Electrodeposition of Molybdenum in LiTFSI-CsTFSI Melt at 150ºC

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Electrodepostion of molybdenum was studied in the eutectic LiTFSI-CsTFSI (0.07: 0.93 in mole fraction, m.p., 112ºC) melt at 150ºC. $MoCl_5$ was selected as molybdenum ion sources. Metallic molybdenum was electrodeposited on nickel substrate. Quality of the deposits was improved by using galvanostatic electrolysis and pulsed current electrolysis.

1. Introduction

LIGA process, a microfabrication technique consisting of lithography, electroforming and molding, allows inexpensive mass production of microstructures. Although many products have already been commercially produced with this method, applicable materials are limited to metals that are able to be electrodeposited in aqueous electrolytes such as copper, gold, nickel and Ni–Fe alloys [1]. The authors believe that electrodeposition of refractory metals, such as Mo, W and Ta in molten salts is a very promising method for the electroforming step of LIGA process owing to their high hardness and high mechanical-strength and excellent corrosion resistance.

Many efforts have been made to develop an electroplating process for the electrodeposition of refractory metals. High temperature molten salts were found to be good baths for the electrodepositon of refractory metals [2, 3]. Senderoff and Mellors obtained refractory metals in fluoride melts at 700-850ºC [4, 5]. Katagiri et al. obtained W metal at 350–450ºC using $NaCl-ZnCl_2$ and $NaBr-ZnBr_2$ melts [6]. Very recently, we have obtained W metal [7] and Mo metal [8, 9] at 250ºC using $NaCl-KCl-KF-ZnCl_2$ melt. WCl_4, $MoCl_3$ and $MoCl_5$ were used as sources of W and Mo, respectively.

However, LIGA process requires the electroforming step under 250ºC and preferably at lower than 200ºC due to the limit of heat resistance of a resist sheet made of polymethylmethacrylate (PMMA). Although some newly developed resists can resist higher temperature, the best microstructures can be only manufactured at temperature of no higher than 150ºC.

It is necessary to develop low temperature molten salts for electrodeposition of refractory metals in the LIGA process. Room temperature molten salts (RTMS) or ionic liquids (IL) are acknowledged as the next generation of electrolytes because of their wide liquid-phase range, low viscosity, nonflammability, very low vapor pressure and wider electrochemical windows than those of aqueous electrolytes. Some attempts have been made to electrodeposit refractory metals in RTMS at low temperatures. Matsunaga et al. have tried to obtain tantalum in a 1-ethyl-3-methylimidazolium chloride (EMIC)-$TaCl_5$ melt (66.7:33.3, in mole fraction) at 100ºC [10] in which Ta (V) can be reduced to Ta (II), and LiF addition enables the further reduction of Ta (II) to metallic tantalum. S. Zein El Abedin et al [11] could not reproduce the results obtained by Matsunaga, but they have obtained metallic Ta at 200ºC using another kind of room temperature ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([BMP]TFSI) using TaF_5 as a source of Ta. In fact, they did not obtain crystalline metallic tantalum unless LiF was added to the electrolyte.

Alkali metal salts of bis[(tri-fluoromethyl)sulfony]amide (MTFSI, M = Li, Na, K, Rb, Cs) and their mixture were studied in our group, including binary phasediagram, ternary phasediagram, thermal properties, physical-chemical properties such as density, viscosity, conductivity, and so on. The eutectic LiTFSI-CsTFSI (0.07/0.93, mole fraction) shows a low melting point of 112°C and good ionic conductivity (18.4 mS/cm, 150°C).

The aim of the present work is to obtain Mo metal by electrodeposition using newly developed LiTFSI-CsTFSI melt at 150°C.

