Electrodeposition of Tungsten from Li₂WO₄-Na₂WO₄-K₂WO₄ Based Melts

Koji NITTA, a,b,* Masatoshi MAJIMA,a Shinji INAZAWA,a Toshiyuki NOHIRA, b,* and Rika HAGIWARA b

a Electronics & Materials R&D Labs, Sumitomo Electric Industries, Ltd. (1-1-3 Shimaya, Konohana-ku, Osaka 554-0024, Japan)
b Department of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University (Sakyo-ku, Kyoto 606-8501, Japan)

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We examined a eutectic Li₂WO₄-Na₂WO₄-K₂WO₄ melt and several its derivative melts at 873 K to develop a stable bath which enables electrodeposition of high quality tungsten. Galvanostatic electrolysis at 25 mA cm⁻² in the eutectic Li₂WO₄-Na₂WO₄-K₂WO₄ melt gave a powdery deposit consisting of both tungsten and tungsten oxide. A dendritic deposit of tungsten was obtained from a Li₂WO₄-Na₂WO₄-K₂WO₄-LiCl-NaCl-KCl melt, which has a lower viscosity, in the same electrolysis condition. The dendrite formation was completely suppressed by vibrating the electrode during the electrodeposition. However, the surface was covered with large and angular crystal grains. By addition of KF to the melt, the size of the crystal grains became much smaller and smooth surface was obtained. The XRD analysis and cross-sectional SEM observation revealed that the addition of KF suppressed the preferential growth of α-W crystal and gave the mixture of α-W and β-W resulting in smaller crystal grain size.

Key Words : Electrodeposition of Tungsten, Molten Salt, β-tungsten, Tungsten Coating

1 Introduction

Tungsten metal has excellent properties for industrial use such as high heat resistance, high strength, and low heat expansion. Thus, tungsten is used for an electrode of CCFL (Cold Cathode Fluorescent Lamp), a heat sink, and a shield for radiation. However, tungsten is difficult to process by machining methods because of its hardness and brittleness. In addition, tungsten is comparatively expensive material. So, the applications of tungsten have been limited so far. If it is possible to plate the designated amount of tungsten at the designated part by electrodeposition, most of the problems will be solved and tungsten will be used more widely. Although the electrodeposition of tungsten from an aqueous solution is extremely difficult, the electrodeposition from molten salt has been reported since the 1960's. Senderoff et al. obtained electrodeposits of tungsten from an alkali metal fluoride melt at 973-1123 K,1,2 and Koyama et al. successfully electrodeposited tungsten from KF-B₂O₃-WO₃ at 1123 K.3 However, such high processing temperatures have bad influences on the substrate such as deformation and softening. As an example of the electrodeposition at lower temperature, Katagiri et al. successfully electrodeposited metallic tungsten from ZnBr₂-NaBr4 and ZnCl₂-NaCl5 melts at 623-723 K. There are, however, problems such as volatilization of ZnCl₂, thus its practical application has not been attained. As another example, we reported the electrodeposition of tungsten at 523 K from of a ZnCl₂-NaCl-KCl melt aiming applications to the LIGA process and the coating of micro parts.6 Although a smooth and dense tungsten film has been obtained from this melt, there is a problem that the deposition rate decreases as time passes. In this study, we examined a eutectic Li₂WO₄-Na₂WO₄-K₂WO₄ melt and several its derivative melts to develop a bath which enables electrodeposition of a thick and smooth tungsten film at 873 K.

