Physicochemical Properties of EMPyrsCl-ZnCl₂ Melts and Electrodeposition of Molybdenum from the Equimolar Melt at 150 °C

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A new molten salt system, N-ethyl-N-methylpyrrolidinium chloride (EMPyrsCl)-ZnCl₂, was investigated for the electrodeposition of molybdenum at intermediate temperature. A phase diagram was constructed for the EMPyrsCl-ZnCl₂ system, which shows the lowest melting point of 45 °C at an equimolar composition. A thermal gravimetry indicated that thermal decomposition starts at 230 °C for the equimolar melt. The viscosity and conductivity of the equimolar melt were 75 cP and 22 mS cm⁻¹, respectively, at 150 °C. The cathode limit of the equimolar melt was confirmed to be the deposition of metallic zinc by XRD analysis. A smooth metallic molybdenum film was electrodeposited on a nickel substrate by potentiostatic electrolysis at 0.01 V vs. Zn(II)/Zn in an equimolar melt containing MoCl₆ (0.9 mol%) and KF (3.0 mol%) at 150 °C.

Key Words : N-ethyl-N-methylpyrrolidinium Chloride, Zinc Chloride, Intermediate Temperature Molten Salt, Electrodeposition of Molybdenum

1 Introduction

Electrodeposition of refractory metals such as molybdenum and tungsten at low temperatures has many advantages from a practical viewpoint. One of the most promising applications is the lithographie-galvanomoung-afomung (LIGA) process that is a microfabrication technique consisting of lithography, electroforming and molding. 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 will be drastically improved. It is still a remarkable achievement only to coat the surface of the conventional LIGA micro-parts with refractory metals.

It had been long recognized that electrodeposition of refractory metals was possible only from high temperature molten salts. 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 in the melt at 250 °C using WCl₆ or WO₄⁻ as a tungsten ion source. We have also succeeded in electrodepositing molybdenum from the same melt at 250 °C using MoCl₅ or MoCl₆. More recently, we have developed a new intermediate temperature molten salt, N-ethyl-N-methylpyrrolidinium chloride (EMPyrsCl)-ZnCl₂, and reported the preliminary result of the electrodeposition of molybdenum at 150 °C using KF and MoCl₆. We have also reported that electrodeposition of molybdenum is possible from a eutectic LiTFSCsTFSI melt at 150 °C using MoCl₆.

In the present study, we focused on the EMPyrsCl-ZnCl₂ system and investigated its physicochemical properties, such as phase diagram, conductivity, viscosity and cathode limit, which had not been clarified in the previous study. Then, electrodeposition of molybdenum was further studied at 150 °C. Some new results, which had not been reported in the previous study, are reported here.

2 Experimental

EMPyrsCl (Yoyulabo Corp.) was purified by recrystallization using acetonitrile and ethyl acetate for three times. The recrystallized EMPyrsCl was dried in vacuum at 423 K for more than 48 hours. ZnCl₂ (99.9 %, Wako Pure Chemical Industries, Ltd.) was dried under vacuum at 453 K for more than 48 hours. They were mixed in various mole fractions to prepare salt samples. The melting point and the decomposition point were measured by differential scanning calorimetry (DSC) and differential thermal analysis-thermal gravimetry (DTA-TG), respectively.

For the electrodeposition, an equimolar EMPyrsCl-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. MoCl₅ (99.5 %, Wako Pure Chemical Industries, Ltd.) was added as a molybdenum ion source. KF (99 %, Wako Pure Chemical Industries, Ltd.) was added as a fluoride ion source. The working electrode in cyclic voltammetry was a molybde-
num wire (99.95%, 1 mm dia.× 10 mm, Nilaco Corp.). The working electrode for the electrodeposition was a molybdenum plate (99.95%, 5 × 10 × 0.2 mm, Nilaco Corp.) or a nickel plate (99.7%, 5 × 10 × 0.2 mm, Furuuchi Chemical Corp.). Prior to the experiment, the nickel plate was electrochemically polished in a sulfuric acid, and then immersed in acid cleaner (Kizai Corp., Kokeisan B) containing NaIF₆ to remove surface oxides. The counter electrode was a zinc spiral wire. The reference electrode was a Zn(II)/Zn electrode. It was composed of a Zn wire (99.98%, 1 mm dia. × 10 mm, Nilaco Corp.) immersed into the equimolar EMPyrCl-ZnCl₂ melt separated from the bulk melt by a Perlex filter (Perlex Corp.).

Cyclic voltammetry with positive feedback IR compensation and potentiostatic electrolysis were 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, Multiflex, CuKα), scanning electron microscopy (SEM, Hitachi, S-2600H), scanning ion microscopy (SIM) with focused ion beam (FIB, FEI, FIB200), and X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9010MC).

