

Available online at www.sciencedirect.com



ELECTROCHIMICA

Electrochimica Acta 53 (2007) 20-23

www.elsevier.com/locate/electacta

Analysis of tungsten film electrodeposited from a ZnCl₂-NaCl-KCl melt

Koji Nitta^{a,*}, Shinji Inazawa^a, Kazunori Okada^a, Hironori Nakajima^b, Toshiyuki Nohira^{b,**}, Rika Hagiwara^b

^a Electronics & Materials R&D Labs, Sumitomo Electric Industries, Ltd., 1-1-3, Shimaya, Konohana-ku, Osaka 554-0024, Japan

^b Department of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

Received 1 February 2006; received in revised form 16 January 2007; accepted 16 January 2007 Available online 30 January 2007

Abstract

Microparts for micro-electro-mechanical systems (MEMS) are becoming increasingly important, and the Lithographie Galvanoformung Abformung (LIGA) process for producing such parts is attracting attention [1]. However, as this process requires the step of electroplating in aqueous solution, only copper, nickel and their alloys can be used because of the limit of the potential window of water. We have been attempting to apply the electroplating of refractory metals in molten salts to the LIGA process or to the surface coating of conventional LIGA microparts in order to give higher strength and heat resistance for the microparts. Herein we report the characteristics of a tungsten film electrodeposited from a ZnCl₂–NaCl–KCl melt at 250 °C.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: MEMS; LIGA; Electrodeposition of tungsten; Tungsten film; Electrodeposition in molten salt

1. Introduction

As a process for manufacturing microparts for micro-electromechanical systems (MEMS), the Lithographie Galvanoformung Abformung (LIGA) process is already in practical use for some cases and holds great promise for the future. The current LIGA process, however, requires the electroforming in aqueous solution, and thus the applicable materials are limited to nickel, copper, and their alloys.

Still, the strength and durability of the material in the microparts are expected to be improved, wherein refractory metals (especially tungsten) have the greatest potential. However, electrodeposition of tungsten from an aqueous solution is extremely difficult. Nevertheless, Senderoff and Mellors obtained electrodeposits of refractory metals from an alkali metal fluoride melt at 700–850 °C [2,3], and Katagiri et al. have been successful with electrodeposition of metallic tungsten from ZnBr₂–NaBr [4] and ZnCl₂–NaCl [5] at 350–450 °C. Yet the resist sheet for the LIGA process deteriorates at such high temperatures (350 °C

** Corresponding author. Tel.: +81 75 753 4817; fax: +81 75 753 5906.

E-mail addresses: nitta-koji@sei.co.jp (K. Nitta), nohira@energy.kyoto-u.ac.jp (T. Nohira).

or more). Also, when such high temperature electrodeposition techniques are applied to the coating of LIGA parts made of electroformed nickel, the heat induces softening and embrittlement of the substrate nickel. We have therefore been investigating tungsten electrodeposition in a temperature range in which the resist deformation and the softening of electroformed nickel material can be prevented. We have already reported that electrodeposition of tungsten is possible in a $ZnCl_2-NaCl-KCl$ melt (m.p. 203 °C), and that the addition of KF to the melt gives better deposits [6]. In this paper, we studied the microstructure and mechanical characteristics of the obtained tungsten film, and demonstrate the tungsten coating on LIGA parts made of nickel.

2. Experimental

2.1. Materials and apparatus

All the chemicals were anhydrous reagent grade. $ZnCl_2$ (99.9%, Wako Pure Chemical Industries, Ltd.), NaCl and KCl (99 each, Wako Pure Chemical Industries, Ltd.) were well mixed into an eutectic composition ($ZnCl_2:NaCl:KCl = 0.6:0.2:0.2$, in mole fraction) and dried in a furnace under vacuum at 250 °C for 3 days or more. The dried mixture was then melted at

^{*} Corresponding author. Tel.: +81 6 6466 5637; fax: +81 6 6466 1274.

