Electrodeposition of Molybdenum from Molten Salt

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A new molten salt system, N-ethyl-N-methyl-pyrrolidinium chloride (EMPyrCl)-$ZnCl_2$, was investigated for the electrodeposition of molybdenum at intermediate temperature. A phase diagram was constructed for the EMPyrCl-$ZnCl_2$ system, which shows the lowest melting point of 45˚C at an equimolar composition. A thermal gravimetry indicated that thermal decomposition starts from 230˚C for the equimolar melt. The viscosity and conductivity of the equimolar melt were 75 cP and 22 mS cm, 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 $MoCl_5$ (0.9 mol%) and KF (3.0 mol%) at 150˚C or $MoCl_3$ (0.2 mol%) and KF (2.0 mol%) at 200˚C.

Keywords: molybdenum, molten salt, electrodeposition, N-ethyl-N-methyl-pyrrolidinium chloride

1. Introduction

Molybdenum and tungsten, which are called refractory metals, are widely used for industrial applications such as heat resistance material because of their high melting point and high strength. However, they are often used in simple shapes, such as plate or rod, because they are hard to be processed. Although the gas phase methods are used when a complicated shape is demanded, there are some problems in the rate or the uniformity of deposition.

On the other hand, thin molybdenum or tungsten foils are increasingly demanded for the thermal emission materials such as heat sink. However, it is difficult to manufacture these foils because of the difficulty in process. So, we are developing the electroplating process to solve these problems [(1), (2)]. Although refractory metals, which are base metals, are not electrodeposited from aqueous solution, they can be electrodeposited from molten salts containing no water [(3)-(8)]. However, a substrate is damaged because molten salts which are reported as the baths for electrodeposition are used at high temperature. In this study, we aimed at the electrodeposition of molybdenum under 200ºC. The key points of the selection of low melting point molten salt are as follows; (i) The electrochemical and thermal stabilities of cation, (ii) High ionic conductivity, (iii) Ease in handling, and (iv) No formation of by-product in anode. Then we selected N-ethyl-N-methyl-pyrrolidinium chloride (EMPryCl; **Fig. 1**)-$ZnCl_2$ melt. In this paper, we report the physicochemical properties, the electrochemical properties and the electrodeposition of molybdenum from this melt.

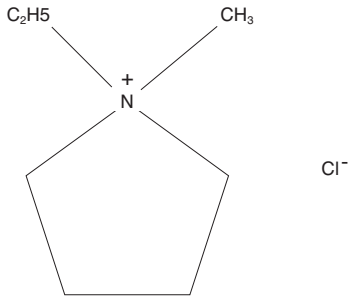

Fig. 1. Structure of N-ethyl-N-methylpyrrolidinium chloride

2. Experimental

2-1 Preparation of salts

EMPyrCl (Yoyulabo Corp.) was purified by recrystallization using acetonitrile and ethyl acetate for three times. The recrystallized EMPyrCl was dried in vacuum at 150ºC for more than 24 hours. $ZnCl_2$ (99.9%, Wako Pure Chemical Industries, Ltd.) was dried under vacuum at 180ºC for more than 24 hours. They were mixed in various mole fractions to prepare salt samples in a glove box filled with argon. $MoCl_3$ and $MoCl_5$ were used as the sources of molybdenum ion. Furthermore, KF was used as additive.

2-2 Measurements of the physicochemical properties

The melting point of EMPyrCl –$ZnCl_2$ melt was measured by differential scanning calorimetry (DSC), using an aluminum seal cell. The viscosity was measured by rotary viscometer equipped with thermo controller. The ionic conductivity was measured by the impedance method.

2-3 Electrochemical measurement and electrodeposition

For the electrodeposition, an equimolar EMPyrCl-$ZnCl_2$ melt was used. The working electrode was the nickel plate. The counter and reference electrodes were zinc rods.

The electrochemical measurements and electrodeposition were carried out by potentio-galvanostat in a glove box filled with argon. The deposits were characterized by scanning electron microscopy (SEM), scanning ion microscopy (SIM) with focused ion beam (FIB), and X-ray photoelectron spectroscopy (XPS).