2. Experimental

The cesium bis[(tri-fluoromethyl)sulfonyl]amide salt (CsTFSI) was prepared by neutralization of ethanol solution of HTFSI (Morita Chemical Industries Co., Ltd, purity >99%) with cesium carbonate (Aldrich, purity >99.5%), and then dried under vacuum for three days at 115°C. Other chemicals were commercially available and used after appropriate drying treatments. The electrolyte was prepared by mixing LiTFSI (Morita Chemical Industries Co., Ltd, purity >99%) and CsTFSI in the eutectic composition (LiTFSI: CsTFSI = 0.07: 0.93 / mole fraction) in an alumina crucible with high purity. $MoCl_5$ (Aldrich, anhydrous, purity 99.99%) was added to the above mixture at room temperature. (Note: If $MoCl_5$ is added to the LiTFSI-CsTFSI melt at 150°C or higher, some brown gas releases from the melt due to decomposition of $MoCl_5$.). A chromel–alumel thermocouple was used for the temperature measurement.

The working electrode was a Ni plate (Nilaco, 5 mm x 10 mm x 0.2 mm, purity 99.7%), a Mo plate (Nilaco, 5 mm x 10 mm x 0.2 mm, purity 99.7%), or glassy carbon rod (Φ3 mm, Tokai carbon). The nickel plate was electrochemically polished in sulfuric acid then immersed in an acid cleaner containing $NaHF_2$ (Kizai Corp., Kokeisan B) to remove surface oxides. The Mo plate was etched by argon ion beam of the XPS. The counter electrode and the reference electrode were made of lithium metal (Aldrich, purity 99.9%). The cyclic voltammetry measurements and electrodepositions were performed in a glove box filled with argon using a PARSTAT 273 Potentiostat/Galvanostat (Princeton Applied Research) controlled by PowerCV, PowerSTEP, PowerPULSE and PowerCORR software. After the electrodepositions, the samples were immersed in acetone, and then rinsed with deaerated distilled water to remove adherent salts. This process was performed in a glove bag filled with nitrogen.

The deposits were characterized by scanning electron microscopy (SEM, Hitachi, S-2600H), energy dispersive X-ray analysis (EDX, Horiba Co., Ltd., EMAX ENERGY EX-200), X-ray diffraction (XRD, Rigaku Industrial Co., Ltd., Multi Flex) with CuKα radiation, and X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9010MC).

3. Results and Discussions

3.1 Electrochemical behavior of LiTFSI-CsTFSI melt.

Cyclic voltammetry was performed on nickel, glassy carbon and molybdenum electrodes in eutectic LiTFSI-CsTFSI melt at 150°C. Curve a in Fig.1 is the voltammogram obtained for the Ni electrode, curve b for the Mo electrode, and curve c for the glassy carbon. Cathodic and anodic currents around 0 V on curves a, b are attributed to the deposition and dissolution of metallic lithium, respectively. The anodic current around 5 V on curve c is attributed to the oxidation of TFSI⁻ ion. Anodic current

appears at around 4 V on curve b, suggesting that molybdenum slightly dissolves into the melt.
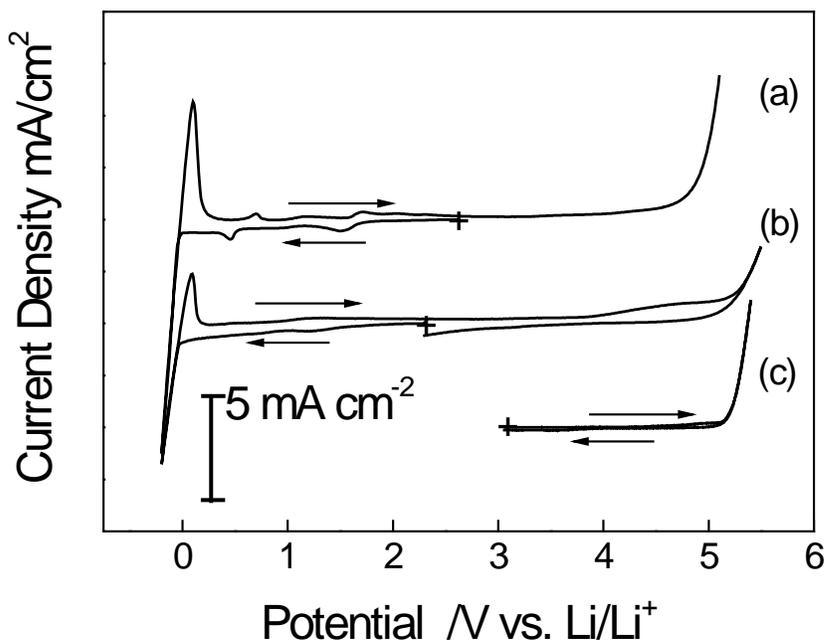
Fig. 1. Cyclic voltammograms in a molten eutectic LiTFSI-CsTFSI system at 150°C. Electrode, (a) Ni plate, (b) Mo plate, (c) glassy carbon rod; Scan rate, 50mVs^{-1}. The marks (+) indicate the starting point, and the arrows shows the direction of potential scan.

