Journal of the Less-Common Metals, *134* (1987) 141 - 151

SMOOTH ELECTRODEPOSITS OF MOLYBDENUM FROM $KF-K_2B_4O_7-K_2MoO_4$ FUSED SALT MELTS

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(Received January 15, 1987)

Summary

An adherent and visually smooth deposit of molybdenum has been electrolytically deposited on copper, nickel, molybdenum, stainless steel, mild steel and graphite substrates in a $KF-K_2B_4O_7-K_2MoO_4$ fused salt melt at temperatures in the range 998 - 1173 K and current densities in the range 110 - 660 A m^{-2}. The deposits were not as hard as those obtained from $KF-B_2O_3-MoO_3$, $KF-B_2O_3-Na_2MoO_4$, $KF-B_2O_3-K_2MoO_4$ and $KF-Na_2B_4O_7-Na_2MoO_4$ fused salt melts, a little harder than the smooth deposits obtained from a $KF-Li_2B_4O_7-Li_2MoO_4$ fused salt melt, and in spite of the use of a graphite cell, comparable with that of a molybdenum button which was prepared by plasma-arc-melting a commercially available molybdenum sheet. The use of a graphite anode also gave a smooth deposit of molybdenum although it contained a small amount of Mo_2C. No chemical compound was electrodeposited from the $KF-K_2B_4O_7-K_2MoO_4$ fused salt melts.

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1. Introduction

Molybdenum metal has good physical properties at high temperatures and excellent corrosion resistance against molten salts, especially against sulphur-containing molten salts [1]. However, it is very expensive and is difficult to fabricate. Therefore, it is worthwhile to coat an inexpensive metallic substrate with molybdenum metal or to obtain molybdenum metal in the form of a sheet or rod. Previous papers [2 - 7] have revealed that visually smooth and adherent coatings of molybdenum can be obtained electrolytically on copper, nickel and molybdenum substrates in $KF-Na_2B_4O_7-K_2MoO_4$, $KF-B_2O_3-K_2MoO_4$, $KF-B_2O_3-Na_2MoO_4$, $KF-B_2O_3-MoO_3$, $KF-Na_2B_4O_7-Na_2MoO_4$ and $KF-Li_2B_4O_7-Li_2MoO_4$ fused salt melts. Analogous to these melts, a $KF-K_2B_4O_7-K_2MoO_4$ fused salt melt was also expected to give visually smooth and adherent coatings of molybdenum. Thus this work was undertaken to study the electrodeposition of molybdenum in a $KF-K_2B_4O_7-K_2MoO_4$ fused salt melt and, in particular, to

0022-5088/87/$3.50 © Elsevier Sequoia/Printed in The Netherlands

determine the ranges of bath composition, temperature and current density that gave a visually smooth and adherent deposit of molybdenum. This salt was found to give molybdenum deposits with a hardness comparable with that of a commercially available molybdenum metal. Furthermore, no chemical compound was electrolytically deposited in the whole compositional range examined. The literature on the electrodeposition of molybdenum from fused salts has been reviewed in a previous paper [2].

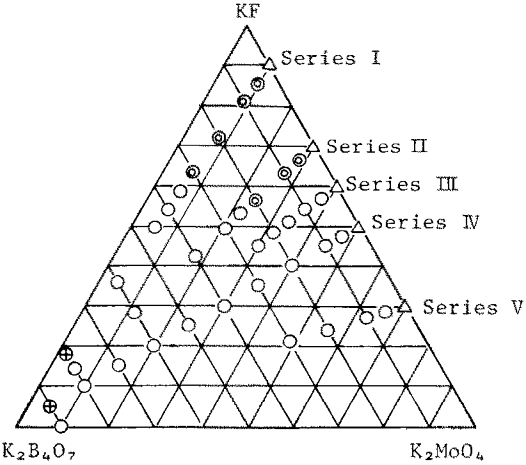
2. Experimental details

The apparatuses for electrolysis and the preparation of electrodes were the same as described in ref. 7. The fused salts were prepared from KF (special reagent grade), $K_2B_4O_7$ (guaranteed reagent grade) and K_2MoO_4 (chemical reagent grade). The method for the preparation of the baths was the same as described in ref. 7. The electrolysis was carried out at constant current densities (110, 220, 330, 440, 550, 660 and 770 A m^{-2}) and at constant temperatures (998, 1023, 1073, 1123 and 1173 K). The procedures for electrolysis and the examination of electrodeposits were the same as described in ref. 7.

