suggest that some (unelucidated) inhibition processes and reactions control the growth and texture of molybdenum.

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1. Introduction

An increasing number of applications are being found for molybdenum in high-technology areas such as nuclear power, missile, space industry or microelectronics due to its chemical and mechanical properties. However, the production methods, such as compact power sintering and arc casting, are expensive and useful forms of molybdenum metal are difficult to fabricate.

Electrodeposition of molybdenum power and coating from molten electrolytes is a more advanced method, but the literature containing relative very little fundamental information on the behavior of molybdenum compounds in molten systems and electrocrystallization phenomena and texture of electrodeposited molybdenum in special.

The present investigation was undertaken in order to study the electro reduction of Mo^{6+} compounds and to elucidate the nucleation, electrocrystallization and texture of Mo deposited on Ni surface.

2. Experimental

The electrolysis cell: -- The electrodeposition was carried out in a 15 cm diameter argon atmosphere electrolytic cell. The cell consisted of a lower chamber, electrolytic chamber and an upper chamber, act as the receiver for molybdenum deposits. The receiver was equipped with a water cooled receiver-lock where the cathode deposit was held for cooling in argon atmosphere before removal from the cell in order to prevent oxidation of molybdenum metal, deposited at high temperatures. A stainless steel crucible (12 cm internal diameter, 13 cm outer diameter and 20 cm long) was used to contain the electrode. This crucible also acts as anode. A nickel strip (0.8 to 1.0 cm.) was used as cathode. The experiments

were conducted at 1023 K and 1123 K temperature controlled within ± 5 K.

Upon completion of electrolysis, the cathode deposit was lifted to the receiver chamber, locked and permitted to cool to room temperature before removal. The molybdenum, thus obtained, were dipped in dilute HCl solution, stripped from the cathode, washed and rinsed repeatedly, first with water and then with acetone in order to remove the entrained electrolyte from the crystals. The electrolytic bath consists of a NaCl-KCl-NaF (Merck) eutectic mixture (60.5-22.5-17 mol %) [1]; all are of advanced purity so that no previously purification was needed. The salts were then melted in argon atmosphere. The Mo compounds were introduced into the bath in the form of K_2MoO_4 (Merck high purity).

The surface morphology, granulometry and composition of the electrodeposits of Mo were observed using SEM (Scanning Electron Microscopy) and XPS (X-ray Photoelectron Spectroscopy) methods.

3. Results and discussion

Preliminary tests, with baths containing different alkali halide compounds and different concentrations of the molybdenum salt, indicate that the best deposits were obtained in NaCl-KCl-NaF (60.5-22.5-17 mol %) molten electrolyte containing nearly saturated with the K_2MoO_4 . The deposition was carried out over a range of current densities from 0.05 to 1.5 A/cm² and over a temperature of 1123 K. The experimental conditions and other observations is given in Table 1.

The deposits usually consisted of rather coarse powder with an average diameter of about 0.05 mm. In many instances, however, a layer of deposit immediately

next to the cathode, about 0.01 mm in thickness, was adherent to the cathode and appeared quite dense. Typical deposits obtained from this electrodeposition experiments is shown in Fig. 1.

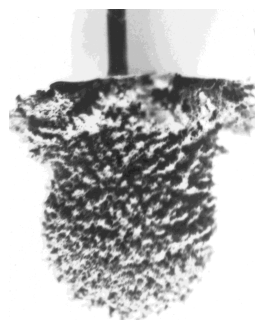


Fig. 1. Typical deposit at electrodeposition of Mo on Ni electrode: $i_c = 0.50 \text{ A/cm}^2$; $C_{K_2MoO_4} = 42 \cdot 10^{-3} \text{ mol\%}$; $T = 1123 \text{ K}$.

It has been established [2] that in a wide range of cathode densities the phase overvoltage depends on current density logarithmically, similarly to the Tafel dependence:

$$\eta = a + b \log i \quad (1)$$

Analysis of the data reported in literature [3-6] shows that the values of the coefficient a and b vary widely between different electrode – deposited metal – electrolyte systems: $a = 40\text{-}230 \text{ mV}$ and $b = 10\text{-}85 \text{ mV}$. The coefficient a decreases with increasing temperature and/or concentration of the deposited metal in the melt. These dependences are accounted for by the fact that the interaction between metal and the substrate becomes stronger at highest temperatures.

Table 1. Molybdenum deposit from NaCl-KCl-NaF- K_2MoO_4 molten electrolyte.

