ELECTRODEPOSITION OF MOLYBDENUM AND MOLYBDENUM CARBIDE COATINGS FROM OXIDE BASED MOLTEN SALTS

B. Aladjov*, D. Topor and J. R. Selman

Department of Chemical Engineering
Illinois Institute of Technology, Chicago, IL 60616

* Bulgarian Academy of Sciences,
Central Laboratory of Electrochemical Power Sources
1113 Sofia, BULGARIA

ABSTRACT

Dense, well-adherent molybdenum and molybdenum carbide coatings have been deposited on mild steel substrates by electrochemical deposition from a Na2WO4 - K2WO4 molten bath containing alkali molybdates and carbonates. Coatings with a thickness of up to 30 μm have been prepared at cathodic current densities between 30 and 50 mA.cm⁻² under air as ambient atmosphere. The coating morphology depends strongly on melt composition, temperature and moisture content. Addition of Na2B4O7 to the basic non-lithium bath composition causes significant quality and morphology improvements.

INTRODUCTION

Recently, considerable attention has been focused on the development of coatings of molybdenum and molybdenum carbide by molten salt electrochemical deposition (MSECD). These coatings are considered candidate materials for coating the container and positive-electrode current collector of high-temperature power sources such as the sodium-sulfur and lithium-FeS₂ batteries.

MSECD is a powerful method which can be used to produce various compound-based coatings having improved properties compared with those of the pure single chemical elements. This method offers the ability to coat complex shapes and provides good process control by making use of current/potential variation.
Formation of refractory metal and metal carbide deposits by MSECD using several different bath composition (chloride, chloride-oxide, fluoride) has been demonstrated by many authors (1-11). However, all these methods have difficulties in practical use, especially: inert atmosphere is required; complicated treating steps, special purity requirements for the electrolyte baths etc., so the practical potential of these methods is insufficient. Recently, a different method was found, using a non-fluoride based electrochemical deposition from a melt consisting completely of oxides, with air as ambient atmosphere (12-16).

The method can be summarized as follows. Mo2C coatings are deposited directly on mild steel from a Na2WO4-K2WO4-Li2MoO4-Li2CO3 melt at 900 °C. Dense coatings with a thickness of up to 50 μm are obtained at cathodic current densities between 20 and 100 mA.cm−2.

The authors attribute the deposition of Mo2C from oxide melts to the instantaneous chemical reaction of carbon and molybdenum produced from the corresponding oxygenated anions. As a result of this reaction a compact pore-free deposit of molybdenum carbide is obtained with good adhesion to the low carbon steel substrate.

Preliminary results on the corrosion and electrochemical behavior of Mo2C coatings deposited electrochemically on low carbon steel show good promise for corrosion protection of the cathode container in lithium/iron sulfide and sodium/sulfur batteries (17).

The objectives of this study are (a) to produce dense and adherent molybdenum and molybdenum carbide coatings from sodium tungstate-potassium tungstate based melts containing alkali molybdates and carbonates; (b) to determine correlations with process parameters such as temperature, current density, melt composition, moisture content etc.

**EXPERIMENTAL**

The electrochemical plating cell assembly is schematically presented in Figure 1. It consists of an α-Al2O3 crucible positioned on the bottom of an electroresistance furnace, a cover of thermo-insulating material with holes for the anode electrode, a low carbon steel cathode, a platinum flag as quasi-reference electrode, and a chromel-alumel thermocouple. The electrodes and thermocouple passed through the holes of the cover and were immersed in the electrolyte melt which occupied the bulk of the crucible. A small Hoskins (Model FD 101) electric furnace was used to fuse the electrolyte and ensure the necessary working temperature.

A molten bath consisting of an equimolar mixture of Na2WO4 and K2WO4 was used. The molybdenum and carbon species were introduced as alkali molybdate and carbonate, by
direct mixing with the base tungstates as a powder. Initially all individual components were dried at 200-300 °C for 2-3 hours in order to remove as much moisture as possible from the commercially available laboratory chemicals. Following this, the melt components were weighed and mixed to give the desired electrolyte composition. As a second step, in some cases an additional electrochemical purification was carried out. To remove the remaining moisture completely, the melt was electrolyzed at about 1.5-2.0 V at 650 °C between two carbon electrodes until the current dropped to a low constant value typically less than 1 mA.

