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The electrodeposition of improved molybdenum coatings from molten salts by the use of electrolyte additives

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The electrodeposition of molybdenum from molten chlorides has been investigated in two electrolyte systems: $KCl–K_3MoCl_6$ at a temperature of 800° C and $LiCl–KCl–K_3MoCl_6$ at a temperature of 400° C. With the goal of improving the surface quality of the deposits, a search was conducted for electrolyte additives that would act as leveling agents. Activated alumina proved beneficial for deposits produced in the high temperature melt but had little or no effect on deposits generated at low temperatures. Molybdenum disulfide adversely affected the deposits by promoting the growth of surface irregularities.

1. Introduction

Surface quality is a very important consideration in the development of high performance materials. Carefully prepared surfaces can offer improved mechanical properties such as better abrasion or wear resistance and enhanced corrosion resistance. The refractory metals (elements of groups 4, 5 and 6) in general and molybdenum in particular, with their high melting points, good thermal and electrical conductivities and excellent mechanical properties, are very attractive as surface coatings. Molybdenum, however, appears to be dangerously close to exhaustion and has consequently been classified as a strategically sensitive material [1]. Conservation of molybdenum may thus become a priority. Electroplating from molten salts allows one to generate coatings which exploit the properties of molybdenum without having to fabricate the entire product out of the metal, thereby minimizing its consumption.

Molybdenum has been electrodeposited from a variety of electrolyte systems including fluorides [2] and fluoromolybdates [3, 4]. Previous results in chloride-based electrolytes are summarized in Table 1.

The electrochemistry of molybdenum in molten chlorides has been the subject of a number of investigations attempting to elucidate the elementary steps in the mechanism of the electrodeposition reaction [15–25]. As for the electrodeposition of coatings in molten chlorides, the relationship between process variables and deposit morphology has been studied [26–28].

Although coherent molybdenum coatings have been obtained from molten chlorides the surface quality of the deposits has not been satisfactory; in fact, in some cases only powder, rather than a coating, was produced. In aqueous electroplating, leveling agents are added to the bath to improve surface quality. Typically these are organic compounds which are unstable under the conditions reported in Table 1. Identifying suitable inorganic leveling agents was the purpose of this study. Two candidates were chosen on the basis of their potential to act as surfactants in chloride melts: activated alumina and molybdenum disulfide. Activated alumina had been tested by Senderoff [29] who found it to be promising.

2. Experimental details

Potassium hexachloromolybdate, K_3MoCl_6, was obtained from Climax Molybdenum Company, where it had been prepared by electrosynthesis under an inert atmosphere of nitrogen. Chemical analysis confirmed that the compound was 99.74 wt % pure, the remainder being excess potassium chloride. This compound was purified prior to use by heating under a vacuum of 4 Pa (30 μm Hg) for 3 h at 120° C.

The alkali chlorides were of analytical grade and were dehydrated by heating under vacuum according to the procedure recommended in the literature [30]. MoS_2 and activated alumina (Alcoa type F-20) were heated to 100° C under a vacuum of 4 Pa (30 μm Hg) for at least 8 h before use.

Electrodes were made of either graphite or molybdenum. Graphite was used both as cathode substrates and as electrodes for pre-electrolysis. Spectroscopic grade graphite was purified in a fused quartz tube by heating under vacuum for about 12 h at 900° C followed by chlorination at 800° C for a period of 3 h. This

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Table 1. Previous work on the electrodeposition of molybdenum in molten chlorides.