3.2 Electrodeposition of metallic molybdenum in LiTFSI-CsTFSI-MoCl$_5$ melts at 150 °C.

Figure 2 (A) shows a cyclic voltammogram of the nickel electrode in LiTFSI-CsTFSI-MoCl$_5$ (0.5 mol% added) melt at 150°C. Because a portion of MoCl$_5$ remained not dissolved, the melt was regarded to be saturated on MoCl$_5$. Compared to curve (a) in Fig. 1, two new cathodic current shoulders were observed. The first cathodic wave, which appears at around 2.5 V, is assumed to be correlated to the reduction of Mo (V) to Mo (III). The second cathodic wave, which appears at around 1.3 V, is considered as electrolytic reduction of Mo (III) to Mo (0). In the reverse scan, the anodic peak, which appears at around 2.2 V, might be attributed to the dissolution of Mo (0) to Mo (III). However, as shown in Fig. 2 (B), a new anodic peak appears at around 1.85 V in the linear sweep voltammograms, in which a 60 s deposition at the initial potential was performed before each measurement. This anodic peak disappeared when the initial potential is more positive than 1.7 V, and it might be attributed to the oxidation of Mo (0) to some higher valences.
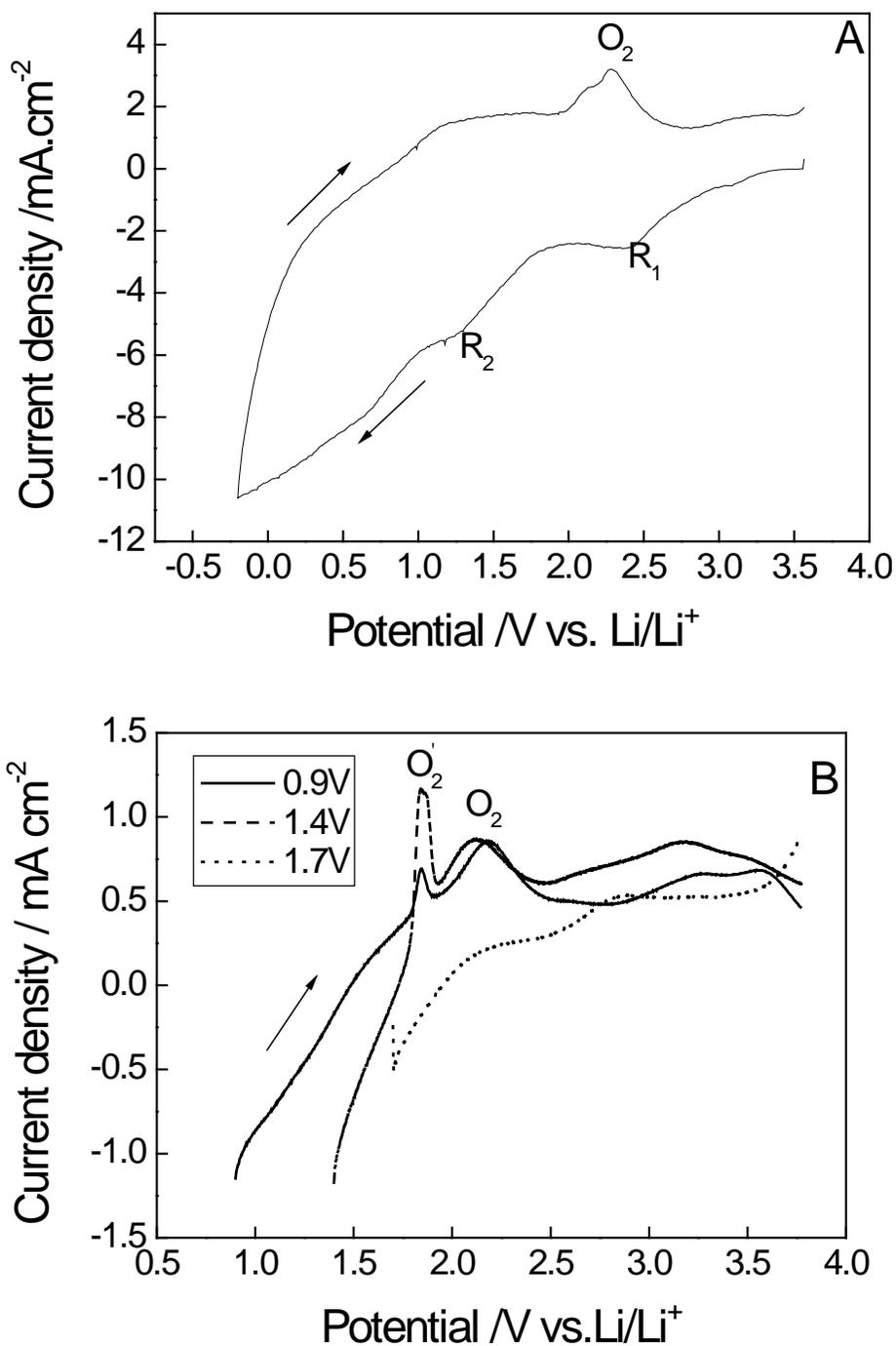
Fig. 2. (A) Cyclic Voltammogram and (B) linear voltammograms on nickel electrode in LiTFSI-CsTFSI-MoCl₅ (0.5 mol% added) melts at 150°C. Scan rate: 50 mV/s; 60 s deposition was performed at the initial potential before sweep in the linear voltammetry.