^{0013-4686/\$ –} see front matter © 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2007.01.032

250 °C in a Pyrex glass beaker installed in a four-necked separable flask on a heating plate. WCl₄ (97%, Sigma-Aldrich Co.) was added in the melt as a tungsten ion source. KF (99%, Wako Pure Chemical Industries, Ltd.) was added as a fluoride ion source. The working electrode was made of a nickel plate $(99.7\%, 5 \text{ mm} \times 10 \text{ mm} \times 0.2 \text{ mm}, \text{Furuuchi Chemical Corp.})$ that was fully immersed in the melt. The nickel plate was electrochemically polished in a sulfuric acid and then immersed in an oxide remover solution (Kokeisan B, Kizai Corp.). The counter electrode was a glassy carbon rod (Ø 3 mm, GC-20, Tokai Carbon Co. Ltd.). A zinc wire (99.99%, Ø 0.5 mm, Nilaco Corp.) immersed in the melt was used for the reference electrode. A nickel micro contact probe electroformed on a stainless substrate was used as the working electrode in the examination of the surface coating of the micro parts. All the electrochemical measurements were carried out in a glove box filled with argon. A chromel-alumel thermocouple was used for the temperature measurement.

2.2. Electrodeposition and characterization

Potentiostatic electrolysis was 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. The deposits were characterized by scanning electron microscopy (SEM, Hitachi, S-800), energy dispersive X-ray analysis (EDX, edax, S-UTW), scanning ion microscopy (SIM) with focused ion beam (FIB, FEI, FIB200), transmission electron microscopy (TEM, Hitachi, H-9000UHR) with FIB and energy dispersive X-ray analysis (EDX, Noran Instruments Inc., TN-5500). The hardness of the film was measured by nanoindentation (MTS System Corp., Nanoindenter XP).

3. Results and discussion

3.1. Deposition of metallic tungsten from a ZnCl₂-NaCl-KCl-KF-WCl₄ melt

A potentiostatic electrolysis was performed at 20 mV versus Zn(II)/Zn in ZnCl₂–NaCl–KCl-KF (4 mol% added)–WCl₄ (0.05 mol kg⁻¹ added) melt at 250 °C. A metallic gray film was obtained after the potentiostatic electrolysis. Fig. 1 shows the surface SEM image of the film, which exhibited a smooth surface. Fig. 2 shows the EDX spectrum of the film, in which nickel, tungsten and zinc peaks are observed. This result is consistent with our previous study that a metallic tungsten layer formed on a nickel–zinc alloy layer in the same electrolysis condition [6].

3.2. Analysis of the cross-section of the film

Fig. 3 shows a cross-sectional SIM image after FIB crosssectioning. A fine layer of 0.65 μ m on a course layer of 0.87 μ m is observed on the nickel substrate. According to our previous result [6], the fine layer should be metallic tungsten, which is confirmed in the next section, and the course layer should be nickel–zinc alloy. formation of nickel–zinc alloy easily occurs



Fig. 1. The surface SEM image of the electrodeposited film.



Fig. 2. The EDX spectrum of the electrodeposited film.



Fig. 3. The cross-sectional SIM image of the electrodeposited film.

compared with tungsten electrodeposition for the present condition. Thus, the nickel-zinc alloy formation is thought to mainly occur in the initial period. However, the nickel-zinc alloy formation stops after the surface of the electrode is fully covered with the metallic tungsten layer. Assuming that the metallic tungsten is electrodeposited from the tetravalent tungsten species, the current efficiency is calculated to be 6.9%. The causes of the low current efficiency are assumed to be, in addition to the formation of a nickel-zinc alloy, the reduction of water and other impurities residing in the salts, and the so-called shuttle reaction. When high valence ion is reduced to low valence ion at the cathode and the reverse reaction occurs at the anode, it is called a shuttle reaction. Since tungsten exhibits a wide variety of oxidation states, ranging from +6 to 0, there is a possibility that the shuttle reaction takes place.

3.3. TEM observation of the tungsten film

To observe the microstructure of the film, TEM analysis was performed. The TEM image and the EDX spectrum of the film are shown in Figs. 4 and 5. These results show that the film is extremely compact, and that the melt and other impurities are not included in the film. Fig. 6 shows an electron diffraction image. Plain rings can be seen in the diffraction image indicating that the obtained tungsten is polycrystalline in structure.

