

MOLYBDENUM COATINGS BY MOLTEN SALT ELECTROLYSIS

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The electrodeposition of molybdenum from molten salts is being studied in order to develop a technology capable of making refractory metal coatings on low-cost base metals. The experiments have shown that it is possible to electroplate molybdenum onto various substrates such as molybdenum or graphite from an electrolyte consisting of $KCl-K_2MoCl_6$ at a temperature of $800^{\circ}C$. As part of a comprehensive investigation of the ternary phase diagram of $KCl-LiCl-K_3MoCl_6$, the binary systems, $KCl-K_3MoCl_6$ and $LiCl-K_3MoCl_6$, have been studied with the goal of identifying a low-melting plating melt.

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 IVB, VB, and VIB) 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.

Although molybdenum has been electrodeposited from molten chlorides (1-5) the surface quality of the deposits has not been satisfactory; in fact, in some cases only powder, not coatings, was produced. Thus, the goal of the present study was to make smooth deposits of high purity.

A separate but related issue 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-K₃MoCl₆ system, the phase diagrams of the two binaries, LiCl-K₃MoCl₆ and KCl-K₃MoCl₆, were determined.

Experimental

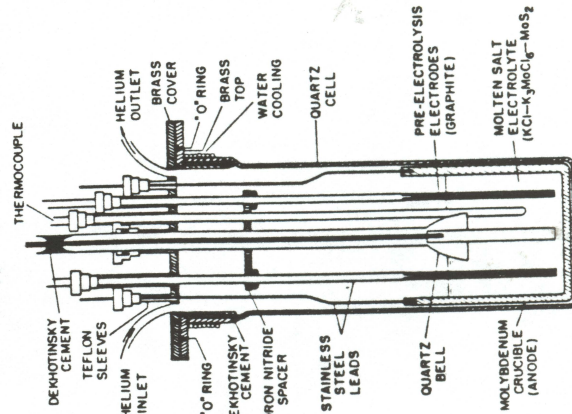


Figure 1. Cell for Electroplating Molybdenum

Phase diagrams were determined by cryoscopy. Evacuated fused quartz ampoules containing the salts were heated in an electrical resistance furnace whose temperature was programmable. Cooling rates varied from 0.5 to 2.5 K min⁻¹. Phase changes were observed in the measured temperature versus time curves (6).

Electroplating experiments were conducted in the cell shown in Fig. 1. A fused quartz tube fitted with a brass flange contained a molybdenum crucible which held the electrolyte and served as the anode. A rod-shaped cathode substrate was positioned at the center of the crucible and surrounded by a fused quartz bell. As well, there were two graphite electrodes for pre-electrolysis.

In a typical experiment the crucible is charged in a glove box under an argon atmosphere and quickly transferred to the cell, which is immediately evacuated. After the cell and its contents have been slowly heated under vacuum to 500°C, purified helium is introduced. To melt the electrolyte the temperature is increased to 800°C. Following several hours of pre-electrolysis, electrodeposition of molybdenum is conducted. The deposit is washed with acidified water followed by alcohol, air-dried, and then chemical, metallographic, and mechanical tests are performed.

Results and Discussion

The phase diagram of the KCl-K₃MoCl₆ system is shown in Figure 2a. The melting point of the K₃MoCl₆ compound was determined to be 882°C. The system KCl-K₃MoCl₆ is a simple eutectic (18.4 mole % K₃MoCl₆ at 697°C). The binary LiCl-K₃MoCl₆ is also a simple eutectic (10.5 mole % K₃MoCl₆ at 483°C.)

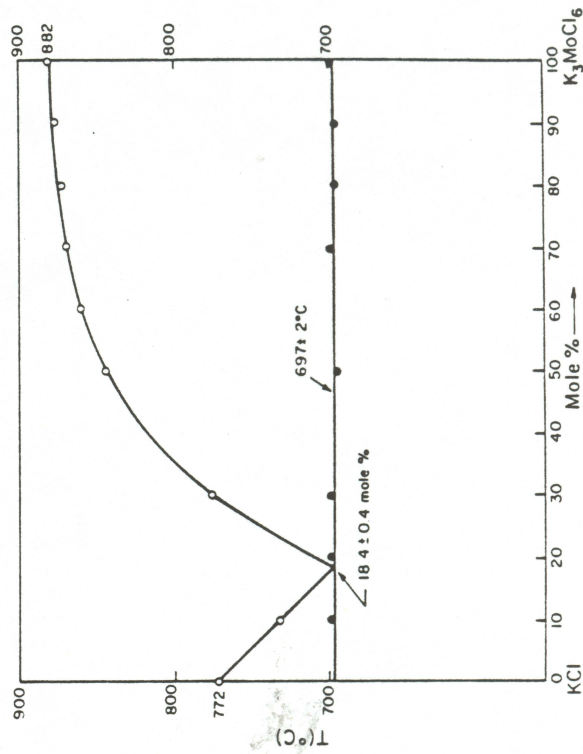


Figure 2a. Phase diagram of KCl-K₃MoCl₆ system.

