Electrodeposition of tungsten from EMPyrCl-ZnCl₂ melts at 150°C

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Electrodeposition of tungsten has been achieved at 150°C, which is the lowest temperature to this day, by using a new molten salt (ionic liquid), \(N\)-ethyl-\(N\)-methylpyrrolidinium chloride (EMPyrCl)-ZnCl₂. Metallic tungsten was electrodeposited on a nickel substrate by potentiostatic electrolysis at 0.01 V vs. Zn(II)/Zn in an equimolar EMPyrCl-ZnCl₂ melt after adding KF and WCl₄. A denser and smoother tungsten film was obtained by the same electrolysis condition when WCl₄ was used as a tungsten ion source.

Key words: electrodeposition, tungsten, molten salt, ionic liquid, EMPyrCl, ZnCl₂

1. INTRODUCTION

It had been long recognized that electrodeposition of refractory metals such as tungsten and molybdenum was possible only from high temperature molten salts. Electrodeposition of refractory metals at low temperatures has many advantages from a practical viewpoint. One of the most promising applications is the LIGA process that is a microfabrication technique consisting of lithography, electroforming and molding [1]. Currently, electrodeposition of nickel from aqueous solutions is mainly used as the electroforming step of the LIGA process. If the electrodeposition of refractory metals is applied to the electroforming step of the LIGA process, performance and reliability of micro-parts should be drastically improved. It is still a remarkable achievement only to coat the surface of the conventional LIGA micro-parts with refractory metals. However, the electroforming step of the LIGA process must be conducted below 250°C, preferably less than 200°C, due to the thermal instability of the resin resist. For coating the conventional LIGA parts, the process temperature should be kept as low as possible to avoid the heat induced softening and embrittlement of the electroformed nickel substrate.

From this background, we have developed a new molten salt, NaCl-KCl-ZnCl₂ eutectic melt, and reported that electrodeposition of tungsten is possible at 250°C using WCl₄ [2,3] or WO₃ [4] as a tungsten ion source. We have also succeeded in electrodepositing molybdenum from the same melt at 250°C using MoCl₅ [5] or MoCl₃ [6] as a molybdenum ion source. More lately, due to the requirement of lower processing temperature, we have developed a new low temperature molten salt (also referred to as an ionic liquid recently), \(N\)-ethyl-\(N\)-methylpyrrolidinium chloride (EMPyrCl)-ZnCl₂ [7,8]. According to the phase diagram of EMPyrCl-ZnCl₂ system [8], it has the lowest melting point of 45°C at an equimolar composition. Electrodeposition of molybdenum was achieved at as low as 150°C by using an equimolar EMPyrCl-ZnCl₂ melt containing MoCl₅ [8]. We have also reported that electrodeposition of molybdenum is possible from a eutectic LiTFSI-CsTFSI melt at 150°C using MoCl₅ [9].

In the present study, we selected the EMPyrCl-ZnCl₂ system and investigated the electrodeposition of tungsten at 150°C using WCl₄ or WCl₆ as a tungsten ion source. For the electrodeposition, an equimolar EMPyrCl-ZnCl₂ melt was used. The mixture was put in a Pyrex beaker placed in a five-necked separable flask on a heating plate in an Ar-filled vacuum glove box. WCl₄ (97%, STREM) or WCl₆ (99.9%, Wako Pure Chemical Industries, Ltd.) was dried under vacuum at 453 K for more than 48 hours. Electrodeposition of tungsten was performed using an electrochemical measurement system (Hokuto Denko Co., Ltd., HZ-5000 or Princeton Applied Research, PARSTAT 2273). The obtained samples were immersed in acetone, and then rinsed with distilled water to remove adherent salts. The deposits were characterized by X-ray diffraction (XRD, Rigaku,
3. RESULTS AND DISCUSSION

3.1 An EMPyrCl-ZnCl₂-WCl₄-KF melt

A cyclic voltammogram was recorded for a tungsten electrode in a blank melt, which is shown as a dashed curve in Fig. 1. A cathodic current at more negative than 0 V vs. Zn(II)/Zn corresponds to the deposition of metallic zinc. A voltammogram obtained after adding KF (3.0 mol%) and WCl₄ (4.5 mol%) is shown as a solid curve in Fig. 1. Since the smooth and dense tungsten films were obtained by the addition of KF in our previous studies of NaCl-KCl-ZnCl₂-WCl₄ [2,3] and NaCl-KCl-ZnCl₂-WO₃ [4] at 250°C, KF was also added in the present study. A cathodic current shoulder is observed at potential more negative than 0.6 V, suggesting the electrodeposition of tungsten.

