Electrodeposition of Refractory Metals in Medium-Temperature Molten Salts

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Introduction

LIGA process, a microfabrication technique consisting of a lithography and an electroforming, has attracted considerable attention. The authors believe that electrodeposition of refractory metals such as W, Mo, 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. If this method is realized, it would extremely contribute to the technical development of the Micro-Electro-Mechanical Systems (MEMS).

Senderoff and Mellors have obtained refractory metals in fluoride melts at 700-850°C[1, 2]. Katagiri et al. have obtained W metal at 350-450°C using $ZnCl_2$-NaCl and $ZnBr_2$-NaBr melts[3, 4].

However, LIGA process requires the electroforming step under 250 °C due to the limit of heat resistance of a resist sheet made of polymethylmethacrylate (PMMA). Electrodeposition of refractory metals in molten salts under 250 °C has not been reported so far.

The aim of the present work is to obtain refractory metals by electrodeposition in molten salts at medium-temperatures around 250 °C.

Experimental

All the chemicals used were anhydrous reagent grade. $ZnCl_2$, NaCl and KCl were well mixed into eutectic composition ($ZnCl_2$: NaCl : KCl = 0.54 : 0.21 : 0.25 / mole fraction) in a high purity alumina crucible and dried in a furnace under vacuum at 130 °C for at least 24 hours. After that it was melted at 250 °C. $TaCl_5$ was added in the melt as a tantalum ion source. The working electrode was a Ni plate (5 mm x 10 mm x 0.2 mm) which was fully immersed in the molten salt. The Ni plate was electrochemically polished in a sulfuric acid as a pretreatment. The counter electrode was a glassy carbon rod (3 mm). The reference electrode was a Zn wire (1 mm) immersed in a molten salt of the same composition of the melt, which was separated from the melt by Pyrex tube with a junction of a thin Pyrex. Cyclic voltammetry and potentiostatic electrolysis were performed in this cell. The deposits were analyzed by XRD, SEM and EDX.

Results and discussion

Figure 1 shows a cyclic voltammogram for the Ni electrode in a molten $ZnCl_2$-NaCl-KCl-$TaCl_5$ (0.05 mol kg^{-1} added) system at 250 °C. A blank plot is shown for comparison. Cathodic currents were observed for both the plots from 0.04 V to -0.08 V, which correspond to the formation of Ni-Zn alloy and deposition of Zn metal. Since no distinctive current was observed in more positive potential region than 0.04 V for both the plots, electrodepositon of Ta metal is not likely to proceed in this region. On the other hand, the cathodic current from 0.04 V to -0.08 V became smaller by addition of $TaCl_5$. The smaller cathodic current resulted in the smaller anodic current in the region 0 - 0.2 V. The decrease of the cathodic current is possibly due to the electrodeposition of Ta metal, that is, the deposited Ta metal prevents the formation of Ni-Zn alloy and deposition of Zn metal. Since electrodeposition of Ta metal was suggested in more negative potential region than 0.04 V, potentiostatic electrolysis was performed at -0.4 V for 0.7 hours, where codeposition of Zn and Ta metal was expected.

As the result, dendritic deposit was obtained. XRD analysis of the deposit clearly showed the existence of Zn metal and suggested the codeposition of Ta metal.

Acknowledgements

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References

[1] S. Senderoff and G. W. Mellors, Science, **153**, 1475 (1966).
[2] S. Senderoff and G. W. Mellors, J. Electrochem. Soc., **114**, 586 (1967).
[3] A. Katagiri, M. Suzuki, and Z. Takehara, J. Electrochem. Soc., **138**, 767 (1991).
[4] M. Masuda, H. Takenishi, and A. Katagiri, J. Electrochem. Soc., **148**, C59 (2001).

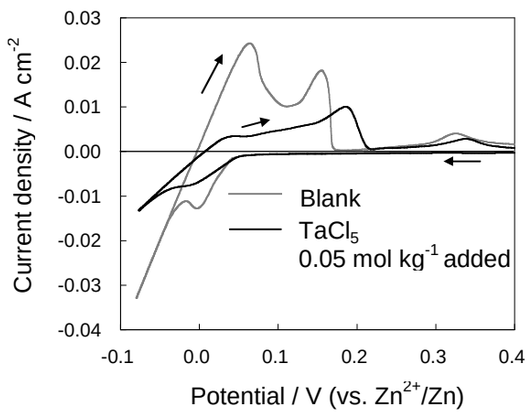

Fig. 1. Cyclic voltammograms for Ni electrodes in a molten $ZnCl_2$-NaCl-KCl (blank) and in a molten $ZnCl_2$-NaCl-KCl-$TaCl_5$ (0.05 mol kg^{-1} added) system at 250 °C.
Scan rate : 0.05 V s^{-1}