Design of Molten Salt Bath on the Basis of Acid-Base Cooperative Reaction Mechanism. Smooth Electrodeposition of Tungsten from KF-B₂O₃-WO₃ Molten Salt

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This investigation was carried out to find a molten salt which enables a smooth electrodeposition of tungsten. The KF-B₂O₃-WO₃ molten salt was selected on the basis of the acid-base cooperative reaction theory. A composition of KF(67 mol %)-B₂O₃(26 mol %)-WO₃(7 mol %) was selected as the preferred bath composition. Using a tungsten anode, smooth electrodepositions were obtained at 1123 K and at a current density ranging from 250 Am⁻² to 550 Am⁻² on nickel, copper, stainless steel, and mild steel substrates. When a graphite anode was used, smooth electrodepositions accompanied by dendrites were obtained. The Vickers microhardness number of the electrodeposit was 422 (load 0.49 N). The smooth electrodeposit had tendencies to form the 111 fiber texture or a mixed texture of the 111, 211, and 321 fiber textures.

Key Words: Tungsten, Smooth Electrodeposition, Molten Salt Electrolysis, Acid-Base Cooperative Reaction

1 Introduction

Tungsten metal has the highest melting point (3660 K) of the nine refractory metals, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W. Thus tungsten metal exhibits a high tensile strength and a high yield strength as well as a high modulus of elasticity at elevated temperatures, and accordingly is used as a heat-resistant metal and as a main constituent of heat-resistant, high-hardness and/or wear-resistant materials. For example, it is used for filaments and electrodes of lamps and cutting tools. Also, tungsten metal shows excellent corrosion resistance against some special corrosion environments such as sulfur-containing molten salts.

However, tungsten metal is brittle at ambient temperatures and is not cold-deformable, and thus, it is only used in simple forms. Moreover, it is very expensive. Therefore, it has been desired to develop an industrial method to coat inexpensive metallic substrates with tungsten metal or to produce tungsten metal in the form of sheets and rods. Hitherto, molten salt electrolysis, CVD, PVD, plasma spraying and so on have been proposed as the method for the tungsten coating and some part of them are used in industry, but none has been entirely satisfactory. Of these methods, molten salt electrolysis is considered to be the most promising.

The molten salts which have been proposed for obtaining thick tungsten coatings are: (1) the fluoride bath by Mellors and Senderoff, (2) the NaLiB₂O₄(67 mol %)-NaLiWO₄(22 mol %)-WO₃(11 mol %) bath by Davis and Gentry and by McCawley, Kenahan and Schlain, (3) the chloride bath and the chlorobromide bath by Zuckerbrod and Bailey, and (4) the ZnBr₂-NaBr-WBr₃ bath and the ZnCl₂-NaCl-WCl₄ bath by Katagiri, Suzuki and Takehara. Also, White and Twardoch mentioned the possibility of obtaining coherent tungsten deposits from a chloride bath. Yabe et al. also stated the possibility of obtaining a smooth tungsten deposit from the LiF-KF-K₂WO₄-Na₂O bath.

One of the authors (K. Koyama) has succeeded in obtaining thick smooth electrodeposits of molybdenum using KF-MoO₃ (or molybate) molten salt baths to which B₂O₃ (or tetraborate), AlF₃, or metaphosphate is added. To explain the reason for the success, he proposed a new concept of the acid-base cooperative reaction as follows: B₂O₃ (or tetraborate), AlF₃, and metaphosphate act as strong acids, and F⁻ acts as a strong base. The acid and the base cooperate to pull away some of the oxygen ions off MoO₃ or MoO₄, and alternatively F⁻ coordinates to the molybdenum ion in place of the oxygen ions. As a result, some oxyfluoride ion of molybdenum is
formed, and this ion can easily discharge at a cathode to give a smooth electrodeposition of molybdenum.

In the present investigation, on the basis of this theory, we selected the KF-B₂O₃-WO₃ molten salt, and attempted the smooth electrodeposition of tungsten.

2 Experimental

Figure 1 shows the outline of the experimental procedure.

2.1 Preparation of KF-B₂O₃-WO₃ bath

The reagents for the components KF, B₂O₃, and WO₃ were of reagent grade. Prior to weighing, KF and B₂O₃ were dried at 773 K for 3.6 ks (1 h) in air, and WO₃ was dried at 523 K for 10.8 ks (3 h) in air. Each reagent was weighed in a prescribed ratio, placed together in a bath container, dried at 773 K for 10.8 ks (3 h) in a vacuum which was produced by use of a rotary oil pump equipped with a trap chilled by liquid nitrogen, and then fused in an argon atmosphere to use as an electrolytic bath. A platinum crucible (diameter: 70 mm, height: 40 mm) or a graphite crucible (inner diameter: 74 mm, height: 145 mm) was used as the bath container. The amount of the bath was 220 g when using the platinum container and 500 g when using the graphite container. The graphite crucible was used when graphite anodes were used.