The system $\text{KCl-K}_3\text{MoCl}_6$ may be considered as a pseudobinary of the composite system KCl-MoCl_3 . The latter has been studied by Drobot and Saprano (10) using differential thermal analysis on sealed samples containing intimate mixtures of the principal components. Thermal features were identified by heating the specimens, which weighed as little as 2.5 g, at rates of 4 to 8 K/min. Based on the results of only four samples over the composition range from KCl to K_3MoCl_6 , those authors reported a melting point of 865°C for the compound K_3MoCl_6 , which is lower than the 882°C determined in this work. This is probably due to the presence of impurities in their samples since they prepared MoCl_3 by reducing MoCl_5 with anhydrous tin (II) chloride. Temperature gradients caused by the relatively high heating rates and weighing errors may also account for the discrepancy with the values found in this work.

Drobot and Saprano report the $\text{KCl-K}_3\text{MoCl}_6$ eutectic temperature to be 698°C which is in excellent agreement with the value of $697 \pm 2^\circ\text{C}$ found in the present study. Furthermore, those authors report the eutectic composition to be 12 mole percent MoCl_3 which is equivalent to 18.8 mole percent K_3MoCl_6 in the $\text{KCl-K}_3\text{MoCl}_6$ subsystem. This is in excellent agreement with the value 18.4 ± 0.4 mole percent determined in this work.

The phase diagram of the $\text{LiCl-K}_3\text{MoCl}_6$ system is shown in Figure 2b. There are no data reported in the literature to compare with our results. Our study indicates that the ternary system $\text{KCl-LiCl-K}_3\text{MoCl}_6$ offers the possibility of conducting the electroplating operation at substantially lower temperatures than in the $\text{KCl-K}_3\text{MoCl}_6$ binary system.

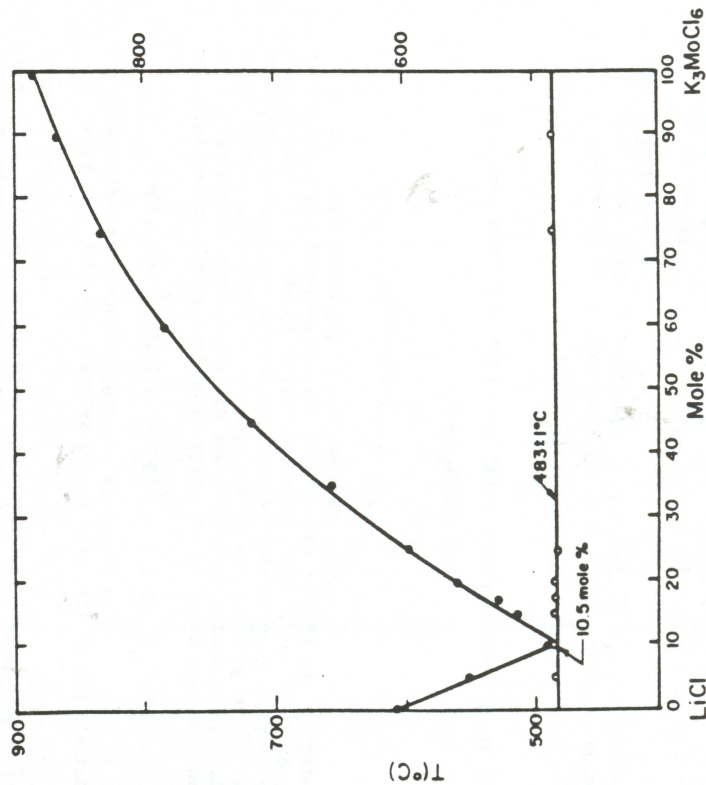


Figure 2b. Phase diagram of $\text{LiCl-K}_3\text{MoCl}_6$ system.