After placing the crucible with the dried powder mixture in the furnace, the temperature was raised slowly to 600 °C at which point the electrolyte started to melt. One to two hours were necessary after melting to produce a clear melt. After melting, the temperature of the electrolyte was raised to 650 °C, the carbon electrodes for pre-electrolysis were positioned above the crucible, and after thermal equilibration they were very slowly immersed. The pre-electrolysis electrodes were removed immediately after completion of pre-electrolysis. The plating electrodes were then positioned above the crucible, and after some additional equilibration, they were very slowly immersed in the molten electrolyte to avoid thermal shock. After reaching thermal equilibrium (usually in 1-1.5 hours), the temperature was raised again very slowly to the working temperature, 900 °C. Electrolysis was started within 1 hour after reaching this temperature.

Following electrolysis the temperature was decreased again very slowly, and at 600°C the electrode assembly was removed. After complete cool-down, the electrodes were ultrasonically stripped of adherent frozen melt.

Cylindrical cathodes of 3.1 or 6.3 mm dia and about 30 mm length were cut from a low-carbon steel rod (AISI 1018). Each cathode substrate was screwed or compressed into a long low-carbon steel holder of 6.3 mm dia to ensure excellent electrical connection. The cathodes were initially etched with 10% hydrochloric acid followed by rapid rinsing by water and acetone. Later, they were cleaned mechanically using successively finer grades of silicon carbide paper (240, 320, 400, 600), and then rinsed again by alcohol and water. Next, in most cases, they were polished with Alfa Micropolish Alumina Solution - 1.0 μm (Buehler), followed by a final ultrasonication in alcohol and acetone.

The anodes were pure metallic molybdenum or carbon rod of 6.3 mm dia. They were installed as the central electrode of the electrochemical cell assembly.

The measuring instrumentation consisted of an EG&G PAR Model 175 Universal Programmer, a Model 179 Potentiostat/Galvanostat provided with Model 179 Digital Coulometer plug-in option, a Hewlett-Packard ColorPro Plotter and a Nicolet 310 Explorer II Digital-Storage Oscilloscope.
RESULTS AND DISCUSSION

Electrolyte Bath Composition

The electrolyte bath composition was varied in order to study the influence of the kind and amount of alkali molybdate and carbonate on the resulting deposits and on this basis to choose the optimal composition. Later, the process parameters of molybdenum and Mo$_2$C deposition from a fixed bath composition were studied in order to generate satisfactory coatings with reproducible surface topology and thickness.

Several different bath composition have been utilized with approximately 8 - 10 mol% alkali molybdate and variable amounts of alkali carbonate. Table 1 lists the chemical composition of the electrolyte baths used, while Table 2 shows the different plating conditions performed. The experiments, which were performed without pre-electrolysis of the electrolyte, gave in most cases un reproduceable results. After pre-electrolysis, coatings of a more reproducible quality were obtained. Using non-lithium alkali molybdates and carbonates, coatings of an even better quality were obtained. Adding 3-8 mol% Na$_2$B$_4$O$_7$ to the basic non-lithium bath composition was observed to cause significant morphology and quality improvements. These bath compositions produce a more uniform small-grain-size coating, moreover they do not require extensive purification because they are apparently not very sensitive to moisture in the atmosphere.

Significant information about the coating quality was obtained from examination of sample cross-sections. Typical microscope cross-section pictures for the samples plated under different conditions are shown in Figures 2, 3 and 4. Generally it indicates approximately uniform thickness over irregular substrate profiles and a virtually dense pore-free coating. The deposit seems to consists of two zones: a) a region near the iron interface containing both iron and molybdenum, which is probably a molybdenum interlayer and/or Fe-Mo diffusion zone; b) a zone further out, which constitutes the true carbide coating - Figure 4. A typical ED-Analysis for a good quality sample plated under the conditions described above is shown in Figure 5.

Inert Atmosphere

To determine the influence of the inert atmosphere on the coating quality, several plating experiments were carried out in an argon-filled glove box. The results show significant changes in coating quality and morphology in the case of lithium-based electrolyte baths and no significant changes in the case of non-lithium salt baths.

Temperature

The working temperature was varied from 900 to 1000 °C. Below 850 °C no deposit was observed. Non-lithium electrolytes in all cases required higher working temperatures.
Moreover, when adding borate the temperature must be increased by 50 - 80 °C. Increase of temperature causes significant changes. Larger grain sizes are found at higher temperatures.