	Melt		*Temperature* (°C)	*Electrochemical process*	*Electrodes*		*Current density* ($mA\ cm^{-2}$)	*Quality of deposit (comments)*	*References*
	Electrolyte	*Solute*			*Anode*	*Cathode*			
1.	$NaCl–AlCl_3$	$MoCl_5$	200	Electrowinning	–	–	–	Metallic	[5]
2.	ACl–BCl A: Na, K; and B: Ca, Sr, Ba	$MoCl_3 + MoCl_4$	850	Electrorefining	Comminuted Mo	Graphite	54	Coarsely crystalline (av. valence 3.2–3.5)	[6]
3.	NaCl	$MoCl_5$	–	Electrowinning	Carbon	Carbon	1000–1500	Porous	[7]
4.	$CaCl_2$	$MoCl_5$	–	Electrorefining	Cast Mo	Fe,Pb	1000–1500	Pb–Mo Alloy	[7]
5.	KCl,LiCl–KCl	K_3MoCl_6	600–900	Electroplating	Mo	W,Mo	30–100	Powdery, coherent	[8, 9]
6.	KCl–NaCl	K_3MoCl_6	800–840	Electrorefining	Mo scrap	Mo sheet	80–520	Needles	[10]
7.	KCl	K_3MoCl_6,MoO_3–C	900–1000	Electrorefining	MoO_3–C	Mo	160–860	Dendritic	[11]
8.	KCl	K_3MoCl_6,Mo_2C	930	Electrorefining	Mo_2C	Mo	325	Dendritic	[12]
9.	ACl (A:Li,Na,K,Cs)	K_3MoCl_6, Cs_3MoCl_6	770–820	Electroplating	Mo	Mo,W,C,Ag	30–100	Coherent	[13, 14]
10.	ACl (A:Li,Cs)	K_3MoCl_6	530	Pulse plating	Mo	Ni, stainless steel	6–50	Gray or bright	[15]

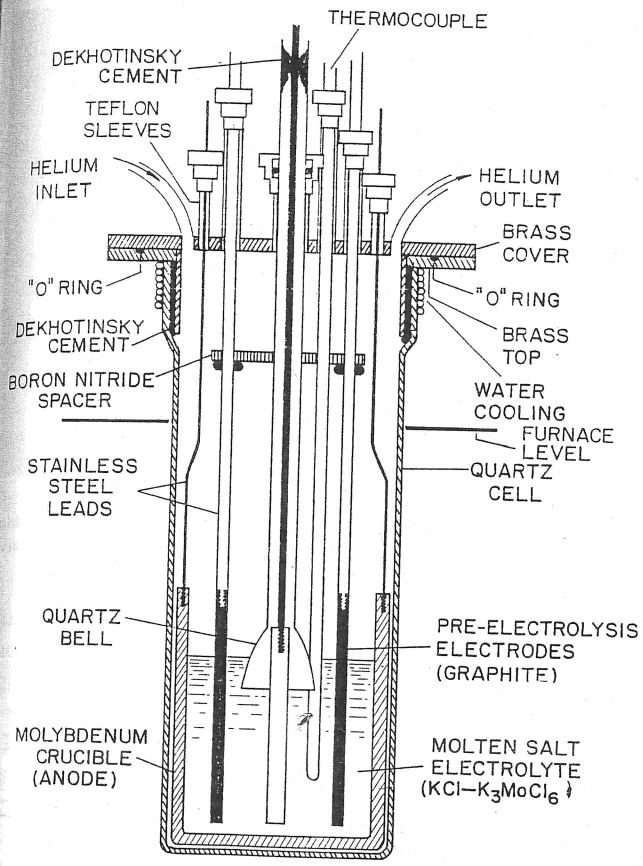

Fig. 1. Cell for electroplating molybdenum.

produced a small amount of an oily substance which condensed onto the wall of the glass tube where it remained cool during the purification procedure. The graphite electrodes were polished with fine sandpaper and were immersed in liquid nitrogen to remove the fines [31].

Molybdenum electrodes were in the form of rods about 6 mm in diameter and 10 cm long. Prior to use they were polished and then etched with a solution containing 200 g l^{-1} $K_3Fe(CN)_6$ and 75 g l^{-1} KOH [32]. Also, the molybdenum crucibles which served both as anodes and containers were etched in the same solution. The effective interelectrode distance in this cell was 3 cm.

Electroplating experiments were conducted in the cell shown in Fig. 1. A fused quartz tube fitted with a brass flange contained a molybdenum crucible of about 400 ml capacity. This crucible held the electrolyte and served as the anode. A rod-shaped cathode substrate was positioned at the centre of the crucible and surrounded by a fused quartz bell [13]. Also, there were two graphite electrodes for pre-electrolysis or conditioning of the electrolyte. The electrode configuration was maintained by a boron nitride spacer. The electrode leads were insulated from the brass cap by the insertion of Teflon sleeves in the brass fittings. The cell was heated by an electrical resistance furnace. Temperature was measured with a chromel–alumel thermocouple, ASTM type K.

