# SMOOTH ELECTRODEPOSITS OF MOLYBDENUM IN KF–Na $_2B_4O_7$ –Na $_2MoO_4$ FUSED SALT MELTS

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#### Summary

An adherent and visually smooth deposit of molybdenum has been electrolytically deposited on copper, nickel, molybdenum, stainless steel and mild steel substrates in a KF-Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-Na<sub>2</sub>MoO<sub>4</sub> fused salt melt at temperatures in the range 998 - 1173 K and current densities in the range 110 - 660 A m<sup>-2</sup>. The use of a graphite anode gives a molybdenum deposit containing a small amount of Mo<sub>2</sub>C.

#### 1. Introduction

Refractory metals obtained by fused salt electrolysis are mostly dendritic or powdery. This is one of the reasons why the winning or coating of refractory metals by fused salt electrolysis is seldom used. This paper describes part of a programme to develop a new method for coating substrate metals with molybdenum or obtaining molybdenum in the form of a sheet or rod by fused salt electrolysis. Previous papers [1-3] have revealed that visually smooth and adherent coatings of molybdenum can be obtained electrolytically on copper, nickel and molybdenum substrates in KF-Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>- $K_2MoO_4$ ,  $KF-B_2O_3-K_2MoO_4$  and  $KF-B_2O_3-Na_2MoO_4$  fused salt melts. Analogous to these melts, a  $KF-Na_2B_4O_7-Na_2MoO_4$  fused salt melt was expected to give visually smooth and adherent coatings of molybdenum. Thus, this work was undertaken to study the electrodeposition of molybdenum from a  $KF-Na_2B_4O_7-Na_2MoO_4$  fused salt melt and, in particular, to determine the ranges of bath composition, temperature and current density that give a visually smooth and adherent deposit of molybdenum. The literature on the electrodeposition of molybdenum from fused salts melts has been reviewed in a previous paper [1].

# 2. Experimental details

The molten salts were prepared from KF (special reagent grade),  $Na_2B_4$ -O<sub>7</sub> (guaranteed reagent grade) and  $Na_2MoO_4$  (guaranteed reagent grade) in the same manner as previously described [1]. Before use, the KF, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and Na<sub>2</sub>MoO<sub>4</sub> were dried in air at 773 K, 723 K and 773 K respectively. A platinum evaporating dish (diameter, 50 mm; height, 25 mm) or a graphite crucible (inside diameter, 72 mm; outside diameter, 90 mm; height, 160 mm) was used as a container for the molten salts. The platinum dish contained about 100 g and the graphite crucible held about 500 g of the molten salt baths. The electrolytic apparatus, electrolysis procedures and method for examining the electrodeposits were also the same as previously described [1]. The surface area of each electrode was  $2 \times 10^{-4}$  m<sup>2</sup> (2 cm<sup>2</sup>) when the platinum container was used and  $9 \times 10^{-4}$  m<sup>2</sup> (9 cm<sup>2</sup>) when the graphite container was used.

# 3. Results and discussion

### 3.1. Effects of bath composition on the molybdenum deposition

To determine the optimal bath composition range, that which gave a visually smooth and adherent molybdenum deposit, 39 different baths were used for the electrolysis. Figure 1 shows the results of the visual examination and X-ray diffraction analysis of the deposits. The KF-Na<sub>2</sub>MoO<sub>4</sub> binary baths which did not contain any Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> gave no cathodic deposit of molybdenum metal or molybdenum-containing compound. However, the addition of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> to the binary baths gave cathodic deposits of molybdenum metal. A visually smooth and adherent deposit of molybdenum



△:no deposit, ②:smooth, adherent Mo,
O:smooth, adherent Mo with dendrites,
O:smooth, adherent Mo with powdery Mo,
O:smooth, adherent Mo with black compound.
O:black compound.

Fig. 1. Results of visual examination and X-ray diffraction analysis (electrolytic conditions: platinum cell, 1123 K, 330 A m<sup>-2</sup>,  $1.1 \times 10^6$  C m<sup>-2</sup>, molybdenum anode and nickel cathode).

without dendrites was obtained over a wide range of bath composition. However, the addition of large amounts of  $Na_2B_4O_7$  gave deposits of powdery molybdenum or an unknown black compound. Also, high concentrations of  $Na_2MoO_4$  gave cathodic deposits of the same unknown compound as in the addition of  $Na_2B_4O_7$ . This unknown compound was the same unknown compound, C, found during the electrolysis of  $Na_2B_4O_7-K_2MoO_4$  [1] and  $KF-B_2O_3-Na_2MoO_4$  baths [3].