3. Results and discussion

3.1. Effects of bath composition on the molybdenum deposition

To determine the optimal bath composition range which gave a visually smooth and adherent deposit of molybdenum, 42 different baths were used for the electrolysis. The results of the visual examination and X-ray diffraction analysis for the electrodeposits are shown in Fig. 1. The KF–K_2MoO_4 binary baths gave no cathodic deposits of molybdenum metal or molybdenum-containing compounds. The addition of $K_2B_4O_7$ to the binary baths of series I and II gave visually smooth and adherent deposits of metallic molybdenum without dendrites at the edges of the substrates. However, the addition of large amounts of $K_2B_4O_7$ changed the deposit from a visually smooth adherent deposit of metallic molybdenum without dendrites at the edges of the substrate to a deposit with dendrites at the edges of the substrate, and then to a deposit of powdery molybdenum. The addition of $K_2B_4O_7$ to the KF–K_2MoO_4 binary baths of series III, IV and V gave visually smooth and adherent deposits of metallic molybdenum with dendrites at the edges of the substrates. Furthermore, it is worth noting that even the 90mol.%$K_2B_4O_7$–10mol.%K_2MoO_4 binary bath which did not contain any KF did not give a chemical compound but gave a visually smooth and adherent deposit of metallic molybdenum although it was accompanied by dendrites at the edges of the substrate. Therefore, it was found that the KF–$K_2B_4O_7$–K_2MoO_4 fused salt system gave only metallic molybdenum electrodeposits. This is in contrast to the behaviour of KF–$Na_2B_4O_7$–K_2MoO_4,



△:no deposit, ◎:smooth adherent Mo,
○:smooth adherent Mo with dendrites,
⊕:powdery Mo.

Fig. 1. Results of visual examination and X-ray diffraction analysis (electrolytic conditions: platinum cell, 1123 K, 330 A m^{-2}, 1.1 × 10^6 C m^{-2}, molybdenum anode and nickel cathode).

$KF-B_2O_3-K_2MoO_4$, $KF-B_2O_3-Na_2MoO_4$, $KF-B_2O_3-MoO_3$, $KF-Na_2B_4O_7-Na_2MoO_4$ and $KF-Li_2B_4O_7-Li_2MoO_4$ fused salt systems which give electrodeposits of not only metallic molybdenum but also molybdenum compounds.

The variation in cathode current efficiency with concentration of $K_2B_4O_7$ is shown in Figs. 2 and 3. The cathode current efficiencies for smooth and adherent deposits with or without dendrites at the edges of the substrates were almost 100%. When powdery molybdenum deposits were obtained, the cathode current efficiencies were much lower than 100%. This is thought to be due to the detachment of parts of the powdery deposits from the substrates into the baths during electrolysis.

The variation in anode current efficiency with the concentration of $K_2B_4O_7$ is shown in Figs. 4 and 5. The anode current efficiency changed in a similar way to that in the KF–borate–molybdate systems described previously [2 - 7], *i.e.* it was greater than 100% when the amount of $K_2B_4O_7$ was small, it decreased to almost 100% with an increasing amount of $K_2B_4O_7$ and decreased further to less than 100% when powdery molybdenum deposited at the cathodes. The reason for such behaviour of the anode current efficiency has been discussed in a previous paper [6].

The variation in cell voltage with the concentration of $K_2B_4O_7$ is shown in Fig. 6. The cell voltage varied with the concentration of $K_2B_4O_7$ in a similar way to that in the KF–borate–molybdate systems described previously. The reason for such behaviour of the cell voltage has also been discussed in a previous paper [6].