In a typical experiment the crucible was charged with approximately 400 g of electrolyte in a glove box under an argon atmosphere and quickly transferred to the cell which was immediately evacuated. After the electrolyte had been slowly heated under vacuum to the melting temperature, purified helium was introduced into the cell. It is essential to exclude nitrogen and oxygen for which molybdenum metal has a high affinity. Moisture must also be excluded as it causes hydrolysis of the electrolyte. Accordingly, helium gas was dehydrated by passing through a drying column containing calcium chloride, and oxygen was removed by flowing the gas through a fused quartz tube containing titanium pellets wrapped in a copper foil and maintained at a temperature of 900° C. This purified helium was passed through the electrolysis cell. Pre-electrolysis of the supporting electrolyte was conducted between the two immersed graphite electrodes for several hours at a current density of 200 mA cm^{-2}. Following the pre-electrolysis K_3MoCl_6 was added, and electrodeposition of molybdenum began. Depending on the composition of the electrolyte and the applied current density, the potential ranged from 0.1 to 1 V. At the end of the experiment the cathode substrate was withdrawn from the melt, left for about 1 h in the hot zone of the cell in order to allow the electrolyte to drain, and then lifted to the upper part of the cell to cool.

The deposit was washed ultrasonically in acidified water, rinsed in alcohol and then air-dried and weighed. Typically a molybdenum deposit weighing 10–15 g was produced in a 20 h run. The deposit was subjected to metallographic examination, microhardness testing and chemical analysis by energy dispersive X-ray analysis. The composition of one of the samples was further studied quantitatively by atomic absorption to determine its aluminum and potassium contents.

Table 2. Summary of electroplating experiments

Experiment No.	*Melt composition (wt %) -additive*		*Substrate*	*Cathodic current density ($A\,m^{-2}$)*	*Coulombic Efficiency (%)*		*Comments*
					Anode	*Cathode*	
ia	93 KCl $7K_3MoCl_6$	–	Molybdenum	220	26	47	Graphite crucible, Molybdenum foil as anode
ib	92.2 KCl 7.8 K_3MoCl_6	–	Molybdenum	250	18	65	Graphite crucible, Molybdenum rods as anodes
ic	As above	–	Graphite	500	25	70	Graphite crucible, Molybdenum rods as anodes
iia	90.4 KCl 9.0 K_3MoCl_6	0.6 MoS_2	Graphite	300		99.9	Molybdenum crucible as anode
iib	As above	As above	Graphite	300	Av. 92	100	As above
iic	As above	As above	Graphite	250		73	Large melt-surface deposit
iid	As above	As above	Graphite	250		31	Large melt-surface deposit
iiia	91.3 KCl 8.1 K_3MoCl_6	0.6 Al_2O_3	Molybdenum	250	–	100	Smooth deposit
iiib	91.6 KCl 7.6 K_3MoCl_6	0.8 Al_2O_3	Molybdenum	250		87	Smooth deposit
iiic	88.5 KCl 10.5 K_3MoCl_6	1.0 Al_2O_3	Molybdenum	250		100	Test of throwing power
iiid	87.3 KCl 10.9 K_3MoCl_6	1.8 Al_2O_3	Molybdenum	330		89	Test of throwing power
iiie	As above		Molybdenum	350		100	Test of throwing power
iva	50.7 KCl 41.2 LiCl 6.9 K_3MoCl_6	1.2 Al_2O_3	Molybdenum	200		82	Dendritic deposit
ivb	As above		Graphite	150		–	Deposit washed away
ivc	As above		Stainless steel	300		120	Salt inclusions

3. Results and discussion

The results of the investigations on the electroplating of molybdenum metal in molten alkali chloride electrolytes are given in Table 2 which summarizes the experimental conditions.

Coulombic current efficiencies were calculated by comparing the measured amount of molybdenum deposited, which was determined from weighing the cathode substrate before and after electrolysis, with the Faradaic equivalent produced by the following three-electron process:

$$MoCl_6^{3-} + 3e \longrightarrow Mo(s) + 6Cl^- \qquad (1)$$

This method of calculating cathodic current efficiency is justified by the confirmed absence of any impurity in the deposit, at least in substantial amounts. In fact, quantitative atomic absorption analysis has shown that the suspected impurities, such as aluminum from the use of activated alumina and potassium from entrapped electrolyte, were 0.002 and 0.004 wt %, respectively.