The results obtained in the electroplating experiments are summarized in Table I. In a first series of experiments, the electroplating of molybdenum from fused $\text{KCl-K}_3\text{MoCl}_6$ electrolytes was studied. The experimental conditions, such as composition of the electrolyte, substrate material, temperature, applied voltage, and cathodic current density, are given in Table I. A cross-section of molybdenum electroplated on graphite is shown in Fig. 3, while Fig. 4

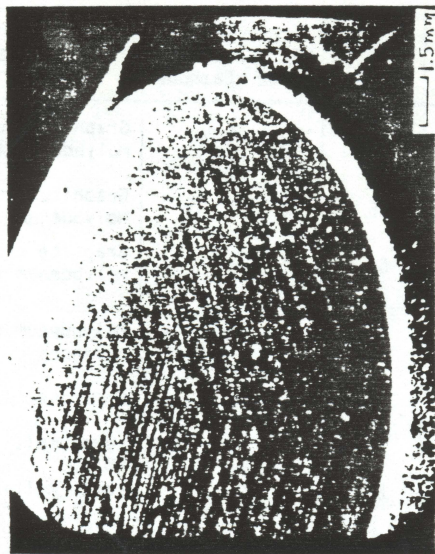


Figure 3. SEM micrograph of electrodeposited molybdenum-graphite substrate interface (7X).



Figure 4. SEM micrograph of molybdenum deposit on graphite showing characteristic columnar structure (1000X).

is an SEM micrograph of the same deposit. The thickness of the molybdenum deposit on graphite is approximately 0.25 mm. Its microhardness is comparable to the starting molybdenum anode and thus indicates low levels of interstitial carbon, nitrogen, and oxygen. As shown in Fig. 4, the molybdenum deposit has an uninterrupted columnar structure and appears to be free of voids.

A feature of refractory-metal electrodeposition in molten salts is the extremely high rate of growth of the deposit at the melt surface (7). To contain this and prevent shorting of the cell, a fused quartz bell shrouds the cathode (8). Addition of MoS₂ did not improve the situation; in fact, it appeared to promote accelerated growth at the melt surface. These phenomena are unexplained and need further investigation.

The expected cathodic reaction is



The anodic reaction should be the reverse of reaction (1).

According to Senderoff's reaction (1) represents an irreversible single step in the electrodeposition of molybdenum and may be preceded by a slow step:



On the basis of the present electrochemical study it is not possible to determine whether the polyatomic cluster anion, Mo₂Cl₆³⁻, is present and, if so, whether reaction (2) or (1) is rate limiting. Initial attempts to elucidate the mechanism of electrodeposition in these melts by Raman spectroscopy were impeded by their deep coloration. However, work is underway to design suitable spectrocells.

Doubts have been expressed as to the stability of the electrolyte. Senderoff (9) has suggested disproportionation according to



Our experiments seem to contradict this. In the phase diagram studies which used fused quartz ampoules and in the electrodeposition studies conducted in graphite crucibles there was no evidence of evolution of MoCl₅. However, when molybdenum crucibles were used substantial amounts of a volatile substance were observed to condense on the cool upper part of the glass cell. These observations taken together are consistent with loss of MoCl₆³⁻ through the oxidation of molybdenum metal by the reaction



Acknowledgements

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TABLE I. SUMMARY OF ELECTROLYSIS EXPERIMENTS

Experiment #	Melt Composition (Wt. %)	Substrate	Cathodic Current Density (mA/cm ²)	Coulombic Efficiency (%)	Anode Cathode	Comments
1	93 KCl 7 K ₃ MoCl ₆	Molybdenum	22	26	Graphite crucible, Molybdenum foil as anode	Graphite crucible, Molybdenum rods as anodes
2	92.2 KCl 7.8 K ₃ MoCl ₆	Molybdenum	25	18	Graphite crucible, Molybdenum rods as anodes	Graphite crucible, Molybdenum rods as anodes
3	As above	Graphite	50	25	Graphite crucible, Molybdenum rods as anodes	Graphite crucible, Molybdenum rods as anodes
4	90.4 KCl 9.0 K ₃ MoCl ₆ 0.6 MoS ₂	Graphite	30	30	Molybdenum crucible	Molybdenum crucible as anode
5	As above	Graphite	30	--	As above	As above
6	As above	Graphite	25	73	Large melt-surface deposit	Large melt-surface deposit
7	As above	Graphite	25	31	Large melt-surface deposit	Large melt-surface deposit
			(Avg. 4±7)	92		

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