3 Results and discussion
3.1 Physicochemical properties of EMPyrCl-ZnCl₂ melts

When Lewis-acidic ZnCl₂ is mixed with Lewis-basic EMPyrCl, a new molten salt having lower melting point is obtained. Figure 1 shows the phase diagram of EMPyrCl-ZnCl₂ system determined by DSC. The lowest melting point in this system is ca. 45°C at equimolar composition. In the TG measurement, weight loss was observed from 230°C for the equimolar melt, which was probably caused by the decomposition of EMPyr⁺ cation. Thus, it was confirmed that the equimolar melt is stable at 45-200°C. Nevertheless, the viscosity of equimolar melt was considerably high at lower temperatures, ex. 2.8 × 10³ cP at 60°C, which is unfavorable for electrochemical applications like electrodeposition. At higher than 100°C, however, the viscosity became considerably low, 75 cP at 150°C, for example.

Figure 2 shows the temperature dependence of conductivity for the melts with different compositions (X(ZnCl₂) = 0.45, 0.50 and 0.60 in mole fraction). The conductivity is the highest for the equimolar melt which exhibits 22 mS cm⁻¹ at 150°C. Thus, the equimolar EMPyrCl-ZnCl₂ melt was selected as an electrolyte and the temperature was set at 150°C in the following electrochemical measurements.

3.2 Electrodeposition of molybdenum from an EMPyrCl-ZnCl₂ melt at 150°C

A cyclic voltammogram was recorded for a molybdenum electrode in a blank melt (X(ZnCl₂) = 0.50), which is shown as a dashed curve in Fig. 3. A cathodic current at more negative than 0 V vs. Zn(II)/Zn possibly corresponds to the deposition of metallic zinc. To confirm this, galvanostatic electrolysis was conducted at ~80 mA cm⁻² for one hour using a molybdenum plate electrode. Figure 4 shows an XRD pattern of the deposit, in which distinct peaks of zinc and weak peaks of ZnO are observed. Since ZnO was considered to be formed during washing with distilled water, the deposit was confirmed to be zinc metal. A voltammogram obtained after addingKF (3.0 mol%) and MoCl₅ (0.9 mol%) is shown as a solid curve in Fig. 3. Since the smooth and dense molybdenum films were obtained by the addition of KF in our previous studies of NaCl-KCl-ZnCl₂-MoCl₅ and NaCl-KCl-ZnCl₂-

![Fig. 1](image1.png) The phase diagram of EMPyrCl-ZnCl₂ system.

![Fig. 2](image2.png) Temperature dependence of conductivity for EMPyrCl-ZnCl₂ melts. X(ZnCl₂) = 0.45(×), 0.50(●) and 0.60(○).

![Fig. 3](image3.png) Cyclic voltammograms for an Mo electrode in equimolar EMPyrCl-ZnCl₂ and equimolar EMPyrCl-ZnCl₂-KF(3.0 mol% added)-MoCl₅(0.9 mol% added) melts at 150°C. Scan rate: 0.01 V s⁻¹.
MoCl$_6$ at 250°C, KF was also added in the present study. A cathodic current shoulder is observed at potential more negative than 0.75 V, suggesting the electrodeposition of molybdenum. A deposition sample was prepared on a nickel substrate by potentiostatic electrolysis at 0.01 V for 3 h in the same melt. Since nickel is often used for the conventional LIGA process and the preparation of clean surface is easy, it was selected as the substrate material. Here, there was no significant difference in electrodeposition potential of molybdenum between a nickel substrate and a molybdenum substrate. After washing with distilled water, a deposit with metallic luster was obtained. Figure 5 shows (a) surface SEM and (b) cross-sectional SIM images of the deposit. The surface is smooth and the thickness is ca. 0.2 μm. The current efficiency was estimated to be 24% from the thickness and the quantity of electricity, assuming five-electron reduction. A reason for such low efficiency has not been clarified yet. The deposit was further analyzed by XPS. Figure 6 shows an Mo 3d spectrum of the deposit, in which Mo 3d 3/2 and Mo 3d 5/2 peaks are observed at 231 eV and 228 eV, respectively. These energy values confirm that molybdenum exists in zero valence state (metallic) in the deposit. Moreover, other elements such as zinc, chlorine and fluorine were not detected by XPS. Thus, the deposit was confirmed to be pure metallic molybdenum. Since no distinct peak except for nickel was observed from an XRD analysis, the deposited molybdenum was considered to be amorphous.

4 Conclusion

A phase diagram has been constructed for the EMPyrean-ZnCl$_2$ system. The lowest melting point is 45°C at an equimolar composition. The equimolar melt is stable at 45-200°C and its viscosity and conductivity are 75 cP and 22 mS cm$^{-1}$ at 150°C. The cathode limit of the equimolar melt is the deposition of metallic zinc. A metallic molybdenum film was electrodeposited on a nickel substrate from the EMPyrean-ZnCl$_2$-KF (3.0 mol% added)-MoCl$_6$ (0.9 mol% added) melt at 150°C, which was confirmed by SEM, SIM and XPS. The EMPyrean-ZnCl$_2$ system is promising as a new electrolyte which enables the electrodeposition of refractory metals at lower temperatures than before.

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References