The anodic reaction should be the reverse of Reaction 1. Anodic coulombic efficiencies were estimated upon the completion of a series of experiments by weighing the empty molybdenum crucible before and after electrolysis.

The current densities shown in Table 2 were calculated on the basis of the initial geometric surface area of the part of the cathode substrate immersed in the melt. As the deposition proceeds, however, the deposit grows and its surface area increases. Therefore, current density values reported in Table 2 actually represent initial or apparent current density values.

Four distinct electrolyte compositions were employed. All used K_3MoCl_6 as a source of soluble molybdenum and KCl as the principal constituent of the supporting electrolyte.

Composition (i): K_3MoCl_6–KCl. Base composition without additives to serve as standard electrolyte for comparison with subsequent results.

Composition (ii): K_3MoCl_6–KCl–MoS_2. Composition (i) to which MoS_2 has been added as a candidate leveling agent.

Composition (iii): K_3MoCl_6–KCl–Al_2O_3. Composition (i) to which Al_2O_3 has been added as a candidate leveling agent.

Composition (iv): K_3MoCl_6–KCl–LiCl–Al_2O_3. Composition (iii) to which LiCl has been added as a major constituent of the supporting electrolyte in order to decrease the liquidus temperature.

As reported in Table 1 it is possible to obtain good quality coherent metal from an electrolyte of composition (i) [8, 9]. Our experiments, conducted at a temperature of 800° C, confirmed this. Figure 2 shows a cross section of a molybdenum deposit on a graphite substrate obtained from experiment ib. A uniform coating, approximately 0.5 mm thick and having

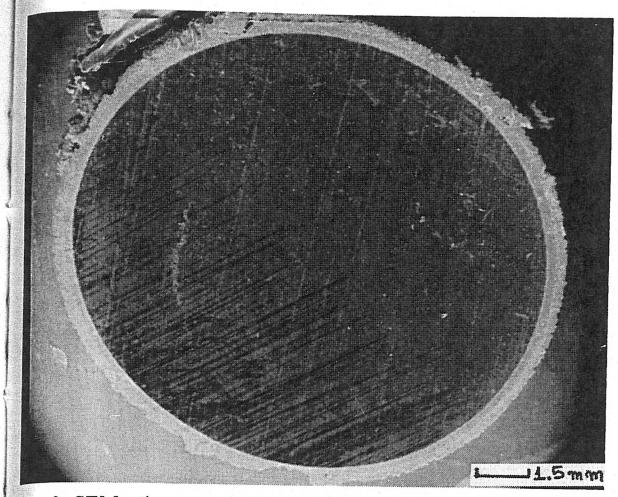

Fig. 2. SEM micrograph of a molybdenum deposit on a graphite substrate. Electrolyte composition (i). Current density 500 A m^{-2}. Temperature 800° C. Experiment ib.

the characteristic uninterrupted columnar structure shown in Fig. 3, was produced. The deposit appears to be free of voids, and its microhardness (234 HK) is comparable to that of the starting molybdenum anode (235 HK). This is indicative of low levels of interstitial carbon, nitrogen and oxygen, which all tend to increase hardness when present.

The surface quality of these deposits was not considered to be satisfactory, as evidenced by the protrusion of large 'spikes' of the type shown in Fig. 4. The texture of the compact metal deposits obtained by molten salt electrolysis has been studied by Soviet investigators [26–28], who concluded that the texture axis is the direction of the crystal's longest diagonal. For molybdenum deposits there is preferential growth of the ⟨1 1 1⟩ orientation perpendicular to the substrate [13].

As it was the purpose of the present investigation to produce smooth deposits of molybdenum metal, it was felt that their texture should be altered in order to minimize preferential growth. Accordingly, the addition of surfactants was studied.