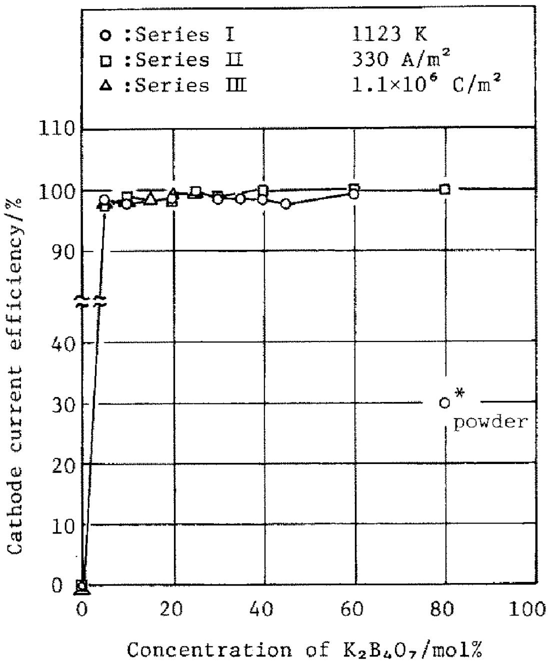


Fig. 2. Variation in cathode current efficiency with $K_2B_4O_7$ concentration (series I, KF:K_2MoO_4 = 9:1; series II, KF:K_2MoO_4 = 7:3; series III, KF:K_2MoO_4 = 6:4).

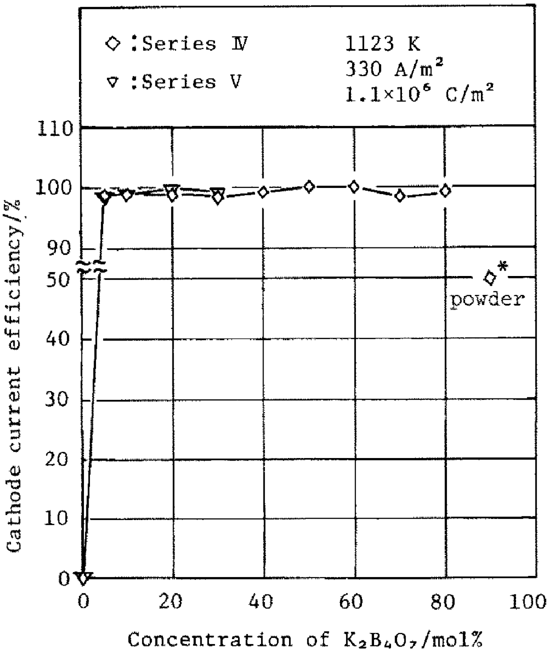


Fig. 3. Variation in cathode current efficiency with $K_2B_4O_7$ concentration (series IV, KF:K_2MoO_4 = 5:5; series V, KF:K_2MoO_4 = 3:7).

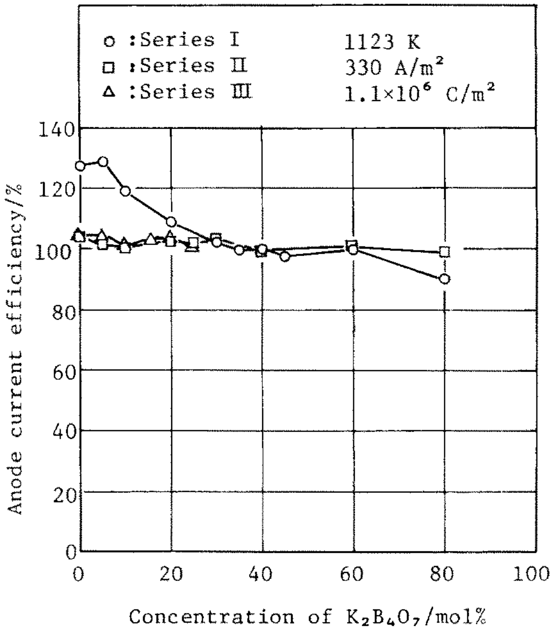


Fig. 4. Variation in anode current efficiency with $K_2B_4O_7$ concentration (series I, KF:K_2MoO_4 = 9:1; series II, KF:K_2MoO_4 = 7:3; series III, KF:K_2MoO_4 = 6:4).