3. Results and Discussion

3-1 The physicochemical properties of EMPyrCl – $ZnCl_2$ melts

Figure 2 shows the phase diagram of EMPyrCl-$ZnCl_2$ system determined by DSC. The mixture, which were $0.4 \leqq X(ZnCl_2) \geqq 0.9$, were melt under 200°C. Then, the lowest melting point in this system is ca. 45°C at equimolar composition. **Figure 3** shows the temperature dependence of viscosity for the mixture which were $X(ZnCl_2)$ = 0.45, 0.5, 0.6. The viscosities of these systems were very sensitive to temperature. The melt which had the lowest melting point ($ZnCl_2$ = 0.5) showed the lowest viscosity. Furthermore, **Fig. 4** shows the temperature dependences of ionic conductivity for the mixture of $X(ZnCl_2)$ = 0.45, 0.5, 0.6. The ionic conductivities of this system were also very sensitive to temperature. The melt which had the lowest melting point ($ZnCl_2$ = 0.5) showed the highest ionic conductivity. A dendrite deposition was often formed from a high viscosity bath because the supply of ion on the surface of the electrode was not sufficient. Furthermore, the uniformity of the film decreases in a low ionic conductivity bath. The low viscosity and high ionic conductivity are desirable for the bath of electrodepositrion. From these points of view, it is considered that this melt should be used at 150-200°C.

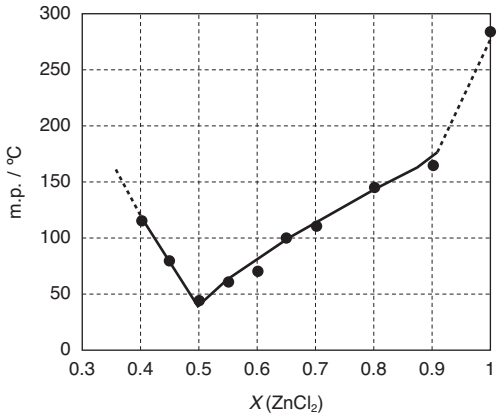

Fig. 2. Binary phase diagram of EMPryCl-$ZnCl_2$

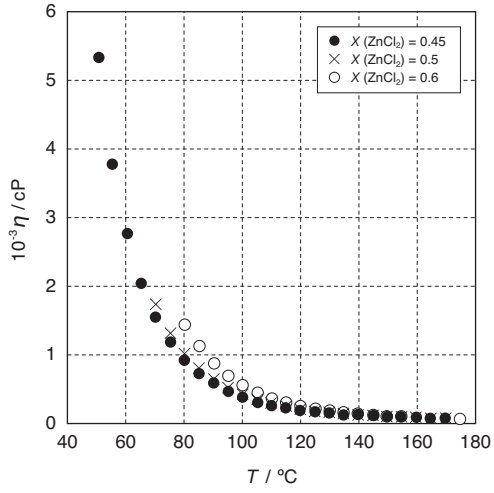

Fig. 3. Temperature dependence of viscosity for EMPryCl-$ZnCl_2$ melt

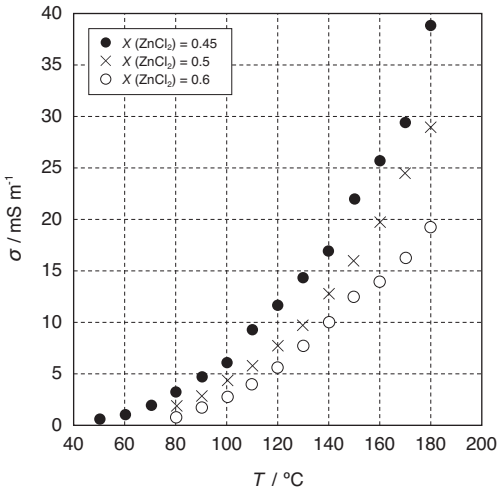

Fig. 4. Temperature dependence of ionic conductivity for EMPryCl-$ZnCl_2$ melt

3-2 Electrochemical measurement and electrodeposition

A cyclic voltammogram was recorded in the equimolar melt containing 0.8 mol% of $MoCl_5$ and 3 mol% of KF at 150°C, as shown in **Fig. 5**. The cathodic current, which was considered to be caused by the molybdenum electrodeposition, was observed from 0.75 V vs. Zn(II)/Zn. The cathodic current about 0 V was due to the formation of zinc-nickel alloy. On the other hand, the anodic current at about 0.2 V was due to the dissolution of zinc from zinc-nickel alloy. The anodic current was decreased in the voltammogram in the bath with $MoCl_5$ because the formation of alloy was prevented by molybdenum electrodeposited. It was therefore considered that molybdenum was electrodeposited from this melt. To confirm this, the