A series of experiments, summarized as iia–iid in Table 2, was conducted in electrolyte of composition

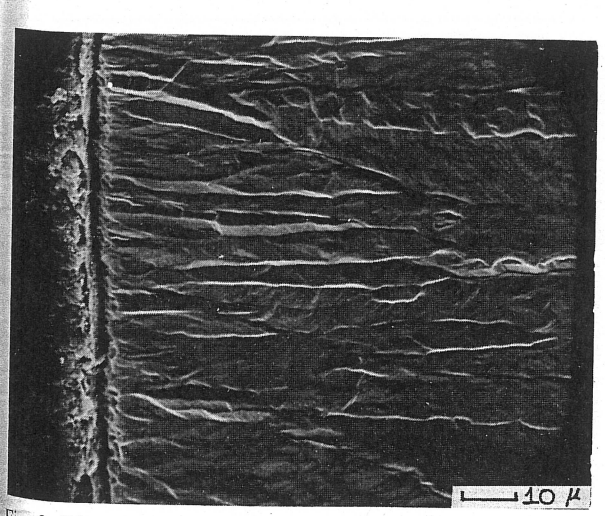

Fig. 3. SEM micrograph of molybdenum deposit of Fig. 2 showing characteristic columnar structure.

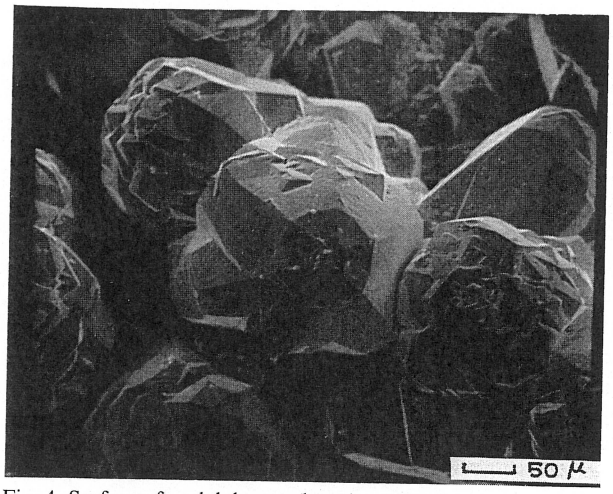

Fig. 4. Surface of molybdenum deposit of Fig. 2.

(ii). A small addition of MoS_2 was made in order to study its effect on the surface morphology of the deposits. The experiments were conducted at 800° C using a molybdenum crucible as anode.

During electrolysis a small amount of a light brown powder condensed on the cold upper part of the electrolysis cell. Upon exposure to air the powder turned yellow, presumably due to hydrolysis, while upon dissolution in water it produced a blue-coloured solution. Samples of the powder were collected and analysed by X-ray diffraction using nickel-filtered copper Kα radiation. The Debye Scherrer powder pattern of the substance revealed it to consist of a mixture of KCl and $MoCl_2$. The powder diffraction pattern of the latter had been determined previously [33]. These findings are consistent with the suggestion that the loss of molybdenum from the melt occurs by the oxidation of molybdenum metal according to the reaction:

$$2Mo^{3+} + Mo(\text{crucible}) = 3Mo^{2+} \qquad (2)$$

In attempting to account for the precipitation of molybdenum powder in their cells, Senderoff and Mellors [21] suggested the following reaction which involves the evaporation of volatile $MoCl_5$:

$$MoCl_6^{3-} = 2/5Mo(s) + 3/5MoCl_5(v) + 3Cl^- \qquad (3)$$

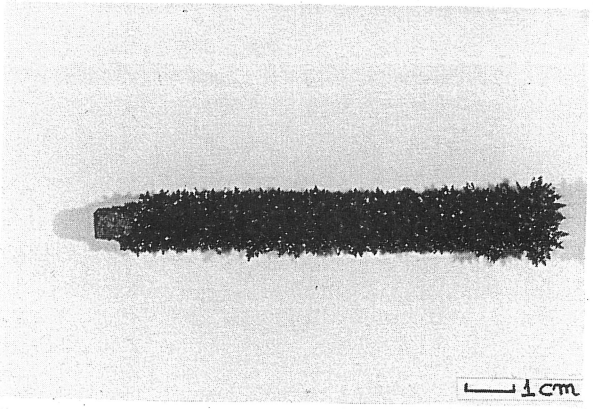

Fig. 5. Molybdenum deposit on a graphite substrate. Electrolyte composition (ii). Current density 300 A m^{-2}. Temperature 800° C. Experiment iia.