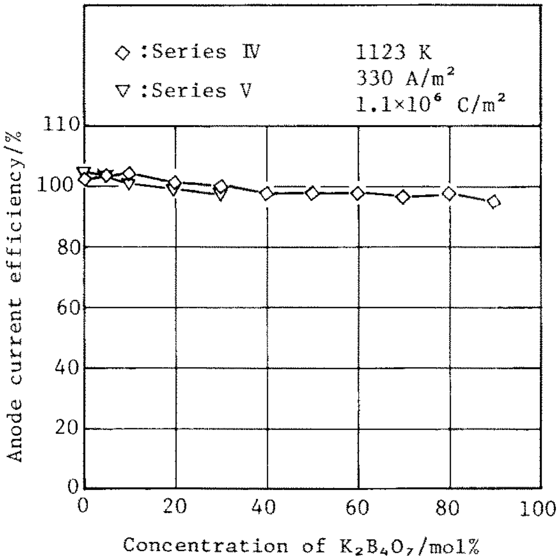


Fig. 5. Variation in anode current efficiency with $K_2B_4O_7$ concentration (series IV, KF:K_2MoO_4 = 5:5; series V, KF:K_2MoO_4 = 3:7).

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 70mol.%KF–10mol.%$K_2B_4O_7$–20mol.%K_2MoO_4

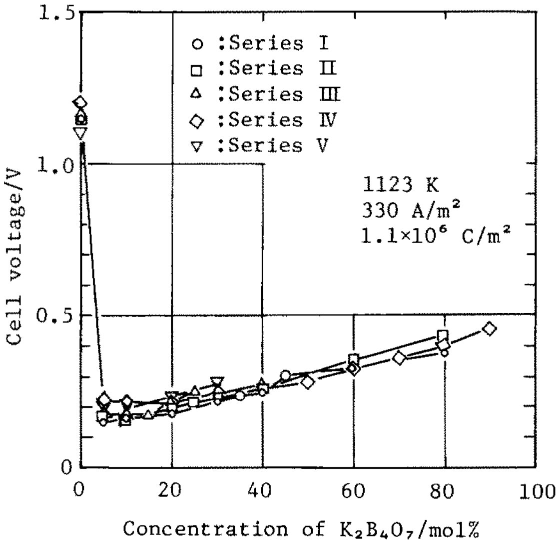


Fig. 6. Variation in cell voltage with $K_2B_4O_7$ concentration (series I, KF:K_2MoO_4 = 9:1; series II, KF:K_2MoO_4 = 7:3; series III, KF:K_2MoO_4 = 6:4; series IV, KF:K_2MoO_4 = 5:5; series V, KF:K_2MoO_4 = 3:7).

bath with a melting point of 961 K was selected as a representative of the baths which gave smooth and adherent deposits of molybdenum under the electrolytic conditions described earlier. The electrolytic conditions and the results are listed in Table 1. The lowest temperature which gave a visually smooth and adherent deposit without dendrites at the edges of the substrate was 998 K (725 °C). This is lower than the lowest temperatures of the 76mol.%KF–20mol.%B_2O_3–4mol.%MoO_3, 41.25mol.%KF–13.75-mol.%$Na_2B_4O_7$–45mol.%K_2MoO_4, 65mol.%KF–25mol.%B_2O_3–10mol.%K_2-MoO_4, 75mol.%KF–15mol.%B_2O_3–10mol.%Na_2MoO_4 and 77.5mol.%KF–7.5mol.%$Li_2B_4O_7$–15mol.%Li_2MoO_4 baths, and equal to the lowest temperatures of the 60mol.%KF–20mol.%$Na_2B_4O_7$–20mol.%K_2MoO_4 and 80mol.%-KF– 5mol.%$Na_2B_4O_7$–15mol.%Na_2MoO_4 baths [2 - 7].