Electrolyte mol %	K_2MoO_4 mol %	Current density A/cm^2	Deposition time, h	Type of deposit
NaCl-KCl-NaF 60.5-22.5-17	$4.2 \cdot 10^{-3}$	0.05	0.5	Nonmetallic black powder
		0.5	2	Metallic black powder
		1.0	4	Powder consists of small platelets over adherent plate
		1.5	6	Granular metallic powder over adherent layer
	$21 \cdot 10^{-3}$	0.05	0.5	Nonmetallic black powder
		0.5	2	Amorphous metallic powder
		1.0	4	Microdendrites
		1.5	6	Well shaped metallic dendrites
	$42 \cdot 10^{-3}$	0.05	0.5	Amorphous metallic powder
		0.1	1	Powder consists of small platelets over adherent plate
		0.5	2	Bright, compact and adherent deposit
		1.0	4	Dendrites with principal and secondary direction of growth
	$84 \cdot 10^{-3}$	0.05	0.5	Nodular superficial coherent molybdenum deposit overlying thin coherent layer
		0.5	2	Dendritic Mo powder overlying adherent layer
		1.0	4	Powder consists of small platelets over adherent plate
		1.5	6	Granular metallic powder over adherent layer

In the case when dilute solutions of a salt of the metal being deposited are subject to electrolysis in a melt, the growth rate of a crystal nucleus is determined by diffusion of discharging ions its surface.

The influence of duration of electrolysis and cathode current density on the nucleation and growth mechanism is demonstrated in Fig. 2 and 3:

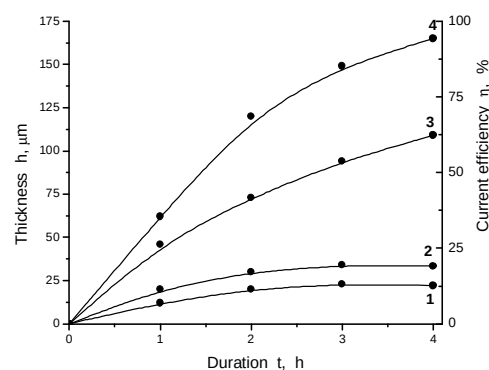


Fig. 2. The thickness of a molybdenum coating and its current efficiency on nickel electrode vs. the duration of electrolysis at: 1) $i_c = 0.01 \text{ A/cm}^2$; 2) $i_c = 0.1 \text{ A/cm}^2$; 3) $i_c = 0.2 \text{ A/cm}^2$; 4) $i_c = 0.5 \text{ A/cm}^2$.

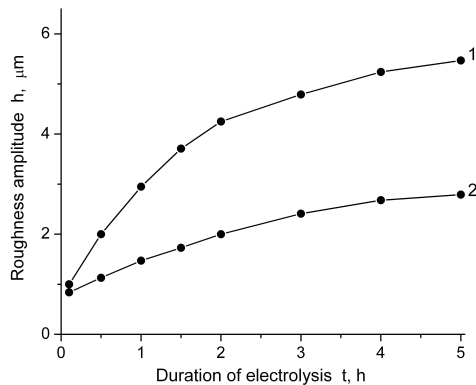


Fig. 3. The roughness amplitude of molybdenum coating on nickel vs. the duration of electrolysis at: $i_c = 0.5 \text{ A/cm}^2$; 2) : $i_c = 0.05 \text{ A/cm}^2$.

The average grain size increases from about $13.5 \mu\text{m}$ at a current density of 0.10 A/cm^2 to about $20 \mu\text{m}$ at 0.20 A/cm^2 . The quantitative estimation of the phase over-voltage yields values of 10-40 mV for nickel electrode at 1123 K.

The current-time transient were recorded by applying a potential pulse from an initial value for which zero or minimal current was detected. The shapes of the current-time profiles were related to nucleation and three-dimensional growth behaviour. The interesting feature of the current-time transient is the rising region of the peak, which corresponds to the density of nuclei before overlapping of the first monolayer of the growing nuclei occurs. This region therefore can be used to derive the kinetics of the nuclei growth. The typical current-time behaviour is presented in Fig. 4. There are three characteristic regions in the current-time curves. The first is an initial pulse of very short duration corresponding to a high current intensity, which is probably related to the double layer charging transient. This is then followed by a second region where a short and essentially small constant current is observed indicating an induction period. As molybdenum nucleates and grows the current increases with time to give the third region.

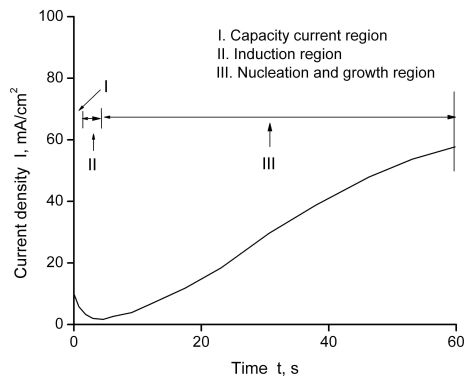


Fig. 4. The current – time transients for molybdenum electrodeposition on nickel surface.

The sets of I/t transients measured at different molybdenum concentrations and potentiostatic pulse for electrodeposition of molybdenum obtained on the nickel electrode substrate are presented in Fig. 5 (applying different potentiostatic pulse for a period of 160 s in a molten electrolyte containing $42 \times 10^{-3} \text{ mol \% K}_2\text{MoO}_4$). In all the transient curves, a maximum current I_{max} is observed at time t_{max} that is dependent both on the pulse potential. The current then fall and maintains a near constant value up 140 s. Then results show that the potentiostatic pulse play an important role during electrocrystallization. This t_{max} value can be related to the time at which full coalescence of the molybdenum crystallites occurs.