2 Experimental

2.1 Materials and apparatus

All the chemicals were anhydrous reagent grade. Li₂WO₄ (98%, Mitsuwa Chemicals Co., Ltd.), Na₂WO₄ (99%, Stream Chemicals Inc.), K₂WO₄ (99%, Wako Pure Chemical Industries, Ltd.), LiCl, NaCl, KCl and KF (99% each, Wako Pure Chemical Industries, Ltd.) were dried in a furnace under vacuum at 423 K for a day or more. The dried Li₂WO₄, Na₂WO₄ and K₂WO₄ were mixed into a eutectic composition (Li₂WO₄ : Na₂WO₄ : K₂WO₄ = 0.45 : 0.35, in mole fraction7) and melted at 873 K in a graphite crucible in a muffle heater. To decrease the viscosity of melt, LiCl, NaCl and KCl were added to the melt in the same cation ratio (Li₂WO₄ : Na₂WO₄ : K₂WO₄ : LiCl : NaCl : KCl = 0.2 : 0.45 : 0.35 : 0.4 : 0.9 : 0.7, in mole fraction for the final composition). As another derivative melt, 3.2 mol% KF was added to the above melt. The working electrodes were a nickel wire (99.9%, 5 × 0.3 mm in diameter, Nilaco Corp.) for cyclic voltammetry and a nickel plate (99.9%, 10 × 10 × 0.2 mm, Nilaco Corp.) for galvanostatic electrolysis. The nickel plate was electrochemically polished in a sulfuric acid beforehand. The counter electrode was a tungsten plate (99.95%, 10 × 20 × 0.2 mm, Nilaco Corp.). A tungsten wire (99.95%, 0.5 mm in diameter, Nilaco Corp.) immersed in the melt was used as the reference electrode. All the electrochemical measurements were carried out in a glove box filled with argon. A chromel-alumel thermo-
2.2 Electrolysis and evaluation of electrodeposits

Cyclic voltammetry (CV) and galvanostatic electrolysis were carried out using an electrochemical measurement system (Hokuto Denko Co., Ltd., HSV-100). After the electrolysis, electrodes were immersed in distilled water to remove adherent salts. The deposits were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-800), energy dispersive X-ray analysis (EDX, EDAX S-UTW), X-ray diffraction (XRD, Rigaku Co., Ltd., RINT2000), scanning ion microscopy (SIM) with focused ion beam (FIB, FEI, FIB200).

3 Results and Discussion

3.1 Cyclic voltammetry

Figure 1 shows CVs for a nickel wire electrode in (A) eutectic Li$_2$WO$_4$-Na$_2$WO$_4$-K$_2$WO$_4$, (B) (melt (A))+(LiCl-NaCl-KCl), and (C) (melt (B))+KF at 873 K. Cathodic currents are observed from approximately −0.65 V in all CVs, though cathodic current in (A) is smaller than those in (B) and (C). On the anodic scans, current peaks appear around −0.6 V in (B) and (C). In (A), there is no clear anodic peak. From these results, the following assumptions are derived: (i) Cathodic currents in all CVs are caused by electrodeposition of tungsten metal and anodic currents are caused by anodic dissolution of tungsten metal. (ii) Mass transport near the electrode in (A) is slower than those in (B) and (C) due to the high viscosity of melt (A). On the other hand, the equilibrium reaction on a tungsten wire reference electrode would not correspond to “W(VI) + 6 e = W(0)”, because the redox potential was observed at approximately −0.6 V vs W-wire in CVs. Although the tungsten wire reference electrode exhibited a stable potential, its potential is assumed to be determined by the equilibrium reaction between the surface tungsten oxide and the residual oxide ions in the melt. It should be noted that no volatilization was found for all the melts.