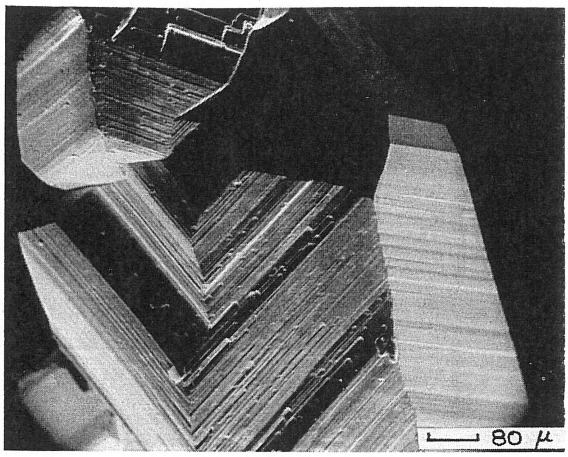

Fig. 6. SEM micrograph of the tip of the needles of the deposit shown in Fig. 5.

The deposit obtained from experiment iia, representative of this series, is shown in Fig. 5. Initially the deposit grows as a compact coating up to a limited thickness, typically measuring 200 μm, beyond which needle-like structures develop. An SEM micrograph of the tips of the needles, shown in Fig. 6, depicts a change in the deposition habit from columnar to epitaxial. Evidently, MoS_2 promotes preferential growth, i.e. acts as a negative leveling agent.

The presence of MoS_2 in the electrolyte also promoted accelerated growth at the melt surface. The associated deposit is shown in Fig. 7. The purpose of the fused quartz bell shrouding the cathode is to prevent this deposit from shorting across to the anode [13]. This rapid growth of metal at the free surface of the melt is not fully understood. However, this behavior is consistent with what one would expect if there were a variation in electrolyte composition along the cathode. Temperature gradients in combination with surface tension effects may act so as to enhance the concentration of molybdenum-bearing species at the melt surface. As the kinetics of charge transfer are expected to be fast at these temperatures, higher molybdenum concentrations should result in higher deposition rates.

The effect of the addition of activated alumina to the electrolyte was studied in the series of experiments

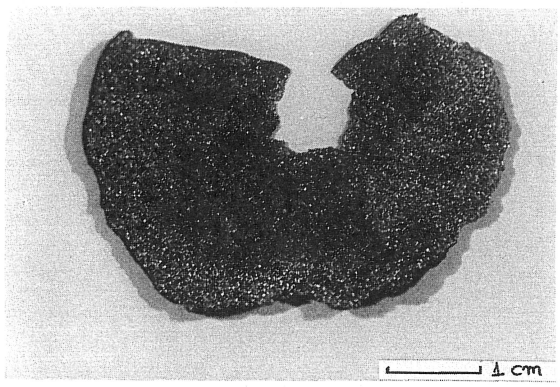

Fig. 7. Plate-like molybdenum deposit grown on the surface of the electrolyte. Experiment iia.

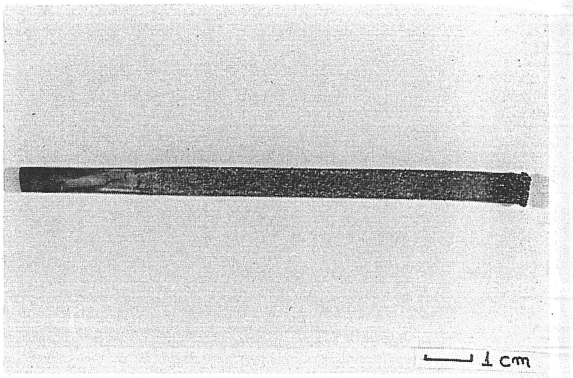

Fig. 8. SEM micrograph of a molybdenum deposit on a molybdenum substrate. Electrolyte composition (iii), 0.6% Al_2O_3. Current density 250 A m^{-2}. Temperature 800° C.

summarized as iiia to iiie in Table 2. Substantially smoother deposits were obtained, as evidenced in Fig. 8 from experiment iiia. Comparison of Fig. 4 generated from electrolyte of composition (i) and Fig. 9 generated from electrolyte of composition (iii) suggests that the presence of activated alumina promotes grain refinement. Energy dispersive X-ray spectra revealed that the composition of the molybdenum deposit and that of the parent molybdenum anode were identical; at the interface between the deposit and the cathode substrate the presence of aluminum was detected. The latter observation could be evidence either of physical entrainment of alumina or of alumina solubility in the electrolyte. Oxide solubility in chloride melts has been reported [34].