A deposition sample was prepared on a nickel substrate by potentiostatic electrolysis at 0.01 V for 3 h in the same melt. After washing with distilled water, a deposit with metallic luster was obtained. Fig. 2 shows a surface SEM image of the deposit. The surface is not smooth and the formation of dendrite is observed. The deposit was further analyzed by XPS. Fig. 3 shows an W 4f spectrum of the deposit after Ar⁺ ion etching, in which W 4f⁷/₂ (31.5 eV) and W 4f⁵/₂ (33.5 eV) peaks are observed. These energy values confirm that tungsten exists in zero valence state (metallic) in the deposit [10]. Moreover, other elements such as zinc, chlorine and fluorine were not detected by XPS. Thus, the deposit was confirmed to be pure metallic tungsten. Since no distinct peak except for nickel was observed from an XRD analysis, the deposited tungsten was considered to be amorphous.

3.2 An EMPyrCl-ZnCl₂-WCl₆-KF melt

Fig. 4 compares cyclic voltammograms for a tungsten electrode before (dashed curve) and after (solid curve) adding KF (3.0 mol%) and WCl₆ (1.0 mol%). In the solid curve, a cathodic current rises from approximately 1 V and a current shoulder appears at 0-0.5 V. Electrodeposition of tungsten is speculated to occur at the current shoulder. After the reversal of scan direction, anodic current is observed only at more positive than 1.5 V, suggesting high irreversibility of the electrodeposition reaction.

To prepare a sample, potentiostatic electrolysis was conducted at 0.01 V for 3 h in the same melt. Fig. 5 shows a surface SEM image of the deposit. The surface is covered with spherical particles. The deposit was also analyzed by XPS. Although the outermost surface was shown to be covered with tungsten oxide, peaks ascribed to zero valence state appeared in a W 4f spectrum after etching with Ar⁺ ion (Fig. 6). In the XPS analysis, zinc, chlorine and fluorine were not detected, indicating that pure metallic tungsten was obtained. Since the XRD pattern did not show any distinctive peak corresponding to a tungsten crystal, the obtained tungsten is considered to be amorphous.
Fig. 4. Cyclic voltammograms for a W electrode in EMPyrCl-ZnCl₂ and EMPyrCl-ZnCl₂-WCl₆ (1.0 mol% added)-KF (3.0 mol% added) melts at 150°C. Scan rate: 0.01 V s⁻¹.

Fig. 5. A surface SEM image of the deposit obtained by potentiostatic electrolysis at 0.01 V for 3 hours in an EMPyrCl-ZnCl₂-WCl₆ (1.0 mol% added)-KF (3 mol % added) melt at 150°C.

Fig. 6. A tungsten 4f XPS spectrum of the deposit obtained by potentiostatic electrolysis at 0.01 V for 3 hours in an EMPyrCl-ZnCl₂-WCl₆ (1.0 mol% added)-KF (3 mol % added) melt at 150°C. The surface was etched by Ar⁺ ion before the analysis.

4. CONCLUSION

It has been shown that electrodeposition of tungsten is possible at 150°C by using an equimolar EMPyrCl-ZnCl₂ melt. Metallic tungsten was electrodeposited on a nickel substrate after adding KF and WCl₄, which was confirmed by XPS. A denser and smoother tungsten film was obtained when WCl₆ was used as a tungsten ion source. The EMPyrCl-ZnCl₂ system is promising as a new electrolyte which enables the electrodeposition of tungsten at lower temperatures than before.

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REFERENCES


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