Figure 2 shows the variation in cathode current efficiency with the concentration of  $Na_2B_4O_7$ . The cathode current efficiencies for the KF-Na<sub>2</sub>- $MoO_4$  binary baths were almost zero. In these cases, salts deposits caused by splashing were present on parts of the cathode specimens above the surface of the bath. This suggests that the electrode reaction at the cathode probably involved the discharge of H<sup>+</sup> which was supplied by water in the baths. When visually smooth and adherent deposits of molybdenum were plated, the cathode current efficiencies were in the range of 98% to 105% (these efficiencies were calculated assuming that molybdenum metal was electrodeposited from hexavalent molybdenum ions). The efficiencies for the powdery molybdenum deposits were lower than those for the visually smooth and adherent deposits of molybdenum. This is probably due to the detachment of parts of the powdery deposits into the baths from the cathodes during electrolysis; actually, the baths after electrolysis contained much molybdenum powder. For the deposits of the unknown compound and the codeposits of molybdenum and the unknown compound, the efficiencies in Fig. 3 are not the true efficiencies, because they are based on the assumption



Fig. 2. Variation in cathode current efficiency with  $Na_2B_4O_7$  concentration (series I: KF:  $Na_2MoO_4 = 9:1$ ; series II: KF: $Na_2MoO_4 = 8:2$ ; series III: KF: $Na_2MoO_4 = 7:3$ ):  $\blacktriangle$ ,  $\blacksquare$ , codeposits of metallic molybdenum and the black compound;  $\circ^*$ , powdery molybdenum deposits or smooth, adherent molybdenum deposits with powdery molybdenum.



Fig. 3. Variation of anode current efficiency with  $Na_2B_4O_7$  concentration (series I: KF:  $Na_2MoO_4 = 9:1$ ; series II: KF: $Na_2MoO_4 = 9:1$ ; series II: KF: $Na_2MoO_4 = 7:3$ ):  $\blacktriangle$ ,  $\blacksquare$ , anode current efficiencies for cases where codeposits of metallic molybdenum and the black compound were formed at the cathodes;  $\circ^*$ , anode current efficiencies for cases where deposits of powdery molybdenum or deposits of smooth, adherent molybdenum with powdery molybdenum were formed at the cathodes.

that the deposits are pure molybdenum metal. In addition, the unknown compound was easy to detach from the cathodes during electrolysis.

Figure 3 shows the variation in anode current efficiency with the concentration of  $Na_2B_4O_7$ . The following can be seen from Fig. 3: (1) for the KF- $Na_2MoO_4$  baths, the anode current efficiencies are 110% - 130%. The reason for this may be that the molybdenum anodes dissolved partly in the form of lower valent ions such as  $Mo^{5+}$  and  $Mo^{4+}$ , and also dissolved partly chemically. (2) The addition of 5 mol.%  $Na_2B_4O_7$  to the KF- $Na_2MoO_4$  baths reduced the anode current efficiencies to 104% - 110%, and further additions of  $Na_2B_4O_7$  reduced it to 101% - 96% when molybdenum metal was electrodeposited on the cathodes. If large amounts of  $Na_2B_4O_7$  were added and powdery molybdenum was electrodeposited on the cathodes, the anode current efficiencies further decreased, suggesting that oxygen gas evolution occurred.

Figure 4 shows the variation in cell voltage with the  $Na_2B_4O_7$  concentration. The cell voltage varied with the  $Na_2B_4O_7$  concentration in a way similar to that in the KF- $Na_2B_4O_7$ - $K_2MoO_4$ , KF- $B_2O_3$ - $K_2MoO_4$  and KF- $B_2O_3$ - $Na_2MoO_4$  systems [1 - 3]. The abrupt decrease in the cell voltage on adding 5 mol.%  $Na_2B_4O_7$  to the KF- $Na_2MoO_4$  binary baths is considered to be due to the formation of  $Mo^{6+}$  complex anions which are easily reduced at the cathodes. However, the subsequent gradual increase in cell voltage with