Based on these results, potentiostatic electrolysises were carried out on Ni substrates for 1 h at 1.4 V, 2.0 V and 2.2 V. The depositions of metallic molybdenum at these potentials were confirmed by XPS analysis (see Fig. 3). The depositions prepared at these potentials which are black visually do not dissolve into acetone but can be removed easily with water, especially for those obtained at more negative potentials. Perhaps the depositions are mixture of metallic molybdenum and molybdenum compounds which react with water to cause the drop of the deposits from the Ni substrate.

Because of the poor adherence of the deposits obtained by potentiostatic electrolysis, the other techniques such as galvanostatic electrolysis and pulsed current electrolysis were applied to improve the quality of the deposited film.
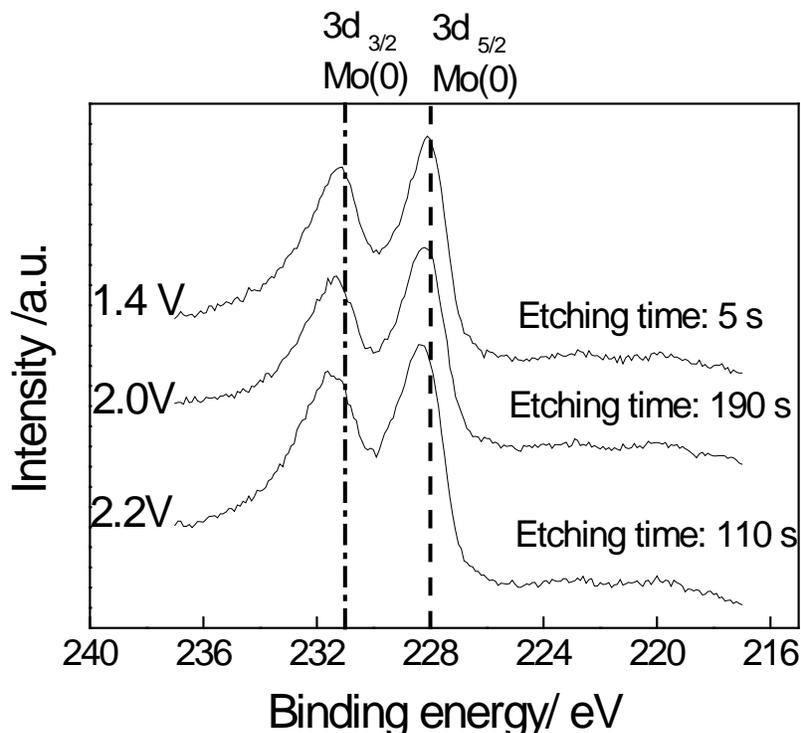
Fig. 3. Mo 3d XPS spectra of the films obtained by potentiostatic electrolysis at 1.4 V, 2.0V and 2.2 V for 1 h in LiTFSI-CsTFSI-MoCl$_5$ (0.5 mol %) melt at 150ºC.

