ELECTRODEPOSITION OF REFRACTORY METALS IN MEDIUM-TEMPERATURE MOLTEN SALTS

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ABSTRACT

Metallic tungsten deposits were obtained by potentiostatic electrolyses in ZnCl₂-NaCl-KCl and ZnCl₂-NaCl-KCl-KF melts containing WCl₆ at 250 °C. Both the deposits obtained after the electrolysis of three hours were about 0.5 μm of thickness. Addition of KF gave a smooth metal deposit. A dense metallic molybdenum deposit was also obtained by potentiostatic electrolyses in molten ZnCl₂-NaCl-KCl-KF containing MoCl₃ at 250 °C. Thickness of the layer was about 3 μm after the electrolysis of three hours. Addition of KF in the melt improved adhesion of the metal deposit.

INTRODUCTION

Electrodeposition of refractory metals such as tungsten, molybdenum, tantalum at low temperatures has many advantages from engineering point of view. One of the examples is the application of such a technique to the LIGA (Lithographie Galvanoformung Abformung) process (1) which is a microfabrication technique consisting of lithography, electroforming and molding. Although many products have already been commercially produced with this method, materials applicable to this process are restricted to the metals such as copper, gold, nickel and Ni-Fe alloys which are able to be electrodeposited in aqueous electrolytes. Electrodeposition of refractory metals is highly expected to be used as the electroforming step of the LIGA process owing to their high hardness and mechanical strength. However, it has not been achieved except for chromium in aqueous solutions mostly due to the narrow electrochemical window of water.

Senderoff and Mellors obtained refractory metals in alkali metal fluoride melts at 700-850 °C (2, 3). After that, refractory metals have been obtained in chloride, fluoride and oxide melts at above 500 °C (4). Katagiri et al. succeeded to obtain metallic tungsten at 350 to 450 °C using ZnBr₂-NaBr (5) and ZnCl₂-NaCl melts (5, 6). Electrodeposition of smooth and dense refractory metals becomes more difficult as the operation temperature decreases. Such electrodepositions of refractory metals at temperatures below 350 °C have not been reported, except for the case of chromium.

Electrodeposition is made at lower than 250 °C for the LIGA process due to the limit of heat resistance of the resist sheet made of polymethylmethacrylate (PMMA). Thus the aim of the present study is to obtain smooth and dense tungsten and molybdenum metal films by electrodeposition in molten salts at medium-temperatures around 250 °C. A molten ZnCl₂-NaCl-KCl eutectic (ZnCl₂ : NaCl : KCl = 0.6 : 0.2 : 0.2,
in mole fraction, mp. 203 °C (7) was selected as an electrolyte for the first time to this process. Refractory metal chlorides with low valences, WCl₄ and MoCl₃, were used as ion sources. The melts containing KF were also examined since fine deposits have been obtained in fluoride melts at high temperature in the previous works (4), which is possibly related to the formation of fluorocomplex ions.

EXPERIMENTAL

Materials and apparatus All the chemicals were anhydrous reagent grade. ZnCl₂ (99.9 %, Wako Pure Chemical Industries, Ltd.), NaCl and KCl (99 % each, Wako Pure Chemical Industries, Ltd.) were well mixed into an eutectic composition (ZnCl₂ : NaCl : KCl = 0.6 : 0.2 : 0.2, in mole fraction) and dried in a furnace under vacuum at 130 °C for three days or more. The dried mixture was then melted at 250 °C in a Pyrex beaker installed in a four-necked separable flask on a heating plate. A band-shaped heater was wound around the beaker to have uniform temperature distribution. WCl₄ (97 %, Sigma-Aldrich Co.) and MoCl₃ (99.5 %, Alfa Aesar) were added in the melt as tungsten and molybdenum ion sources, respectively. KF (99 %, Wako Pure Chemical Industries, Ltd.) was added as a fluoride ion source. The working electrode was made of a nickel plate (99.7 %, 5 x 10 x 0.2 mm, Furuuchi Chemical Corp.) that was fully immersed in the melt. The nickel plate was electrochemically polished in a sulfuric acid and then immersed in NaHF₂ solution to remove surface oxides. The counter electrode was a glassy carbon rod (3 mm φ, GC-20, Tokai Carbon Co. Ltd.). A zinc wire (99.99 %, 0.5 mm φ, Nilaco Corp.) immersed in the melt was used for the reference electrode. All the electrochemical measurements were performed in a glove box filled with argon. A chromel-alumel thermocouple was used for the temperature measurement.