The use of activated alumina as a leveling agent in molten salt electrolysis had been tested previously. Mellors and Senderoff added limited amounts of it to an all-fluoride bath for electroplating zirconium [35]. Similarly, Pint and Flengas used small additions of activated alumina to improve the quality of zirconium deposits from an all-chloride bath [36]. In both cases a Zr–Al alloy was produced. The absence of aluminum in the deposits obtained in this work is perhaps due to the fact that molybdenum oxides are thermodynamically less stable than alumina, and thus the electrodeposited molybdenum cannot reduce the stabler

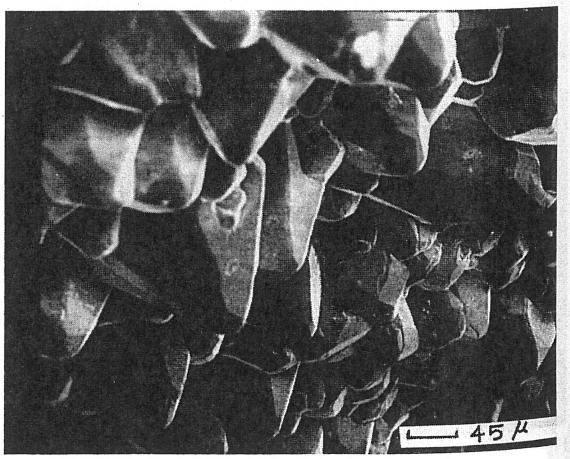

Fig. 9. SEM micrograph of the surface of deposit shown in Fig. 8.

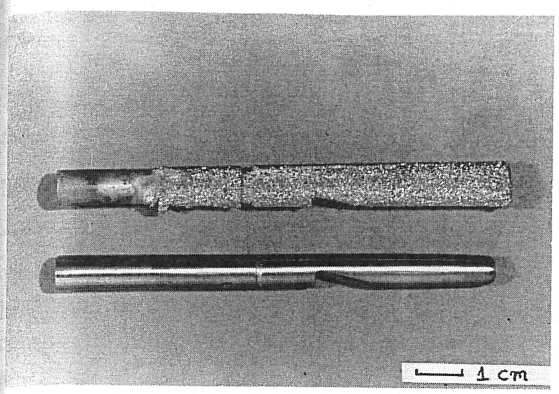

Fig. 10. Specimen for testing the throwing power of the electrolyte. Electrolyte composition (iii), 1.8% Al_2O_3. Current density 330 A m^{-2}. Temperature 800° C. Electroplated specimen (top), machined and polished substrate before plating (bottom).

Al_2O_3 to aluminum metal which would in turn be incorporated into the deposit.

The throwing power of the electrolyte was investigated through the use of specially machined substrates. Fig. 10 shows such a specimen before and after electrolysis. The electroplated specimen was sectioned longitudinally, polished and etched in order to examine the interface between the substrate and the deposit. Fig. 11 shows one such specimen, which is of uniform thickness and follows the contours of the substrate. What appears as a void in the electrodeposit was identified as a piece of abrasive used in polishing the substrate before electroplating. Fig. 12 is an SEM micrograph of the deposit shown in Fig. 11 and reveals in greater detail the high degree of uniformity in the thickness of the coating over right angle bends. Clearly, this is evidence of an electrolyte with excellent throwing power.

While the above observations are consistent with the contention that activated alumina acts as a leveling agent, they do not constitute proof. Despite much work, the mechanism of leveling is not well understood [37]; to establish a scientific criterion to measure the effect of a particular additive some knowledge of the mechanism of electrodeposition is required. Senderoff and Mellors [21] concluded that the electrodeposition of molybdenum metal from these melts proceeds irreversibly according to Reaction 1 which in

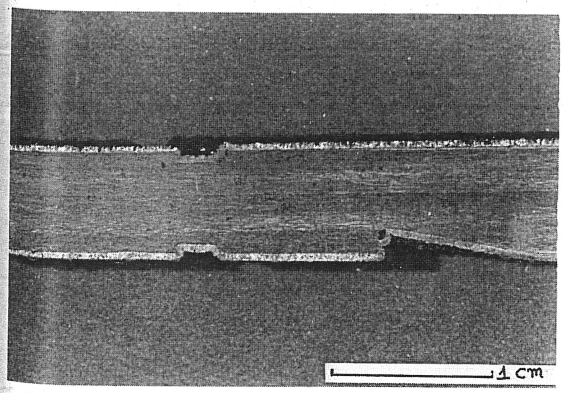

Fig. 11. Longitudinal section of the specimen of Fig. 10 showing excellent throwing power.