2.2 Electrolysis

Electrolysis was carried out on the apparatus whose schematic diagram is shown in Fig. 2. A tungsten sheet or a graphite rod (6 mm in diameter) was used as the anode material, and a nickel (JIS NNCP), copper (JIS C1100), mild steel (JIS SN400B), or stainless steel (JIS SUS304) sheet was used as the cathode substrate; each sheet was 10 mm in width, 0.3 mm in thickness and 100 mm in length. Prior to use, these sheets were polished with #0 emery paper, then degreased with acetone, and then immersed 15 mm (when the platinum crucible was used) or 30 mm (when the graphite crucible was used) into the electrolytic baths.

Electrolysis was performed under a purified argon atmosphere by use of direct current (ripple voltage 0.1 %) without the agitation of the baths or the rotation of the electrodes. After the preparation of the baths, for the purpose of the dehydration, purification and conditioning of the baths, preelectrolysis was carried out before main electrolysis by use of a tungsten anode at a temperature of 1123 K, a current density of 1000 Am⁻², and an amount of electricity of more than 5000 C (when the platinum container was used) or more than 10000 C (when the graphite container was used). After the preelectrolysis, the anode and the cathode were renewed, and then main electrolysis was carried out at a constant temperature, a constant current density, and a fixed amount of electricity. On completion of the main electrolysis, the anode and the cathode were lifted 180 cm over the bath surface.

Fig. 1 Outline of the experiment.

Fig. 2 Schematic diagram of the electrolytic apparatus. 1. Ar gas inlet or outlet, 2. Stainless steel vessel, 3. Ceramics tube, 4. Anode or Cathode, 5. Bath container, 6. Brick, 7. Bath, 8. Cooling tube
allowed to cool there for 0.9 ks (15 min), then taken out of the electrolytic cell assembly, and immersed in a boiling Al(NO₃)₃ aqueous solution in order to remove the adhering salt (the salt taken out together with the anode and cathode). The adhering salt was easily soluble in the above Al(NO₃)₃ aqueous solution.

The anodic and cathodic current efficiencies were calculated from the amount of electricity and the changes in the masses of the anode and cathode, on the assumption that the tungsten atoms dissolved in the form of W⁶⁺ from the anode and deposited from W⁶⁺ on the cathode.

2. 3 Evaluation of electrodeposits

The electrodepositions were observed with the naked eye, and classified into five types: (1) a smooth deposit, (2) dendrites, (3) a smooth deposit + dendrites, (4) a smooth deposit + an umbrella-like deposit, and (5) a smooth deposit + an umbrella-like deposit + dendrites. The umbrella-like deposit means that the electrodeposits grows like an umbrella on the bath surface and extends towards the anode. After the classification of the electrodeposits, they were identified by X-ray diffraction analysis (CuKα). As for the smooth deposits, they were mounted in a resin, sectioned perpendicular to the substrate sheet surfaces, polished like a mirror, etched by an aqueous solution [2 g K₃Fe(CN)₆ + 2 g KOH + 100 g H₂O], and then submitted to metallographic examination and hardness measurement. The hardness number was measured on a Vickers microhardness tester with a load of 0.49 N (50 gf).

3 Results and Discussion

3. 1 Determination of preferred bath composition

In order to find a bath giving a smooth electrodeposits alone, several baths of the KF-B₂O₃-WO₃ system were subjected to electrolysis. The electrolysis was carried out at 1123 K and 300 Am⁻² using a tungsten anode and a nickel substrate in the platinum container. Figure 3 shows the results of the views of the electrodeposits together with freezing points (strictly speaking, primary crystallization temperatures). The X-ray diffraction analysis showed that all deposits were tungsten metal. The KF-WO₃ binary baths only gave dendritic deposits. When B₂O₃ was added to the KF-WO₃ binary baths, however, dendritic deposition was suppressed, and smooth electrodeposits with or without a small amount of dendrites or an umbrella-like deposit were obtained. This result means that some easily reducible tungsten chemical species was formed by an acid-base cooperative reaction. Of the baths which gave smooth deposits without a small amount of dendrites or an umbrella-like deposit, the KF(67 mol %)-B₂O₃(26 mol %)-WO₃(7 mol %) bath has the lowest freezing point (about 975 K). In general, a bath having a lower freezing point enables us to adopt a higher current density and a lower electrolysis temperature. Thus we selected this bath as a preferred bath and used it in the subsequent electrolysis.