3.3 Galvanostatic electrolysis at 150ºC

At 150ºC, galvanostatic electrolysis was performed in eutectic LiTFSI-CsTFSI melt containing 0.5 mol% MoCl$_5$ at -0.5 mA/cm^2 for 2 h, and then a black deposit was obtained. After removing the black layer with deaerated distilled water, a gray deposit was observed. Fig. 4. shows a spectrum of XPS of Mo 3d for the deposit. Mo3d$_{3/2}$ and Mo 3d$_{5/2}$ peaks corresponding to metallic molybdenum are observed at 231 and 228 eV, respectively. The deposit is, therefore, identified as metallic molybdenum. On the other hand, an XRD pattern did not show any distinctive peaks corresponding to a metallic molybdenum crystal. This means that the electrodeposit is amorphous.
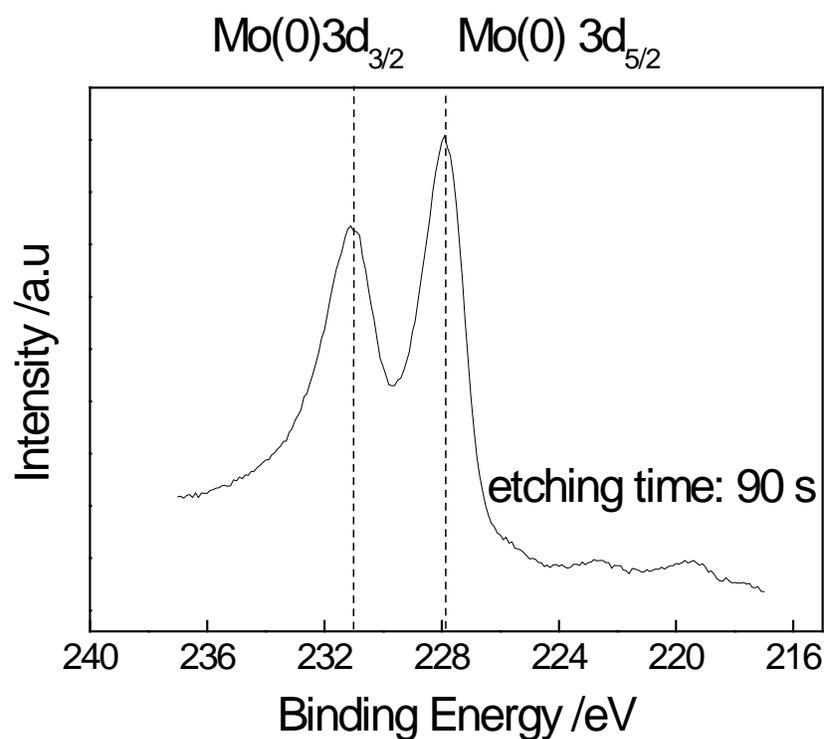
Fig. 4. Mo 3d XPS spectrum of deposition obtained by galvanostatic electrolysis in LiTFSI-CsTFSI-MoCl$_5$ (0.5 mol %) melt for 2 h at 150°C. i = -0.5mA/cm^2.
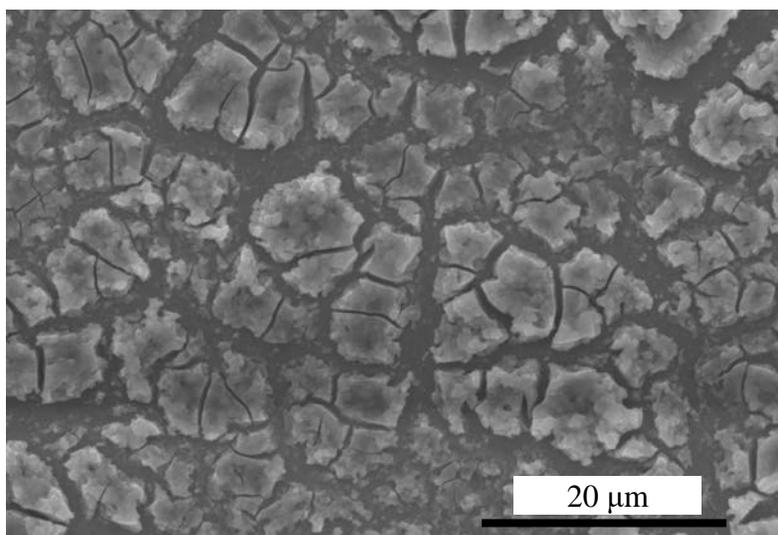
Fig. 5. Surface SEM image of the deposit obtained in LiTFSI-CsTFSI-MoCl$_5$ (0.5 mol % added) melt by galvanostatic electrolysis for 2 h at 150°C. i = -0.5mA/cm^2.