3.2 Galvanostatic Electrolysis

Galvanostatic electrolysis was carried out at 25 mA cm$^{-2}$ for 1 h in the melt (A) at 873 K. A black powdery deposit was obtained. Most part of the deposit dropped off when it was immersed in distilled water to remove adherent salts. Figure 2 shows a surface SEM image and an EDX spectrum of the deposit. The deposit is not dense and contains both tungsten and oxygen. The deposit was confirmed to be consisted of both tungsten metal and tungsten oxide by XRD. The tungsten species in this melt is considered to be oxo-complex ion like WO$_4^{2-}$. When the oxo-complex tungsten ion is electrochemically reduced, oxide ions (O$^2-$) should be produced. A high viscosity of the melt seemed to hinder the supply of tungsten ions to the electrode and/or the removal of oxide ions from the electrode, leading to the inclusions of melt or partially reduced tungsten species in the deposit. Thus, we carried out galvanostatic electrolysis in the melt (B), which has a lower viscosity, in the same electrolysis condition. The obtained deposit was black and did not drop off during the washing treatment. Figure 3 shows a surface SEM image and an EDX spectrum of the deposit. The deposit contains no oxygen but have an angular surface. Furthermore, the influence of addition of fluoride ions was examined to improve the surface smoothness of deposit. According to our previous study, the addition of KF to a ZnCl$_2$-NaCl-KCl melt was effective for smoothing the surface of deposit$^{10}$. Figure 5 shows a surface SEM image and an EDX spectrum of electrodeposits from a Li$_2$WO$_4$-Na$_2$WO$_4$-K$_2$WO$_4$-LiCl-NaCl-KCl melt at 25 mA cm$^{-2}$ for 1 h at 873 K. The range of potential during electrolysis was −0.77 V −0.86 V.

**Fig. 1** Cyclic voltammograms for a nickel wire electrode in (A) Li$_2$WO$_4$-Na$_2$WO$_4$-K$_2$WO$_4$, (B) Li$_2$WO$_4$-Na$_2$WO$_4$-K$_2$WO$_4$-LiCl-NaCl-KCl, (C) Li$_2$WO$_4$-Na$_2$WO$_4$-K$_2$WO$_4$-LiCl-NaCl-KCl-KF melts at 873 K. Scan rate: 0.05 V s$^{-1}$.

**Fig. 2** A surface SEM image and an EDX spectrum of electrodeposits from a Li$_2$WO$_4$-Na$_2$WO$_4$-K$_2$WO$_4$ melt at 873 K at 25 mA cm$^{-2}$ for 1 h. The range of potential during electrolysis was −0.77 V −0.86 V.

**Fig. 3** A surface SEM image and an EDX spectrum of the deposit from a Li$_2$WO$_4$-Na$_2$WO$_4$-K$_2$WO$_4$-LiCl-NaCl-KCl melt at 25 mA cm$^{-2}$ for 1 h at 873 K. The range of potential during electrolysis was −0.80 V −0.89 V.
image and an EDX spectrum of the deposit from the melt (C) under the same electrolysis condition including the vibration of Ni electrode. The deposit has a smooth surface and contains no oxygen. To further investigate the difference in the deposits, XRD patterns and cross-sectional views were measured. Figure 6 shows XRD patterns of the deposits from the melts (B) and (C). The crystal structure of the deposit from melt (B) was β-W and that from melt (C) was the mixture of α-W and β-W. Figure 7 shows cross-sectional SIM images of these deposits. While the deposit from melt (B) has some voids, the deposit from melt (C) is dense and its grain size is smaller than that from (B). These results show that only β-W grows in melt (B) thus forming large grains, and that both α-W and β-W grow in the presence of fluoride ions keeping the grain size small and giving the smooth surface. The thickness of the tungsten film obtained from the melt (C) was approximately 9.7 μm.

4 Conclusion

To develop a stable bath which gives a high quality electrodeposited film, a eutectic Li₂WO₄-Na₂WO₄-K₂WO₄ melt and several its derivative melts were examined at 873 K. A powdery deposit of tungsten and tungsten oxide was obtained in the eutectic Li₂WO₄-Na₂WO₄-K₂WO₄ melt. A dendritic deposit of tungsten was obtained from a Li₂WO₄-Na₂WO₄-K₂WO₄-LiCl-NaCl-KCl melt which has a lower viscosity. The dendrite formation was suppressed by vibrating the electrode during the electrodeposition. However, the surface was covered with large and angular crystal grains. After adding KF to the melt, the size of the crystal grains became much smaller and smooth surface was obtained. The XRD analysis and cross-sectional SIM observation revealed that the addition of KF suppressed the preferential growth of α-W crystal and gave the mixture of α-W and β-W resulting in smaller crystal grain size. The thickness of the tungsten film was approximately 9.7 μm at 25 mA cm⁻² for 1 h.

References