3. 2 Influence of current density on appearance of electrodeposits

The influence of current density on the appearance of the electrodeposits, current efficiency, and bath voltage was examined at a fixed temperature of 1123 K by changing the current density from 200 Am⁻² to 600 Am⁻². Table 1 shows the results. Smooth electrodeposits were obtained in the current density ranging from 250 Am⁻² to 550 Am⁻². Figure 4 shows the appearance and cross-section of an electrodeposits obtained at a current density of 300 Am⁻². Comparing the photograph of this cross-section with that of

<table>
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<th>Current density/Am⁻²</th>
<th>Current efficiency/%</th>
<th>Bath voltage/V</th>
<th>Appearance</th>
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<td>200</td>
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<td>0.13</td>
<td>powder</td>
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<td>116</td>
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</tr>
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<td>107</td>
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<td>0.17</td>
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<tr>
<td>550</td>
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</tr>
<tr>
<td>600</td>
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<td>smooth deposit + dendrites</td>
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the smooth molybdenum electrodeposits previously obtained from the KF-B$_2$O$_3$-MoO$_3$ bath, it was found that the smoothness of the tungsten deposits obtained in the present investigation was inferior to that of the molybdenum electrodeposits, that is, the smooth electrodeposition of tungsten was more difficult than that of molybdenum. From this result, it is inferred that the affinity between the tungsten ion and the oxygen ion is stronger than the affinity between the molybdenum ion and the oxygen ion. As a result, an oxyfluoride ion of tungsten is probably more difficult to be formed by the acid-base cooperative reaction than is an oxyfluoride ion of molybdenum.

The cathodic current efficiency was around 100% while anodic current efficiency scattered and ranged from 107% to 135%. The reason for this is considered to be as follows: (1) Tungsten dissolved in the form of both the hexavalent ion and some lower valent ions, and/or (2) Chemical dissolution accompanied the anodic dissolution. Thus, the rate of chemical dissolution of tungsten was measured in the bath at 1123 K. It was $1.0 \times 10^{-2}$ g cm$^{-2}$ s$^{-1}$. The apparent anodic current efficiencies were corrected with this value. The results are shown in Fig. 5. The corrected anodic current efficiencies approached to 100%. However, the anodic current efficiency at 550 Am$^{-2}$ was much higher than 100%. Therefore, it is reasonable to infer that the tungsten anode dissolved anodically and in part chemically, and that the anodic dissolution proceeded in the form of hexavalent ion and in part some lower valent ions.

Next, in order to examine the influence of the electrolytic temperature on the smoothness of the electrodeposits, the temperature was lowered from 1123 K to 1113 K. Table 2 shows the results. Smooth electrodeposits were obtained at 250 Am$^{-2}$ and 300 Am$^{-2}$. When the temperature was further lowered, no smooth electrodeposits were obtained at any current density. Therefore, in order to obtain a smooth electrodeposition using the present preferred bath, the electrolysis must be carried out at 1123 K or higher temperatures.

### 3.3 Deposition on Different Substrates

Copper, stainless steel and mild steel were tested as substrate materials. The electrolysis was carried out at 1123 K, a current density of 300 Am$^{-2}$, and an amount of electricity of $5.0 \times 10^{6}$ C m$^{-2}$. When mild steel was used as a substrate material, voltage was applied before the immersion of the substrate in the bath because mild steel was immediately attacked by...
the bath on its being immersed in the bath. Figure 6 shows the appearances and microstructures of the electrodeposits. Smooth tungsten electrodeposits were formed on copper, mild steel and stainless steel as well as nickel. Therefore, it can be said that the substrate has no substantial influences on the morphology of the electrodeposited tungsten.

3. 4 Hardness of electrodeposits

The Vickers microhardness number of the electrodeposits, which was obtained from electrolysis at 1123 K and 300 Am−2, was 422 (load 0.49 N). This hardness number is almost the same as that of a commercial tungsten wire which was annealed at 2273 K.21) Thus it can be said that the present molten salt is able to produce a coating of tungsten which corresponds to commercial pure tungsten.

3. 5 X-ray diffraction

The microstructures of the smooth electrodeposits (Figs. 3 and 6) showed that they consisted of columnar grains. Thus, the deposits were supposed to have a fiber texture. In general, electrodeposits obtained in aqueous solutions are well known to have fiber textures. The crystalline orientation of the deposits prepared in the present investigation was examined by X-ray diffraction analysis. To confirm the reproducibility, the electrolysis was carried out more than ten times. The X-ray diffraction pattern showed two types: Sample 1 and Sample 2 as shown in Fig. 7. Figure 7 shows the X-ray diffraction patterns of two typical smooth electrodeposits obtained at a current density of 250 Am−2, an amount of electricity of 5.0 × 10⁶ Cm−2 and 1123 K. Compared with the standard powder pattern of tungsten, the pattern of Sample 1 clearly shows that the 111 fiber axis normal to the deposition plane was predominant. However, the pattern of Sample 2 shows that the 111 axis was predominant, and the 211 and 321 axes were less predominant. Therefore, it was found that the 111 plane and 211 plane and / or 321 plane were apt to grow up faster than the other planes. This trend was
still maintained at higher current densities. This result is consistent with the fact that bcc-typed electrodeposits obtained in aqueous solutions have tendencies to form the 111 fiber texture or a mixed texture of the 111 and 211 fiber textures.22