Cyclic voltammetry and potentiostatic electrolysis Cyclic voltammetry with positive feedback IR compensation and potentiostatic electrolysis were performed using electrochemical measurement systems, Hokuto Denko Co. Ltd., HZ-5000. After the electrolysis, the electrodes were immersed in acetone, then rinsed with distilled water to remove the salts.

Characterization The deposits were characterized by scanning electron microscopy (SEM, Hitachi, S-2600H), X-ray diffraction (XRD, Rigaku Industrial Co. Ltd., Multi Flex) with CuKα radiation and X-ray photoelectron spectroscopy (XPS, Shimadzu Co. Ltd., ESCA-3200-01).

RESULTS AND DISCUSSION

Deposition of metallic tungsten from ZnCl₂-NaCl-KCl-WCl₄ melt

Cyclic voltammetry Figure 1 shows a cyclic voltammogram at the nickel plate electrode in ZnCl₂-NaCl-KCl-WCl₄ (0.05 mol kg⁻¹ added) melt at 250 °C. A blank voltammogram obtained for the same electrode in the melt without WCl₄ is shown for comparison in the figure. In both the plots, a cathodic current shoulder is observed at around 0.03 V as well as an anodic current peak at around 0.12 V. Compared to the results reported for the molten ZnCl₂-NaCl system (8), they are reasonably attributed to
the formation and dissolution of Ni-Zn alloy, respectively. Cathodic and anodic currents around 0 V in both the plots are attributed to the deposition and dissolution of metallic zinc, respectively. In the ZnCl2-NaCl-KCl-WCl4 melt, a cathodic current is also observed in the potential region of 0.04 – 0.4 V, indicating electrodeposition of metallic tungsten. The metallic tungsten deposited on the electrode may have changed the shape of the curve in the potential region of 0 – 0.03 V by suppressing both the deposition of metallic zinc and the formation of Ni-Zn alloy.

**Potentiostatic electrolysis and characterization of the deposit**

Since electrodeposition of metallic tungsten was suggested to occur in the potential region lower than 0.4 V, potentiostatic electrolysis was performed at 0.02 V for three hours, where deposition of metallic tungsten was expected and that of metallic zinc was not.

After the potentiostatic electrolysis, metallic gray deposit was obtained. Figure 2 shows a spectrum of XPS of W 4f for the deposit. W 4f7/2 and W 4f5/2 peaks corresponding to metallic tungsten are observed at 31 and 33 eV, respectively (9). The deposit is thus identified as metallic tungsten. However, an XRD pattern did not show any distinctive peak corresponding to a metallic tungsten crystal (10) other than a weak broad peak at around 40° in 2θ. This is probably due to the small thickness of the layer and/or low crystallinity of the deposit.

The SEM image of the deposit surface includes spherical particles and microcracks. The tensile stress due to electrodeposition in the deposited metallic tungsten or thermal expansion of the nickel substrate would cause the microcracks. Figure 3 shows a cross-sectional SEM image of the deposit. Although the metallic tungsten deposit seems to be dense, the surface is not smooth. The average thickness of the tungsten layer is about 0.5 μm. Until the electrode surface is fully covered with the tungsten layer, the Ni-Zn alloy formation and the metallic tungsten deposition are likely to occur simultaneously at the surface, where zinc atom diffuses into the nickel substrate and the coverage of metallic tungsten increases.

**Deposition of metallic tungsten from ZnCl2-NaCl-KCl-WCl4-KF melt**

**Cyclic voltammetry**

Figure 4 shows a cyclic voltammogram at a nickel electrode in ZnCl2-NaCl-KCl-KF(4 mol% added)-WCl4(0.05 mol kg⁻¹ added) melt at 250 °C. A curve for the melt containing only KF as an additive is also shown for comparison. Addition of KF to the melt causes no distinctive change in the potential region examined in the present study. In the ZnCl2-NaCl-KCl-WCl4-KF melt, a cathodic current is observed in the potential region of 0.04 to 0.4 V. This current is ascribed to electrodeposition of metallic tungsten and is larger than that in the melt without KF.