The upper limits of the cathode current density that gave visually smooth and adherent deposits without dendrites at the edges of the substrates were 110 A m^{-2} at 998 K, 220 A m^{-2} at 1023 K, 330 A m^{-2} at 1073 K and 660 A m^{-2} at 1123 and 1173 K. In comparing these values with the upper limits of the other KF–borate–molybdate baths reported previously [2 - 7], the present bath is roughly comparable with the 76mol.%KF–20mol.%B_2O_3–4mol.%MoO_3, 65mol.%KF–25mol.%B_2O_3–10mol.%K_2MoO_4, 75mol.%KF–15mol.%B_2O_3–10mol.%Na_2MoO_4 and 80mol.%KF–5mol.%Na_2-B_4O_7–15mol.%Na_2MoO_4 baths, and superior to the 41.25mol.%KF–13.75-mol.%$Na_2B_4O_7$–45mol.%K_2MoO_4, 60mol.%KF–20mol.%$Na_2B_4O_7$–20mol.%-K_2MoO_4 and 77.5mol.%KF–7.5mol.%$Li_2B_4O_7$–15mol.%Li_2MoO_4 baths with regard to the upper limit of the cathode current density which gives a smooth deposit of molybdenum.

TABLE 1

Effects of temperature and current density on deposition of molybdenum from the 70mol.%KF–10mol.%$K_2B_4O_7$–20mol.%K_2MoO_4

Temperature (K)	*Current density* ($A\ m^{-2}$)	*Morphology of deposit*	*X-ray diffraction analysis*	*Cathode current efficiency* (%)	*Cell voltage* (V)
998	110	smooth deposit	Mo	99.6	0.17
	220	smooth deposit, dendrite	Mo	98.2	0.24
1023	110	smooth deposit	Mo	98.5	0.12
	220	smooth deposit	Mo	99.4	0.21
	330	smooth deposit, dendrite	Mo	99.1	0.27
1073	110	smooth deposit	Mo	93.0	0.10
	330	smooth deposit	Mo	100.4	0.20
	440	smooth deposit, dendrite	Mo	100.3	0.22
1123	110	smooth deposit	Mo	94.4	0.08
	330	smooth deposit	Mo	99.6	0.16
	660	smooth deposit	Mo	101.5	0.27
	770	smooth deposit, dendrite	Mo	100.3	0.32
1173	110	smooth deposit	Mo	98.7	0.05
	330	smooth deposit	Mo	100.9	0.12
	660	smooth deposit	Mo	103.4	0.26
	770	smooth deposit, dendrite	Mo	99.4	0.33

Electrolytic conditions: molybdenum anode, nickel cathode, amount of electricity of $1.1 \times 10^6\ C\ m^{-2}$, 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. The appearance and microstructure of the deposits which were obtained by using the graphite cell are shown in Fig. 7. In the case of the copper, nickel, molybdenum, stainless steel and graphite substrates, the voltage was applied after the substrates were immersed in the bath, whereas in the case of the mild steel substrate, the voltage was applied before the substrate was immersed in the bath in order to improve the adherence of the deposit to the mild steel substrate. All the deposits were visually smooth without dendritic formation at the edges of the substrates. The deposits were firmly attached to all the substrates tested. However, in the case of the mild steel substrate, the adherence of the deposit was not good when the voltage was applied after the substrate was immersed in the bath. The microstructures of the two mild steel specimens obtained by applying the cell voltage before and after the substrate was immersed in the bath are shown in Fig. 8.