Fig. 4. Variation in cell voltage with Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> concentration (series I: KF:Na<sub>2</sub>MoO<sub>4</sub> = 9:1; series II: KF:Na<sub>2</sub>MoO<sub>4</sub> = 8:2; series III: KF:Na<sub>2</sub>MoO<sub>4</sub> = 7:3):  $\blacktriangle$ ,  $\blacksquare$ , cell voltages for cases where codeposits of metallic molybdenum and the black compound were formed at the cathodes;  $\bigcirc^*$ , cell voltages for cases where deposits of powdery molybdenum or deposits of smooth, adherent molybdenum with powdery molybdenum were formed at the cathodes.

the concentration of  $Na_2B_4O_7$  is probably due to the decrease in the conductivity of the electrolytes. The steep rise in the cell voltage at more than 55 mol.%  $Na_2B_4O_7$  corresponds to the decrease in the cathode current (Fig. 2) and the anode current efficiency (Fig. 3). This may be due to a further change in the form of the Mo<sup>6+</sup> complex and to the contribution of oxygen gas evolution at the anode.

3.2. Effects of bath temperature and current density on the molybdenum deposition

To study the effects of bath temperature and current density on the molybdenum deposition, a  $KF(80)-Na_2B_4O_7(5)-Na_2MoO_4(15 \text{ mol.\%})$  bath with a melting point of 960 K was selected as a representative of the baths which gave smooth and adherent deposits of molybdenum under the electrolytic conditions described above. Table 1 lists the electrolytic conditions and the results. It shows that (1) a visually smooth and adherent deposit without dendrites at the edges of a substrate can be obtained at 998 K (725 °C), (2) the upper limit of the cathode current density that gives a visually smooth and adherent deposit of molybdenum without dendrites at the edges of a substrate increases with increasing temperature and (3) when visually smooth and adherent deposits are formed the cathode current efficiency increases with an increase in the cathode current density.

#### TABLE 1

Temperature (K)	Current density (A m <sup>-2</sup> )	Morphology of deposit	X-ray diffraction analysis	Cathode current efficiency (%)	Cell voltage (V)
998	110	smooth deposit	Мо	89	0.12
	220	smooth deposit, dendrite	Мо	93	0.19
	330	smooth deposit, dendrite	Мо	98	0.24
1023	110	smooth deposit	Мо	96	0.15
	220	smooth deposit	Мо	98	0.21
	330	smooth deposit, dendrite	Мо	99	0.25
1073	110	smooth deposit	Мо	95	0.10
	220	smooth deposit	Мо	98	0.15
	330	smooth deposit	Мо	99	0.18
	440	smooth deposit, dendrite	Мо	100	0.24
1123	110	smooth deposit	Мо	91	0.07
	220	smooth deposit	Мо	97	0.11
	330	smooth deposit	Мо	98	0.14
	550	smooth deposit	Мо	99	0.21
	660	smooth deposit, dendrite	Мо	100	0.26
1173	110	smooth deposit	Мо	89	0.06
	220	smooth deposit	Мо	94	0.09
	330	smooth deposit	Мо	96	0.13
	550	smooth deposit	Мо	99	0.20
	660	smooth deposit	Мо	100	0.24
	770	smooth deposit, dendrite	Мо	100	0.30

Effects of temperature and current density on deposition of molybdenum from KF(80)–  $Na_2B_4O_7(5)-Na_2MoO_4(15 mol.\%)$  bath

Electrolytic conditions: molybdenum anode, nickel cathode, amount of electricity of  $1.1 \times 10^6$  C m<sup>-2</sup>, platinum cell.

#### 3.3. Deposition of molybdenum on different substrates

Copper, nickel, molybdenum, stainless steel (SUS304), mild steel (S20C) and graphite were tested as substrate materials. Figure 5 shows the appearance and microstructure of the deposits. All the layers are visually smooth without dendritic formation at the edges of the substrates. Further, all the deposits, except for that on the graphite substrate, were firmly attached to the substrates. The deposit on the graphite substrate seemed partially nonadherent. On the mild steel substrate a visually smooth and adherent deposit was obtained only when the substrate was immersed in the bath with an applied voltage; when the voltage was applied after immersion of the substrate in the bath, a smooth deposit could not be obtained. This suggests a severe effect on the deposition of molybdenum of ferrous or ferric ions. When a molybdenum anode was used, the cathode current efficiency was in the range of 94% to 100%, the anode current efficiency in the range of 96% to 99% and the cell voltage in the range of 0.18 to 2.2 V. When a graphite anode was used, the anode current efficiency was 97%. This was based on



