



# Electrodeposition of thick metallic amorphous molybdenum coating from aqueous electrolyte



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## ABSTRACT

The electrodeposition of thick metallic molybdenum coating from aqueous electrolyte considered difficult for a long time owing to high reactivity with oxygen. In the present study, a successful attempt was made to electrodeposit thick (~25 μm), metallic bright Mo coating by DC electrolysis from a water deficient aqueous electrolyte containing molybdate ions. Energy-dispersive spectroscopic (EDS) analysis confirmed the presence of Mo along with low content of oxygen on top surface. The crystal structure of as-deposited Mo coating was amorphous in nature, as monitored by in situ XRD investigation, which transformed into crystalline BCC structure upon vacuum annealing. The surface morphology of Mo coatings as investigated by scanning electron microscopy (SEM) revealed the presence of several cracks without any grain structure. Transmission electron microscope micrographs showed the featureless microstructure of amorphous molybdenum, which was further ascertained by the appearance of a continuous ring pattern in the selected area electron diffraction pattern (SAED). XPS analysis confirmed deposition of reduced Mo(0) metal and the top layer converted to Mo oxides upon keeping in ordinary atmosphere. Nanoindentation measurements showed a drastic improvement of nanohardness of as-deposited (2186 ± 455 MPa) to coatings (4187 ± 910 MPa) after annealing at 700 °C.

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## 1. Introduction

Metallic molybdenum (Mo) possesses a high melting point (2623 °C), low thermal expansion coefficient, good thermal shock resistance and wear resistance, which makes it a suitable candidate for high temperature applications, automotive industry and space applications. Molybdenum coatings are normally used to increase thermal and wear resistance of materials [1–3]. These molybdenum coatings are often produced by expensive and energy-consuming techniques like thermal spraying [3,4] and low-pressure plasma spraying [5]. Electrodeposition is considered one of the simple and economical techniques for deposition of coatings on various substrate materials. However, the electrodeposition of molybdenum from aqueous solutions is very difficult due to several factors. Molybdenum exists in its stable oxidation state of +6, mainly in the form of oxides or oxyanions and in aqueous solutions depending on the pH it also forms complex polymeric molybdates [6,7]. The electrodeposition of molybdenum involves reduction of hexavalent molybdate ions (Mo<sup>6+</sup>). In this process, molybdenum might get reduced to lower valence states, resulting in the formation of hydrated

oxides, basic salts or oxides [6,8]. The reduction potential of Mo<sup>6+</sup>/Mo is –0.913 V, and Mo has low hydrogen overpotential (+0.303 V); therefore, a major part of applied current is used in the discharge of hydrogen [8].

Previously, several investigators have attempted to deposit molybdenum from aqueous solutions but ended up with the deposition of poorly adhered oxide films [10,11]. A very few attempts were successful in the electrodeposition of thin metallic molybdenum coatings from aqueous electrolytes, like molybdate and hydrofluoric acid [9], molybdic acid in sulfuric acid [12] and molybdates in acetate ion solutions [8]. A few reports on the electrodeposition of thick metallic molybdenum from fused salts [13,14] or ionic liquids [15] are also available. However, these methods require high temperatures, controlled atmosphere and special setup which makes the plating process cumbersome. The electrodeposition of thick metallic Mo coating from aqueous electrolyte has got continuous attention to investigators over several decades because of economical and simplicity of the aqueous electrolysis. Following the procedure of high concentration acetate electrolyte [8], recent attempts by Morley et al. [16] have been successful in electrodepositing thick (>15 μm) metallic molybdenum from an aqueous electrolyte.

In this study, we have investigated the electrodeposition of metallic Mo coating in detail by adopting a similar aqueous electrolyte containing very high concentrations acetate salts. An effort has been made to

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deposit very thick Mo coating and proposed a plausible mechanism of deposition. Post-deposition, coatings were characterized for their crystal structure, composition, structural transformation by annealing, surface morphology, microstructure and nanohardness.

## 2. Experimental

An aqueous electrolyte containing ammonium molybdate and high concentration of acetate ions following previous literature [8,16] was used for Mo electrodeposition. The composition of the electrolyte consisted of GR grade  $\text{CH}_3\text{COONH}_4$  (8.6 M),  $\text{CH}_3\text{COOK}$  (0.68 M) and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  (0.0034 M) in ultrapure water (resistivity > 18  $\text{M}\Omega\text{ cm}$ ) from the Milli-pore and Milli-Q system. The pH of the electrolyte was maintained at 6.75 by the addition of glacial acetic acid. Due to the high concentration of salts, rigorous stirring was applied to dissolve the salts and obtain a viscous solution. In order to identify the molybdate ion reduction zone, cyclic voltammetry (CV) was carried out in blank acetate electrolyte and with molybdate ions in a 100 ml beaker using AUTOLAB PGSTAT30 potentiostat/galvanostat. A copper foil (area 1  $\text{cm}^2$ ) and a saturated calomel electrode were used as working electrode and reference electrode respectively. A Pt foil was used as counter electrode. The typical scan rate maintained during CV experiments was 10  $\text{mVs}^{-1}$ . The electrodeposition of Mo coating was done on mirror polished copper substrate (area ca. 2–3  $\text{cm}^2$ ) by employing DC current with current density in the range 200–350  $\text{mA cm}^{-2}$ . The temperature of electrolyte was maintained at  $30 \pm 2$  °C with constant stirring throughout the deposition.