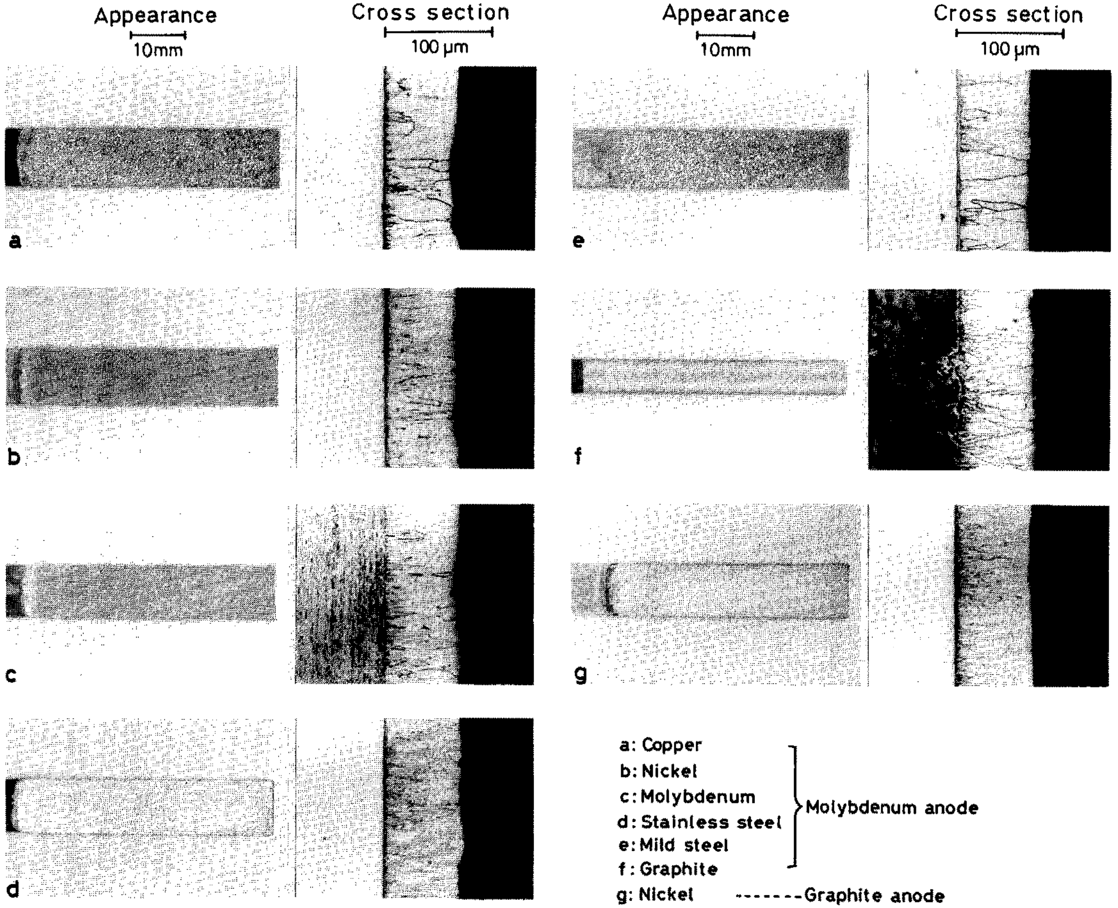


Fig. 7. Appearances and microstructures of deposits (temperature, 1123 K; current density, 220 A m^{-2}; amount of electricity, 5.6×10^6 C m^{-2}; cell, graphite).

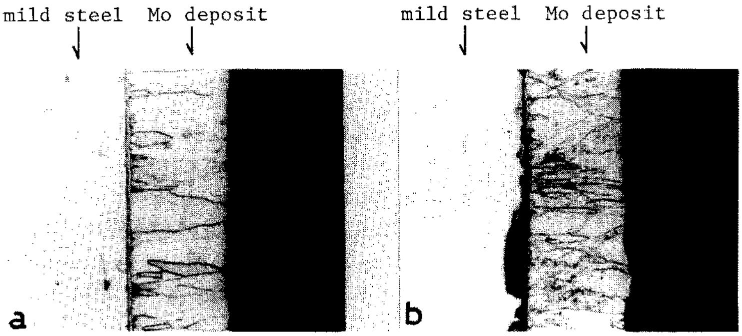


Fig. 8. Microstructures of deposits on mild steel substrates. (a) Voltage was applied before immersion of the substrate in the bath. (b) Voltage was applied after immersion of the substrate in the bath.

The use of a graphite anode also gave a smooth and adherent deposit on a nickel substrate.