Fig. 5. Appearances and microstructures of deposits (temperature, 1123 K; current density, 220 A m<sup>-2</sup>; amount of electricity, 5.6  $\times 10^{6}$  C m<sup>-2</sup>; cell, graphite).

the assumption that the anode reaction was the generation of  $CO_2$  gas. The microhardness of the deposit, obtained by using the graphite anode, was 5.49 GPa (560 kgf mm<sup>-2</sup>) and much higher than that obtained when using the molybdenum anode. The X-ray diffraction analysis showed that the deposits obtained using a graphite anode contained a small amount of Mo<sub>2</sub>C. Therefore, the high hardness of the deposits from the graphite anode is due in part to the carbon (Mo<sub>2</sub>C) in the deposits. The mechanism by which the deposits contained carbon can be explained as follows: the  $CO_2$  gas which was evolved at the graphite anode dissolved in the bath as  $CO_3^{2-}$ ; the  $CO_3^{2-}$  discharged at the cathode to form Mo<sub>2</sub>C by a cathodic reaction such as  $CO_3^{2-} + 4e = C + 3O^{2-}$ .

### 3.4. Comparison of a platinum cell and a graphite cell

Table 2 shows the comparison of the microhardness of the deposits obtained from a platinum cell with that from a graphite cell. The microhardness of the deposits from the graphite cell is much higher than that from the platinum cell. The X-ray diffraction analysis detected small amounts of  $Mo_2C$  in the deposits on the nickel, molybdenum, SUS304 and S20C substrates when the graphite cell was used, but not for that on the copper substrate, whereas  $Mo_2C$  was not found in the deposits when the platinum cell was used. This shows that the carbon in the deposits obtained using the graphite cell came from the graphite cell; the graphite cell probably reacted with the molybdate ions to form  $CO_3^{2^-}$ .

Cell			Substrate		#38#800TT, P
	Cu	Ni	Мо	SUS304	S20C
Platinum cell Graphite cell	2.75 3.23	2.22 3.51	2.20 4.15	3.17 3.54	$\begin{array}{c} 3.50 \\ 6.44 \end{array}$

TABLE 2Vickers microhardness H<sub>v</sub> of the deposits (GPa)

Bath, KF(80)-Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>(5)-Na<sub>2</sub>MoO<sub>4</sub>(15 mol.%); temperature, 1123 K; current density, 220 A m<sup>-2</sup>; amount of electricity,  $5.6 \times 10^6$  C m<sup>-2</sup>.

Even in the case of the platinum cell, the microhardness of the deposits on the copper, SUS304 and S20C substrates is much higher than that of the deposits on the nickel and molybdenum substrates. The reason for this is not clear because the electrodeposits obtained from a  $KF-Na_2B_4O_7-K_2MoO_4$ bath [4] under the same electrolytic conditions as those in the present experiment did not show large differences in microhardness among the substrate materials.

# 4. Conclusions

To find a fused salt bath giving a smooth, adherent deposit of molybdenum,  $KF-Na_2B_4O_7-Na_2MoO_4$  fused salt baths were subjected to electrolysis. The results are summarized as follows.

(1) An adherent and visually smooth deposit of molybdenum was obtained over a wide range of compositions of the  $KF-Na_2B_4O_7-Na_2MoO_4$  fused salt baths.

(2) The electrolytic conditions giving an adherent and smooth deposit of molybdenum in the KF(80)-Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>(5)-Na<sub>2</sub>MoO<sub>4</sub>(15 mol.%) fused salt bath were 110 A m<sup>-2</sup> at 998 K, 110 - 220 A m<sup>-2</sup> at 1023 K, 110 - 330 A m<sup>-2</sup> at 1073 K, 110 - 550 A m<sup>-2</sup> at 1123 K and 110 - 660 A m<sup>-2</sup> at 1173 K.

(3) The use of a graphite anode gave a molybdenum deposit containing a small amount of  $Mo_2C$ .

# References

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