In addition to general α -W structure, β -W structure has been reported for the electrodeposits from molten salts [7]. To identify the crystal structure of the electrodeposited tungsten film, the ratios of radii of the rings in the electron diffraction image are compared with the ratios of plane spacings of the α -W and β -W crystal lattices. When radii of the rings A, B and C in Fig. 6 are defined as r_A , r_B and r_C , the ratios are calculated as $r_A/r_B = 0.696$ and $r_A/r_C = 0.571$. Separately, we calculated the ratios of plane spacings of the major lattice planes using JCPDS cards [8]. For α -W, plane spacings of (100), (200) and (211) are $d_{\alpha 100} = 22.38$ nm, $d_{\alpha 200} = 15.82$ nm and $d_{\alpha 211} =$ 12.92 nm, respectively. They hence yield $d_{\alpha 200}/d_{\alpha 100} = 0.706$ and $d_{\alpha 211}/d_{\alpha 100} = 0.577$. On the other hand, for β -W, $d_{B200} = 25.25$ nm, $d_{B210} = 22.58$ nm, $d_{B211} = 20.62$ nm and



Fig. 4. The TEM image of the electrodeposited film.



Fig. 5. The EDX spectrum of the electrodeposited film.

 $d_{\beta 222} = 14.58$ nm, respectively. Then, they yield $d_{\beta 210}/d_{\beta 200} = 0.912$, $d_{\beta 211}/d_{\beta 200} = 0.624$, $d_{\beta 211}/d_{\beta 210} = 0.913$ and $d_{\beta 222}/d_{\beta 210} = 0.707$. As a result, r_A/r_B and r_A/r_C agree well with $d_{\alpha 200}/d_{\alpha 100}$ and $d_{\alpha 211}/d_{\alpha 100}$, respectively, and do not with the ratios for β -W. The obtained film is thus identified as α -W.

3.4. Hardness measurement of the tungsten film

Nanoindentation was performed to measure the hardness of the tungsten film. A probe was inserted vertically into the substrate from the surface of the film. Fig. 7 shows relationship between insertion depth of the probe and hardness at room temperature. The maximum hardness was 9.1 GPa, however, bulk tungsten was about 7 GPa. The decrease of the hardness as the increase in the insertion depth above 120 nm is due to the effect of the nickel–zinc alloy layer and the nickel substrate.



Fig. 6. The electron diffraction image of the electrodeposited film.



Fig. 7. The hardness of the electrodeposited film determined by nanoindentation.



Fig. 8. The microparts coated with electrodeposited tungsten.

Since the hardness of the glossy nickel electroformed in aqueous solution was 5.4 GPa, the obtained tungsten film has superior hardness.

3.5. Demonstration of tungsten coating on microparts

We demonstrated tungsten coating on microparts manufactured by the LIGA process [9]. Potentiostatic electrolysis was performed on nickel microparts placed on a stainless substrate at 20 mV versus Zn(II)/Zn in ZnCl₂–NaCl–KCl–KF (4 mol% added)–WCl₄ (0.05 mol kg⁻¹ added) melt at 250 °C. Fig. 8 shows an SEM surface image of the microparts after the electrolysis. It is confirmed that a well-adhering and smooth tungsten coating on microparts is feasible using the present method.

4. Conclusion

Potentiostatic electrolysis in a ZnCl₂–NaCl–KCl–KF (4 mol% added)–WCl₄ (0.05 mol kg⁻¹ added) melt at 250 °C gave a smooth tungsten film with no incorporated melts and impurities. The electron diffraction analysis showed that the deposited tungsten film has α -W structure. Nanoindentation analysis revealed that the hardness of the film was 9.1 GPa. Coating on microparts with an adhesive and smooth tungsten film was successfully demonstrated.

Acknowledgements

A part of this study was supported by the Industrial Technology Research Grant Program in 2003 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

- [1] Y. Hirata, Nucl. Instrum. Method B 208 (2003) 21.
- [2] S. Senderoff, G.W. Mellors, Science 153 (1966) 1475.
- [3] S. Senderoff, G.W. Mellors, J. Electrochem. Soc. 114 (1967) 586.
- [4] A. Katagiri, M. Suzuki, Z. Takehara, J. Electrochem. Soc. 138 (1991) 767.
- [5] M. Masuda, H. Takenishi, A. Katagiri, J. Electrochem. Soc. 148 (2001) C59.
- [6] H. Nakajima, T. Nohira, R. Hagiwara, Electrochem. Solid-State Lett. 8 (7) (2005) C91.
- [7] A. Katagiri, M. Suzuki, Z. Takehara, J. Electrochem. Soc. 138 (1991) 767.
- [8] JCPDS No. 47-1319 and No. 04-0806.
- [9] T. Haga, K. Okada, J. Yorita, Y. Hirata, S. Shimada, ICEP Proc. (2002) 421–426.