3. 6 Use of graphite anode

Tungsten metal is expensive. Thus, in order to examine whether a carbon anode can be used in place of a tungsten anode, several experiments were carried out using a graphite anode. Figure 8 shows the views of the deposits prepared by use of a graphite anode at current densities of 250 Am⁻² and 300 Am⁻² in the graphite bath container. The electrolysis temperature was 1123 K, and the amount of electricity was 5.0 × 10⁶ Cm⁻². The view of the deposit which was prepared by use of a tungsten anode has already been shown in Figs. 4 and 6. The use of the graphite anode gave a smooth electrodeposits with dendrites at the edges whereas the use of the tungsten anode gave a smooth electrodeposits without dendrites. This result was in contrast to the results of the molybdenum electrolys in the KF(80 mol %)-B₂O₃(10 mol %)-Li₂MO₄(10 mol %), KF(77.5 mol %)-Li₂B₂O₄(7.5 mol %)-Li₂MO₄(15 mol %), KF(75 mol %)-B₂O₃(15 mol %)-Na₂MO₄(10 mol %), KF(80 mol %)-Na₂B₂O₄(5 mol %)-Na₂MO₄(15 mol %), KF(65 mol %)-B₂O₃(25 mol %)-K₂MO₄(10 mol %), KF(70 mol %)-K₂B₂O₄(10 mol %)-K₂MO₄(20 mol %), KF(60 mol %)-Na₂B₂O₄(20 mol %)-K₂MO₄(20 mol %) baths.5⁻¹⁷ in the case of molybdenum, the use of the graphite anode also gave smooth electrodeposits without dendrites. Therefore, we suppose that the amount of oxyfluoride ion of tungsten was much smaller than that of molybdenum. Consequently, when the graphite anode was used, most of the oxyfluoride ion of tungsten around the cathode was consumed at the early stage of the electrolysis, and as a result, concentration polarization became predominant with time, and as a result, dendrites deposited at the edges.

The above supposition suggests that a molten salt containing much more amount of an oxyfluoride ion of tungsten than the present preferred bath may enable us to use a carbon anode in place of a tungsten anode. When a tungsten anode is used, such a molten salt will also give a smoother electrodeposits than the present preferred bath does. Such a molten salt bath will be the one containing a stronger acid than B₂O₃ or containing more amount of WO₃ than that in the present preferred bath, for example, the KF(72 mol %)-B₂O₃(10 mol %)-WO₃(18 mol %) bath which is one of the double circles shown in Fig. 3.

4 Conclusion

A molten salt for smooth electrodeposition of tungsten was designed on the basis of the acid-base cooperative reaction theory that we proposed previously.

![Fig. 7 X-ray diffraction patterns of electrodeposits.](image)

The electrolysis was carried out at 1123 K, 250 Am⁻² and 5.0 × 10⁶ Cm⁻² in the KF(67 mol %)-B₂O₃(26 mol %)-WO₃(7 mol %) bath by use of a tungsten anode and a nickel substrate.

![Fig. 8 Appearances of electrodeposits obtained by use of a graphite anode at 1123 K.](image)

The electrolysis was carried out at 1123 K and 5.0 × 10⁶ Cm⁻² in the KF(67 mol %)-B₂O₃(26 mol %)-WO₃(7 mol %) bath by use of a nickel substrate. (a): 250 Am⁻², (b): 300 Am⁻².
On the assumption that F⁻(KF) acts as a base and B³⁺(B₂O₃) acts as an acid for WO₃, the KF-B₂O₃-WO₃ molten salt system was investigated. A composition of KF(67 mol %)-B₂O₃(26 mol %)-WO₃(7 mol %) was selected as a preferred bath composition. When a tungsten anode was used, smooth electrodeposits were obtained at 1123 K and at a current density ranging from 250 Am⁻² to 550 Am⁻² on nickel, copper, stainless steel, and mild steel substrates. When a graphite anode was used, smooth electrodeposits accompanied by dendrites were obtained. The Vickers microhardness number of the smooth electrodeposits was 422 (load 0.49 N). The smooth electrodeposits had tendencies to form the 111 fiber texture or a mixed texture of the 111, 211 and 321 fiber textures.

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