The values of the Vickers microhardness of the deposits (a graphite cell was used) are listed in Table 2. When a molybdenum anode was used, in spite of the use of a graphite cell, the value of the hardness was in the range of 195 to 217, and was almost comparable with the value 198 of the molybdenum button which was prepared by plasma-arc-melting the molybdenum sheet which was used as an anode. Furthermore, the hardness of the deposits obtained from the $KF-K_2B_4O_7-K_2MoO_4$ molten salt bath was lower than that of the deposits obtained from the $KF-B_2O_3-MoO_3$, $KF-B_2O_3-K_2MoO_4$, $KF-B_2O_3-Na_2MoO_4$ and $KF-Na_2B_4O_7-Na_2MoO_4$ baths and a little higher than that of the deposits from the $KF-Li_2B_4O_7-Li_2MoO_4$ bath. For example, the values of the hardness of the deposits on the molybdenum substrates

TABLE 2

Deposition of Mo on several substrates

Substrate	*Anode*	*Cathode current efficiency (%)*	*Cell voltage (V)*	*Vickers hardness*[a]	*X-ray diffraction analysis*
copper	Mo	100.9	0.17	198	Mo
nickel	Mo	101.9	0.17	195	Mo
molybdenum	Mo	103.4	0.16	196	Mo
SUS304	Mo	103.4	0.17	217	Mo
S20C	Mo	97.9	0.15	215	Mo
graphite	Mo	101.0	0.16	202	Mo
nickel	C	99.9	0.33	508	$Mo + Mo_2C$

[a] The Vickers microhardness of a molybdenum button, which was prepared by plasma-arc-melting a molybdenum sheet used as an anode, was 198. Bath, 70mol.%KF–10mol.%$K_2B_4O_7$–20mol.%K_2MoO_4; cell, graphite crucible; temperature, 1123 K; current density, 220 A m^{-2}; amount of electricity, 5.6×10^6 C m^{-2}.

obtained from the $KF-B_2O_3-MoO_3$, $KF-B_2O_3-K_2MoO_4$, $KF-B_2O_3-Na_2MoO_4$, $KF-Na_2B_4O_7-Na_2MoO_4$ and $KF-Li_2B_4O_7-Li_2MoO_4$ baths were 226, 346, 295, 423 and 171 respectively [3 - 7].

The value of the hardness of the deposit obtained when using a graphite anode was 508 and much higher than that (196) obtained when using the molybdenum anode. The X-ray diffraction analysis showed that the deposit obtained by using the graphite anode contained a small amount of Mo_2C. Therefore, the high hardness of the deposit from the graphite anode is due to the carbon (Mo_2C) in the deposits. The mechanism which results in a deposit containing carbon was discussed in a previous paper [7].

4. Conclusion

To find a fused salt giving a smooth adherent deposit of molybdenum, $KF-K_2B_4O_7-K_2MoO_4$ fused salt baths were subjected to electrolysis. The results are summarized as follows.

(1) Visually smooth deposits of molybdenum were obtained from $KF-K_2B_4O_7-K_2MoO_4$ fused salt baths.

(2) The electrolytic conditions that gave a smooth deposit of molybdenum in the $70mol.\%KF-10mol.\%K_2B_4O_7-20mol.\%K_2MoO_4$ fused salt bath were as follows: 110 A m^{-2} at 998 K, 110 - 220 A m^{-2} at 1023 K, 110 - 330 A m^{-2} at 1073 K and 110 - 660 A m^{-2} at 1123 K and 1173 K.

(3) The adherence of the smooth deposits of molybdenum to copper, nickel, molybdenum, stainless steel (SUS304), mild steel (S20C) and graphite substrates was very good.

(4) The Vickers microhardness of the smooth deposits was lower than that of the smooth deposits obtained from $KF-B_2O_3-MoO_3$, $KF-B_2O_3-Na_2MoO_4$, $KF-B_2O_3-K_2MoO_4$ and $KF-Na_2B_4O_7-Na_2MoO_4$ fused salt baths, a little higher than that of the smooth deposits obtained from a $KF-Li_2B_4O_7-Li_2MoO_4$ fused salt bath, and in spite of the use of a graphite cell, comparable with that of a molybdenum button which was prepared by plasma-arc-melting a commercially available molybdenum sheet.

(5) The use of a graphite anode also gave a smooth molybdenum deposit although it contained a small amount of Mo_2C.

(6) No chemical compound was electrodeposited from the $KF-K_2B_4O_7-K_2MoO_4$ fused salt melts.

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