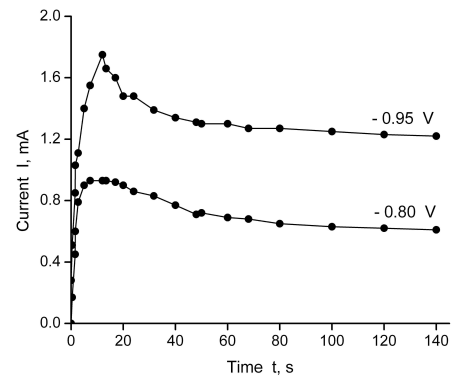


Fig. 5. The current – time curves of molybdenum deposition on nickel substrate.

Microstructural analysis of the dynamics of growth of the new phase (molybdenum deposit) shows a great number of crystallization centers are formed at the beginning of the process. Then, separate crystals grow and merge into a continuous layer with the formation of a plane crystallization front, finally, the deposit transform into massive dendrites or coherent, compact layers.

SEM micrographs of the Mo are presented in Figs. 6 and 7 in order to illustrate the difference in the growth mechanism.



Fig. 6. Mo microdendrites growth on nickel electrode surface at 1023 K.

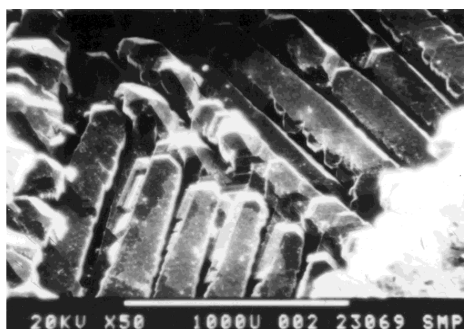


Fig. 7. SEM photograph of a Mo deposit obtained at 1023 K and $i_c = 0.10 \text{ A/cm}^2$.

The structural parameters of single crystals, dendrites and their forms varied as a function of the degree of diffusion complications at the deposit growth front, which settle at different combinations of the given current, the temperature and the concentration of the molybdenum ions in molten electrolyte. In the region of deeper diffusion limitations (Fig. 6) the dendrites had long side branches of practically cylindrical form; a decrease in the diffusion limitations led to the shortening of the side springs, which acquired to form flat petals (Fig. 7).

The XRD patterns from the surface of the coatings more than $30 \mu\text{m}$ in thickness showed that the coatings were single-phase, had a bcc structure, and typically exhibited a well-defined preferential orientation (Fig. 8).

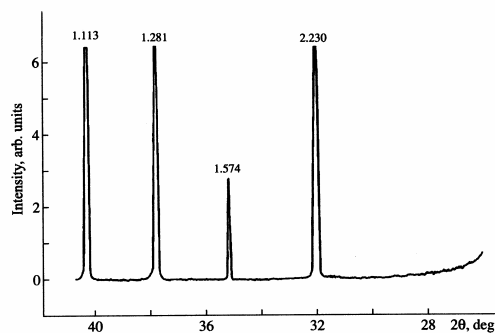


Fig. 8. XRD scan of an electrodeposited Mo coating on nickel electrode surface.

Using a conventional X-ray diffractometer operated in the $2\theta-\Omega$ mode, it was found that the Mo electro deposit exhibits a strong $\langle 111 \rangle$ texture. The lattice parameter a of Mo was $3.1465 - 3.1475 \text{ \AA}$ in good accord with data from literature [7-9]. The total intensities of the peaks were obtained by integration allowing for the intensity factor correction. This gives a distribution of the lowest index directions as follows: $\{111\}$ about 99%, $\{110\} < 1\%$, $\{200\} < 1\%$, $\{211\} < 1\%$, and $\{310\} < 1\%$.

4. Conclusions

Molybdenum coatings were produced on the nickel by electrodeposition from $\text{NaCl-KCl-NaF-K}_2\text{MoO}_4$ molten electrolyte. The kinetics of growth, surface roughness, and chemical purity of the coatings were studied as a function of deposition conditions. The following conclusions were drawn:

1. The surface morphology of Mo electrodeposition on Ni electrode depends on the applied cathodic current density. At low current density such as 0.2 A/cm^2 , a thin and flat layer of Mo was formed without granule type deposits. On the other hand, at 0.5 A/cm^2 or higher, Mo particles with a granule or coherent layer type were formatted on the thin and flat Mo layer.

2. The typical current transient curve for electrodeposition of Mo is divided into three regions: capacitive current region, induction region and nucleation and growth region. The induction time for the nucleation of Mo formed on the Ni electrode, defined as the period from the end of charging double layer to a new nucleus being formed, increased either with decreasing cathodic overpotential or with increasing Mo plating time.

3. Molybdenum electrodeposited on the nickel electrode was initially nucleated and grow according to a three-dimensional diffusion controlled progressive nucleation process, and later according to an instantaneous nucleation process. The period during which nucleation is controlled by the diffusion controlled progressive nucleation process decreases with increasing molybdenum plating time.

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