**Potentiostatic electrolysis and characterization of the deposit**

Since electrodeposition of metallic tungsten was suggested in the potential region of lower than 0.4 V, potentiostatic electrolysis was performed at 0.02 V for three hours, where deposition of metallic tungsten was expected whereas that of zinc was not.

A metallic gray deposit was obtained after the potentiostatic electrolysis. Figure 5 shows the XPS spectrum of W 4f for the deposit. The W 4f7/2 and W 4f5/2 peaks corresponding to metallic tungsten are observed at 31 and 33 eV, respectively.
Nevertheless, again, XRD did not show any distinctive diffraction peaks corresponding to metallic tungsten, which would be explained by the same reasons described above.

The SEM image of the deposit exhibited smooth surface with microcracks. The microcracks are also explained to be formed by the tensile stress in the deposit or thermal expansion of the substrate. The surface of the deposit is smoother than that obtained in the melt without KF. Figure 6 shows a cross-sectional SEM image of the deposit. The average thickness of the layer was about 0.5 μm. The improvement of the surface smoothness and the increase of the cathodic current by addition of KF may be explained in terms of the change of ligand structure of the tungsten complex in the melt giving the increase of solubility of tungsten species as the ion source. This leads to the increase of dissolution of the remaining solid WCl₄ in the melt. The nucleation is considered to exceed the crystal growth, leading to the smooth surface of the deposit. At the electrode surface, zinc atom diffuses into nickel substrate and the coverage of the tungsten increases as in the case of the deposit from the melt without KF.

Deposition of metallic molybdenum from ZnCl₂-NaCl-KCl-MoCl₃ melt

Cyclic voltammetry  Figure 7 shows a cyclic voltammogram at a nickel electrode in ZnCl₂-NaCl-KCl-MoCl₃(0.05 mol kg⁻¹ added) melt at 250 °C. A blank voltammogram obtained for the melt without MoCl₃ is shown for comparison. In the ZnCl₂-NaCl-KCl-MoCl₃ melt, a cathodic current is observed in the potential region of 0.04 to 0.4 V, ascribed to the electrodeposition of metallic molybdenum. Deposited molybdenum may have changed the electrode surface that causes the change of the shape of the curve at 0.00 to 0.02 V by suppressing the deposition of metallic zinc and the formation of Ni-Zn alloy.

Potentiostatic electrolysis and characterization of the deposit  Since electrodeposition of metallic molybdenum was suggested in the potential region of lower than 0.4 V, potentiostatic electrolysis was carried out for three hours at 0.15 V, where metallic molybdenum was expected to deposit without the deposition of metallic zinc.

After the potentiostatic electrolysis, most part of the deposit dropped off from the electrode, small amount of black deposit remained. XPS showed that the deposit is metallic molybdenum. The SEM of the deposit detected spherical particles with microcracks.

Deposition of metallic molybdenum from ZnCl₂-NaCl-KCl-MoCl₃-KF melt

Cyclic voltammetry  Figure 8 shows a cyclic voltammogram at the nickel electrode in ZnCl₂-NaCl-KCl-KF(4 mol% added)-MoCl₃(0.05 mol kg⁻¹ added) melt at 250 °C. A curve for a blank melt with KF is also shown for comparison. In this melt, a cathodic current is also observed in the potential region of 0.04 to 0.58 V, indicating the electrodeposition of metallic molybdenum. The current flow observed is larger than that in the melt without KF. Deposited molybdenum may have changed the shape of the peak at around 0.02 V by suppressing the formation of Ni-Zn alloy.
Potentiostatic electrolysis and characterization of the deposit

Since electrodeposition of metallic molybdenum was suggested in the potential region of lower than 0.58 V, potentiostatic electrolysis was performed for three hours at 0.15 V, where deposition of metallic molybdenum was expected whereas deposition of zinc was not.