Figure 5 shows a surface SEM image of the deposit, where microcracks are observed. It indicates that tensile is generated on the deposited film which would be produced by the deposition induced tensile stress [9].

3.4 Pulsed current electrolysis at 150 ºC

A pulsed current electrolysis was performed in order to obtain a smoother and thicker deposit. Fig. 6 shows the pattern diagram of pulsed current electrolysis in every two cycles. The electrolysis was performed for 420 cycles (34 ks) in the eutectic LiTFSI-CsTFSI melt containing 0.5 mol% $MoCl_5$ at 150ºC. After removing the black layer with deaerated distilled water, gray deposit was observed on Ni substrate. The formation of metallic molybdenum was confirmed by XPS analysis. Fig. 7 shows the surface SEM image and cross sectional image of the deposit. The coverage and adherence of the deposit become better than deposits obtained by the other methods conducted in this study. The thickness of the deposit is about 3 μm, but the microcracks are still observed.
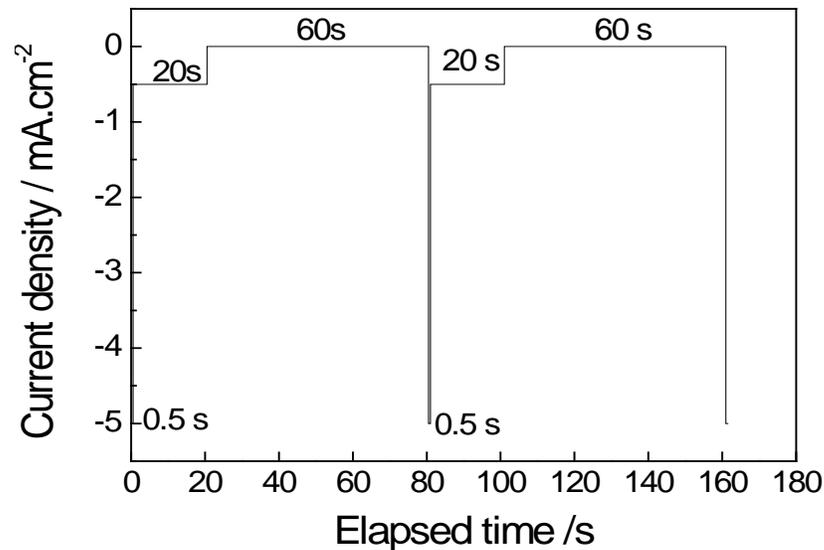
Fig. 6. Pattern diagram of pulsed current electrolysis in every cycle.
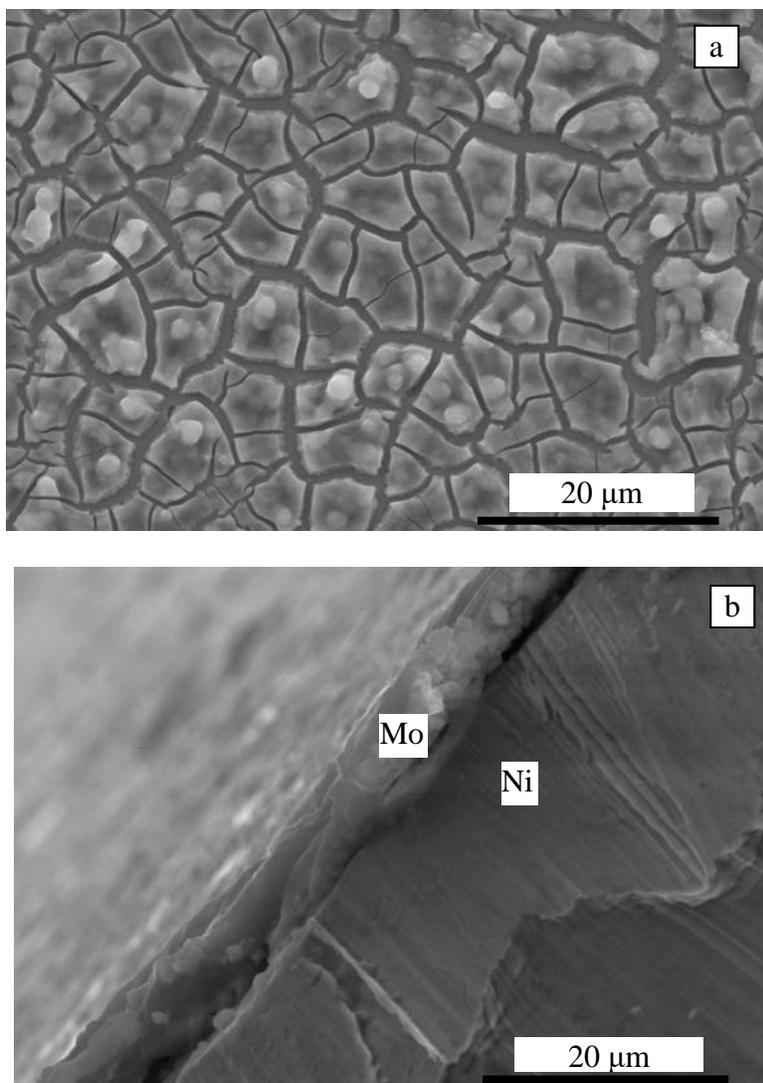
Fig. 7. (a) surface SEM image and (b) cross-sectional image of the deposit obtained in LiTFSI-CsTFSI-MoCl$_5$ (0.5 mol % added) melt by pulsed current electrolysis at 150°C.

Conclusion

We have presented the results on the electroreduction of MoCl$_5$ in the eutectic lithium bis[(tri-fluoromethyl)sulfonyl]amide (LiTFSI) and cesium bis[(tri-fluoromethyl)sulfonyl]amide (CsTFSI) melt (0.07: 0.93, in mole fraction) at 150°C with the aim of metallic molybdenum electrodeposition.

Metallic molybdenum can be obtained at potentials more negative than 2.2 V vs. Li/Li$^+$ at 150°C. The quality and adherence of the electrodeposit were improved by pulsed current electrolysis.

The present process is promising as a new method for molybdenum coating at low temperatures such as the coating on the conventional LIGA parts.

Acknowledgements

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