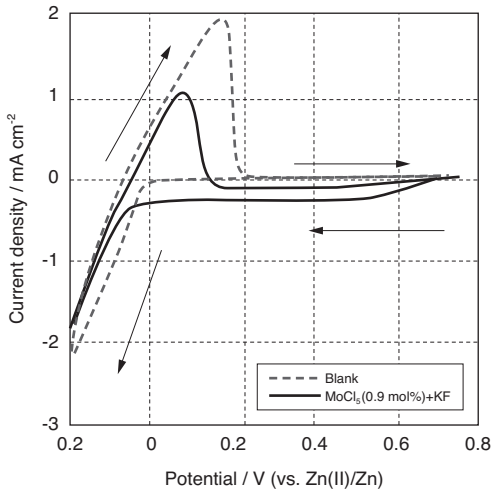

Fig. 5. Cyclic voltammogram for nickel electrode in EMPryCl-$ZnCl_2$-$MoCl_5$(0.8 mol%)-KF(3 mol%) at 150°C

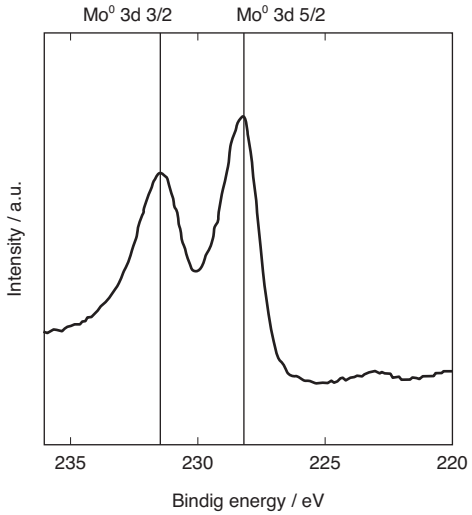

Fig. 6. XPS spectrum of deposit by potentiostatic electrolysis in EMPryCl-$ZnCl_2$-$MoCl_5$(0.8 mol%)-KF(3 mol%) at 0.01 V for three hours at 150°C

potentiostatic electrolysis was carried out at 0.01 V for three hours in the same melt. Then, the metallic gray deposit was obtained. In the electrolysis, the mean current density was 0.4 mA cm^{-2}. **Figure 6** shows an XPS spectrum of the deposit, which confirmed the deposit was pure molybdenum metal [9] without any impurities which were due to zinc deposition or salts. A surface SEM image and a cross-sectional SIM image exposed by FIB were shown in **Fig. 7 and Fig. 8**, respectively. It was confirmed that the deposit was smooth and the thickness of deposit was about 0.2 µm.

Furthermore, the bath containing $MoCl_3$ as a molybdenum ion source was studied. The potentiostatic electrolysis was carried out in the equimolar melt containing 0.5 mol% of $MoCl_3$ and 2 mol% of KF at 0.08 V for fifteen hours at 200°C. In the electrolysis, the mean current density was very small (0.01 mA cm^{-2}). An XPS spectrum of the deposit and a surface SEM image were shown in **Fig. 9 and Fig. 10**, respectively. The deposit was identified as molybdenum metal by the XPS spectrum and formed smooth film by the SEM image. However, the current density in potentiostatic electrolysis in the melt containing $MoCl_3$ was lower than from that of $MoCl_5$ although the temperature during electrolysis was high. This phenomenon was thought to be caused by the difference of molybdenum ion species in this melt. It was reported that the current density in potentiostatic electrolysis decreases in electrodeposition of tungsten from $ZnCl_2$-NaCl-KCl melt,