After the potentiostatic electrolysis, a black deposit was obtained. The adhesion of the deposit was remarkably improved compared to that obtained in the melt without KF. Figure 9 shows a spectrum of XRD pattern of the deposit. The diffraction peaks observed are ascribed to metallic molybdenum (10). The SEM image of the deposit exhibited the formation of dendrites and microcracks. Figure 10 shows a cross-sectional SEM image of the deposit, showing the dense layer of 3 μm.

The improvement of the adhesion and the increase of the cathodic current by KF addition may also be related to the change of ligands of molybdenum complex in the melt. Detailed studies are now under way.

CONCLUSIONS

Metallic tungsten deposits were obtained by potentiostatic electrolyses in ZnCl₂-NaCl-KCl and ZnCl₂-NaCl-KCl-KF melts containing WCl₄ at 250 °C. In the melt containing KF, a smooth and dense deposit was obtained. A dense metallic molybdenum deposit was also obtained by potentiostatic electrolysis in ZnCl₂-NaCl-KCl-KF melt containing MoCl₃ at 250 °C. Addition of KF improved adhesion of the deposit to the nickel substrate.

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Figure 1. Cyclic voltammograms at nickel electrodes in ZnCl2-NaCl-KCl and ZnCl2-NaCl-KCl-WCl4 (0.05 mol kg⁻¹ added) melts at 250 °C. Scan rate: 0.05 V s⁻¹.

Figure 2. A W 4f XPS spectrum of the deposit obtained by the potentiostatic electrolysis at 20 mV vs. Zn²⁺/Zn in a ZnCl2-NaCl-KCl-WCl4 (0.05 mol kg⁻¹ added) melt at 250 °C. Argon ion etching time: 4500 s.

Figure 3. A cross-sectional SEM image of the deposit obtained by the potentiostatic electrolysis at 20 mV vs. Zn²⁺/Zn for three hours in ZnCl2-NaCl-KCl-WCl4 (0.05 mol kg⁻¹ added) melt at 250 °C.
Figure 4. Cyclic voltammograms at nickel electrodes in ZnCl₂-NaCl-KCl-KF (4 mol% added) and ZnCl₂-NaCl-KCl-KF (4 mol% added)-WCl₄ (0.05 mol kg⁻¹ added) melts at 250 °C. Scan rate: 0.05 V s⁻¹.

Figure 5. A W 4f XPS spectrum of the deposit obtained by the potentiostatic electrolysis at 20 mV vs. Zn²⁺/Zn for three hours in ZnCl₂-NaCl-KCl-KF (4 mol% added)-WCl₄ (0.05 mol kg⁻¹ added) melt at 250 °C. Argon ion etching time: 4500 s.

Figure 6. A cross-sectional SEM image of the deposit obtained by the potentiostatic electrolysis at 20 mV vs. Zn²⁺/Zn for three hours in ZnCl₂-NaCl-KCl-KF (4 mol% added)-WCl₄ (0.05 mol kg⁻¹ added) melt at 250 °C.

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Figure 7. Cyclic voltammograms at nickel electrodes in ZnCl₂-NaCl-KCl and ZnCl₂-NaCl-KCl-MoCl₃ (0.05 mol kg⁻¹ added) melts at 250 °C. Scan rate: 0.05 V s⁻¹.

Figure 8. Cyclic voltammograms at nickel electrodes in ZnCl₂-NaCl-KCl-KF (4 mol% added) and ZnCl₂-NaCl-KCl-KF (4 mol% added)-MoCl₃ (0.05 mol kg⁻¹ added) melts at 250 °C. Scan rate: 0.05 V s⁻¹.
Figure 9. An XRD pattern of the deposit obtained by the potentiostatic electrolysis at 150 mV vs. Zn\(^{2+}/\text{Zn}\) for three hours in the ZnCl\(_2\)-NaCl-KCl-KF(4 mol\% added)-MoCl\(_3\)(0.05 mol kg\(^{-1}\) added) melt at 250 °C.

Figure 10. A cross-sectional SEM image of the deposit obtained by the potentiostatic electrolysis at 150 mV vs. Zn\(^{2+}/\text{Zn}\) for three hours in the ZnCl\(_2\)-NaCl-KCl-KF(4 mol\% added)-MoCl\(_3\)(0.05 mol kg\(^{-1}\) added) melt at 250 °C.