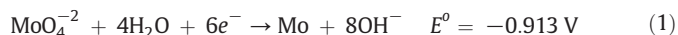
In order to identify the crystal structure, phases and possible structural transformation studies, X-ray diffraction (XRD) was used. The samples were heated in a furnace mounted on a rotating anode based x-ray diffractometer with  $\text{CuK}\alpha$  radiation. XRD data were recorded *in situ* at various temperatures from room temperature to 900 °C with a heating rate of 5 °C  $\text{min}^{-1}$ . At each temperature, the sample was heated for a period of 20 min before starting the x-ray scan.

The surface morphology and composition of the as-deposited films were investigated using scanning electron microscope attached with EDS. Microstructural investigation of the as-deposited Mo coating was done by transmission electron microscope (JEOL 2010 operated at 200 V). For this purpose, Mo coating was deposited on a thin electropolished copper foil. Post-deposition, the copper substrate was removed by grinding which further thinned down by ion milling until electron transparency was achieved and finally placed in a copper grid for TEM examination. In order to ascertain deposited Mo oxidation states, XPS spectra were recorded from the top surface of as-deposited coating and after sputtering out the top layer. Nano-indentation was carried out for as-deposited as well as annealed (700 °C) Mo coatings surface using a Berkovich indenter (UNHT, CSM, Switzerland) with loading and unloading rate of 8  $\text{mN min}^{-1}$  at a load of 4 mN.

## 3. Results and discussion

### 3.1. Electrochemical deposition

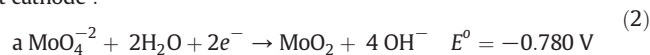
In the present study, heptamolybdate species  $\text{Mo}_7\text{O}_{24}^{6-}$  was taken as an active electrolyte for the electrodeposition of Mo. However, at pH > 6 (pH 6.75), it converts into predominant  $\text{MoO}_4^{2-}$  species form in aqueous solution [7,17]. For conversion of  $\text{MoO}_4^{2-}$  to Mo via electrochemical reduction at the electrode surface requires a very high potential ( $E^\circ = -0.913$  V) [18] is given by the following reaction



Such reaction involving six electron transfers makes  $\text{MoO}_4^{2-}$  to Mo reduction process difficult in aqueous electrolyte. In fact, it competes

with other parallel reduction processes [18] at the cathode surface in aqueous electrolyte as follows

At cathode :



It is seen here that reactions (2) and (3) involve only two electron transfers with lower standard reduction potential as compared to reaction (1). Apart from these,  $\text{MoO}_2$  is a well-known catalyst for electrolytic hydrogen evolution reaction; thus, the nascent oxide layer formed on the cathode surface further accelerates the hydrogen reduction process in reaction (3). As a result, the occurrence of the reduction process in Eq. (1) is of less priority resulting in deposition of black  $\text{MoO}_2$  powder on the cathode surface following Eq. (2) with enormous amount of hydrogen evolution. Therefore, the formation of  $\text{MoO}_2$  and  $\text{H}_2$  gas evolution are predominant reactions leaving behind the Mo formation from such aqueous electrolytes.

Cyclic voltammetry (CV) was carried out in an electrolyte containing only 0.0034 M ammonium molybdate in the potential range of 0 to –2.5 V vs SCE, as shown in Fig. 1. The appearance of a broad peak at –0.8 V vs SCE (inset in Fig. 1) corresponds to reduction of  $\text{MoO}_4^{2-}$  to  $\text{MoO}_2$  in neutral medium according to Eq. (5) confirming the previous literature [19] results. On addition of high concentration of acetate salts:  $\text{CH}_3\text{COONH}_4$  (8.6 M),  $\text{CH}_3\text{COOK}$  (0.68 M) along with comparatively low water content (with a mole ratio  $\text{H}_2\text{O}$ : acetate = 2.46:1) in 0.0034 M ammonium molybdate, a rapid increase in cathodic current was noticed with polarization. It is obvious that the cathodic peak due to  $\text{MoO}_4^{2-}/\text{MoO}_2$  conversion is abolished completely, and the cathodic polarization curve in CV (Fig. 1) become featureless around –0.8 V vs SCE. It seems the current beyond –1.0 V vs SCE is purely governed by the mass-transport phenomenon.

Based on the CV observations, the current density varied from 0 to 700  $\text{mA cm}^{-2}$  for deposition of Mo coating under water deficient conditions. Below current density of 200  $\text{mA cm}^{-2}$ , no coating was observed on the cathode surface. It seems whole current is consumed by the hydrogen evolution reaction. Raising the current density at 200  $\text{mA cm}^{-2}$  and upward, it was found that a bright metallic Mo coating started depositing on the cathode surface. The metallic coating was found to deposit on the cathode surface up to current density of 400  $\text{mA cm}^{-2}$ , and beyond that, the coating turned into black powdery deposit. Under this water deficient condition, the typical two step mechanism of reduction of  $\text{MoO}_4^{2-}$  to Mo could be as follows:

Step 1: Formation of nascent hydrogen



Step 2: Electrolytic reduction of molybdate to molybdenum assisted by nascent hydrogen



In the current density region 200–450  $\text{mA cm}^{-2}$ , reaction (4), hydrogen evolution, is the predominant reaction on the cathode surface including other side reaction (5). It seems the nascent hydrogen just produced at the cathode surface following Eq. (4), a strong reducing agent, facilitates *in situ* electro-reduction of  $\text{MoO}_4^{2-}$  to Mo in the presence of high concentration of acetate ions. A similar mechanism was anticipated by Kyscki et al [8] that just formed  $\text{MoO}_2$  on the cathode surface undergoes *in situ* reduction to Mo by copious volume of hydrogen that is evolved during this high current

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