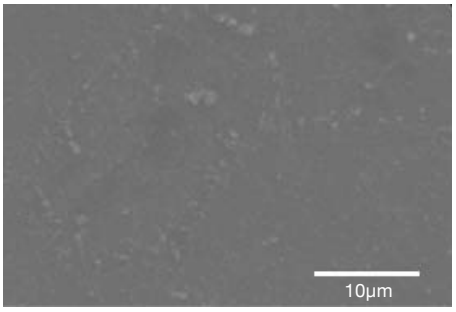

Fig. 7. Surface SEM image of deposit by potentiostatic electrolysis in EMPryCl-$ZnCl_2$-$MoCl_5$(0.8 mol%)-KF(3 mol%) at 0.01 V for three hours at 150°C

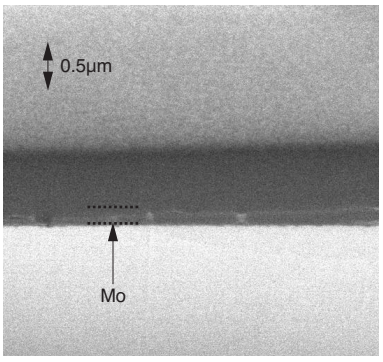

Fig. 8. Cross-sectional SIM image of deposit by potentiostatic electrolysis in EMPryCl-$ZnCl_2$-$MoCl_5$(0.8 mol%)-KF(3 mol%) at 0.01 V for three hours at 150°C

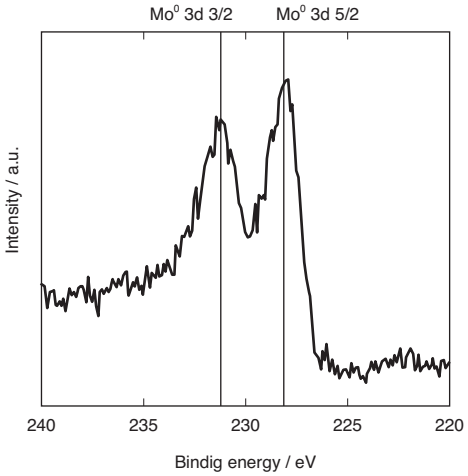

Fig. 9. XPS spectrum of deposit by potentiostatic electrolysis in EMPryCl-$ZnCl_2$-$MoCl_3$(0.5 mol%)-KF(2 mol%) at 0.08 V for fifteen hours at 200°C

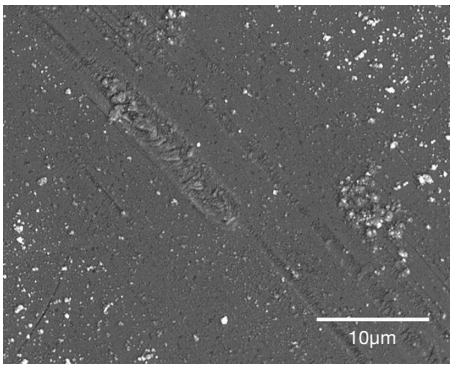

Fig. 10. Surface SEM image of deposit by potentiostatic electrolysis in EMPryCl-$ZnCl_2$-$MoCl_3$(0.5 mol%)-KF(2 mol%) at 0.08 V for fifteen hours at 200°C

which is similar to this system, because of the change of tungsten ion species [10]. It is speculated that the same behavior is observed about molybdenum ion in this melt. Thus, it is important to study and control the states of molybdenum ion.

4. Conclusions

A new molten salt system, N-ethyl-N-methyl-pyrrolidinium chloride (EMPyrCl)-$ZnCl_2$, was investigated for the electrodeposition of molybdenum at intermediate temperature. The physicochemical properties, such as melting point, viscosity and ionic conductivity, were measured. A smooth metallic molybdenum film was electrodeposited on a nickel substrate in an equimolar melt containing $MoCl_5$ (0.9 mol%) and KF (3.0 mol%) at 150ºC or in an equimolar melt containing $MoCl_3$ (0.2 mol%) and KF (2.0 mol%) at 200ºC.

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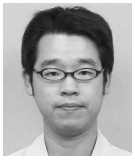

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