**Current Modulation**

Both constant current and reverse current patterns were applied during plating. A reverse current electrolysis was preferred in order to achieve a certain grain structure and thickness. This procedure consisted in applying an initial cathodic current, followed by current reversal characterized by the cathodic current \( I_c \) and the anodic current \( I_a \), by cathodic and anodic current flow times \( t_c \) and \( t_a \) respectively, where \( t_c + t_a = T \) represent the full period of the reversing-current wave – Figure 6. It seems that a very important characteristic of a reversing current is the ratio \( t_c/t_a \). This current modulation produces smaller-grain-size coatings than the constant-current plating at the same working temperature. It also makes higher current densities possible and appears to be most effective in generating good quality coatings.

Using the electrochemical deposition cell described above, good quality well-adherent coatings of Mo₅C were obtained under the following conditions:

| Electrolyte       | Na₂WO₄ - K₂WO₄       | 80 - 90 wt% |
|-------------------|----------------------|------------|
|                   | Na₂MoO₄              | 5 - 10 wt% |
|                   | Na₂CO₃               | 3 - 8 wt%  |
|                   | Na₂B₄O₇              | 0.5 - 3 wt%|
| Temperature       | 950 - 1000 °C        |            |
| Cathode substrate | low-carbon steel      |            |
| Anode material    | carbon, molybdenum   |            |
| Cathodic current density | 30 - 50 mA.cm⁻² |            |

**Chronoamperometry**

A comparative study of nucleation and growth of molybdenum layers was carried out, using a single potential step technique. When the potential of the electrode is pulsed to a potential range where deposition of molybdenum occurs, corresponding current transients follow the dependence \( i \sim t^n \), where \( n \) is a constant depending on the geometry and type of nucleation. The current transients have the shape shown in Figure 7. The transients are characterized by (1) an initial current drop due mainly to double layer charging and to the formation of a supersaturated (metastable) solid solution of molybdenum in the surface layers of the substrate (iron); and, (2) a subsequent current rise to a steady state value associated with the formation and growth of the molybdenum deposit. These curves have the characteristic shape often observed for the deposition of metals on foreign metal surfaces.
A preliminary analysis of the initial rising parts of the experimental current transients for relatively high overpotentials shows that they follow very closely $i-t^{1/2}$ dependence as shown in Figure 8. The initial stages of electrochemical deposition of molybdenum can be explained in terms of a model involving instantaneous nucleation and three-dimensional (3-D) mass-transfer controlled growth, similar to the models for conventional electrolytic metal deposition.

As seen from Figures 7 and 8, with the increase of the applied cathodic potential the slope of the $i-t^{1/2}$ dependence rises greatly and the time required for reaching the steady state current decreases.

CONCLUSIONS

Dense, well-adherent molybdenum and molybdenum carbide coatings can be deposited from oxide-based melts. The coating morphology depends strongly on melt composition, temperature and moisture content. Initial pre-electrolysis significantly changes the composition and morphology of the coatings. Non-lithium electrolyte baths do not require extensive purification. Addition of Na$_2$B$_4$O$_7$ to the basic non-lithium bath causes marked morphology and quality improvements. Significant changes appear to be caused also by variation of deposition temperature.

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Figure 1. Electrochemical Plating Cell Assembly.

Figure 2. Cross-Section of a Sample of Condition D. (Lithium-Based Electrolyte, Pre-Electrolysis Performed, Plating in Air, Working Temperature 950 °C).
Figure 3. Cross-Section of a Sample of Condition M. (Lithium-Based Electrolyte, Pre-Electrolysis Performed, Plating in Air, Working Temperature 1000 °C, using Na₂B₄O₇ addition).

Figure 4. Cross-Section of a Sample of Condition Q. (Non-Lithium Based Electrolyte, Pre-Electrolysis Performed, Plating in Air, Working Temperature 1080 °C, using Na₂B₄O₇ addition).
Figure 5. Typical ED-Analysis for a Sample Shown in Figure 4.

Figure 6. Current Pattern: Reverse Current Modulation.
Figure 7. Typical Current-Time Profiles for Chronoamperometric Experiments.

Figure 8. I vs. $t^{1/2}$ Plots of the Initial Rising Parts of the Transients Shown in Figure 7.
Table 1. Chemical Composition of the Electrolyte Baths Used in the Plating Experiments.

|          | Without Pre-electrolysis | Pre-electrolysis |
|----------|---------------------------|-------------------|
|          | Glove box | Outside | Glove box | Outside |
| Without additions | | | | | |
| Lithium baths | A | B | C | D |
| Non-lithium baths | E | F | G | H |
| Borate additions | I | K | L | M |
| Lithium baths | | | | |
| Non-lithium baths | N | O | P | Q |

Table 2. Different Plating Conditions Performed for MSECD from Oxide Baths.