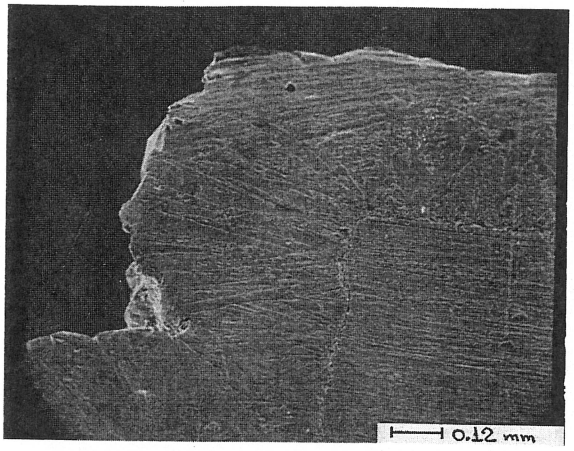

Fig. 12. SEM micrograph of the molybdenum coating of Fig. 11, showing uniformity of thickness around a right angle bend.

turn is perhaps preceded by a slow step represented by the following reaction:

$$Mo_2Cl_9^{3-} + 3Cl^- = 2MoCl_6^{3-} \quad (4)$$

However, they were unable to confirm this. Similarly, on the basis of the results of the present study it is not possible to identify the rate-limiting step in the electrodeposition of molybdenum. It is clear that further investigation is required and that non-electrochemical techniques should be employed as part of this endeavor. For example, as a supplement to electrokinetic studies real time observation of the processes occurring in the electrolyte next to the cathode by fast Raman spectroscopy may reveal the presence of short-lived, kinetic entities and thus identify the rate-limiting step. Furthermore, Raman spectroscopy has the capability of detecting polynuclear cluster ions such as $Mo_2Cl_9^{3-}$ and distinguishing them from simple complex ions such as $MoCl_6^{3-}$. Indeed, Senderoff and Mellors suggested the use of spectroscopic methods without specifying the type of technique [21]. To facilitate the above-mentioned real time study, instrumentation in this laboratory has been reconstructed, and Raman spectra in related refractory metal systems have been measured [38]. This is noteworthy in view of the deep coloration exhibited by these melts.

Finally, there appears to be no limitation on the thickness of the deposited metal. In previous studies deposits of 0.2 mm thickness had been obtained [29]. The deposits shown in this report typically measure 0.5 mm; however, provided that the supply of soluble molybdenum is maintained in the electrolyte through anode dissolution and that the surface of the deposit does not become so irregular as to short out the cell, it appears that plating can continue without limit.

An important issue in the electroplating of molybdenum metal in molten salts is the temperature of the plating process. In order to minimize thermal damage to the substrate, it is imperative that low-temperature electrolytes be found. As part of an investigation of the phase diagram of the LiCl–KCl–K_3MoCl_6 system, the liquidus in the LiCl–K_3MoCl_6 system was deter-

mined [39]. Melts stable at temperatures as low as 380° C were found. However, the molybdenum-bearing complex compound, K_3MoCl_6, is sparingly soluble in LiCl.

Accordingly, an electrolyte consisting of KCl–LiCl–K_3MoCl_6 with a small addition of activated alumina, composition (iv), was tested. The results are summarized as experiments iva–ivc in Table 2. No coherent molybdenum deposits could be produced in these melts at 400° C. Instead, highly dendritic molybdenum metal deposits were obtained which either were washed away or contained salt inclusions. Earlier investigators have also been frustrated in their attempts to plate molybdenum at temperatures below 700° C. Recently, White and Twardoch have reported limited success in a CsCl–LiCl supporting electrolyte at a temperature of 530° C [15].

In view of these reported difficulties in trying to electrodeposit elemental molybdenum in a coherent form at low temperatures, perhaps an alternative approach is warranted, one that goes beyond simply changing the processing parameters such as bath composition and changes the very process itself. For example, it may be that electrodeposition is facilitated by codeposition of a lower melting point metal such as chromium, zinc or tin. For many applications the presence of a second element would not impair the performance of the coating.

Acknowledgements

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