Int. J. Electrochem. Sci., 9 **(2014)** 220 - 226

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Research on Preparation of Multilayers by the Multiple Jet Electrodeposition

Gui-Feng Wang[1,], Li-Da Shen[2], Lin-Ming Dou[1], Zong-Jun Tian[2], Zhi-Dong Liu[2]*

[1] State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology, No. 1 University Road, Xuzhou, Jiangsu 221116, PR China.
[2] College of Mechanical and Electrical Engineering, Nanjing University of Aeronautics and Astronautics, No. 29 Yudao Street, Nanjing, Jiangsu 210016, PR China.
[*]E-mail: wgfskl@163.com

Received: 5 September 2013 / *Accepted:* 23 October 2013 / *Published:* 15 November 2013

The preparation of multilayers by a novel multiple jet electrodeposition (MJED) technology with real-time polishing for deposit surface was studied. The microstructure and microhardness of Ni-Cu multilayers produced by MJED with and without polishing were examined. Factors affecting the structure, such as energized time and current density were discussed. The results indicated that multilayers could be produced by MJED with excellent control of the structure, composition and sublayer thickness. The regularity and microhardness of multilayers were significantly improved compared with that without polishing. And a thicker multilayer deposit up to 1.2 mm was experimentally produced with mirror-like surface and excellent hardness uniformity.

Keywords: jet electrodeposition; multilayers; microhardness

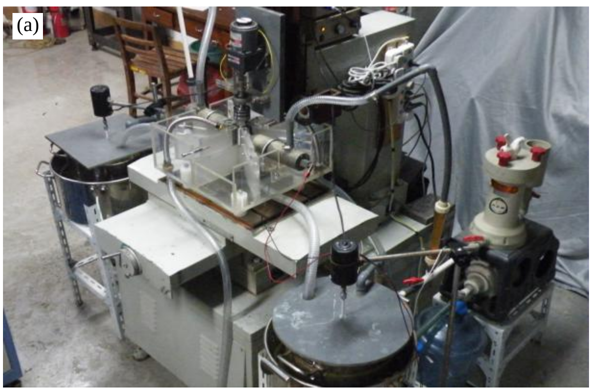
1. INTRODUCTION

Multilayers (compositionally modulated alloys) have received increasing attention in recent years because of their unique properties [1]. These materials comprised of alternating layers of different metals or alloys have been most frequently prepared by physical vapor deposition, but electrodeposition has also possibility to produce multilayers [2-3]. There are mainly two techniques used for electrodeposition of multilayers involving single bath or the dual bath [4-5]. In the former technique, the electrolyte composition, reduction potentials of components and electrodepositing power have very strict requirements, and in the dual bath technique, interruptions during the transfer between baths make the technology difficult to automation and susceptible to the formation of an oxide layer on the substrate. Comparing with the conventional electrodeposition, jet electrodeposition (JED) provides the advantages of selective and high-speed plating, and the grain refining effect is more efficient by a much higher cathode overpotential [6]. Thus, improved multilayers can be expected by this technique with a special JED system.

In this paper, a novel multiple jet electrodeposition (MJED) technology is developed to overcome the above-mentioned drawbacks in production of multilayers by introducing multiple and simultaneous jetting for electrodeposition of various components with a self-made experimental system. Moreover the real-time polishing of dynamical free particles for deposit surface is also introduced to eliminate the irregularity during MJED. This technique can widen the applicability of jet electrodeposition as a production method for multilayers. Structure and properties of the deposits were then investigated. No papers directly addressing this subject have been published so far.

2. EXPERIMENTAL

Experimental system. Fig. 1 shows the photo and the schematic diagram of the self-made MJED system. Electrodeposition room was fragmented into multiple separate chambers. A revolving cathode surrounded by a array of jetting units which were placed in separate chambers, was in the middle of the tank, and rotated under the control of CNC unit. Each jetting chamber was followed by a rinsing chamber in which deposit surface was sprayed with deionized water, and a grinding chamber in which deposit surface was continuously polished with dynamical free particles. The electrolyte was jetted locally onto the cathode surface from the jetting units, and was continuously recirculated to electrolyte tank. The powers of these jetting units can be supplied simultaneously or alternatively in accordance with the CNC commands to control the electrodeposition time of each sublayer. Current density, nozzle size, jetting speed and so on also can be changed variously. Thus multilayers with a variety of compositionally modulated structure can be produced. Further details similar to the geometry of traditional JED system can be found elsewhere [7-9]. Deposition experiments. The electrodepositing bath of Ni sublayers was composed of $Ni_2SO_4{\bullet}6H_2O$ 280 g/L, $NiCl_2$ 40 g/L, H_3BO_3 38 g/L, and the bath of Cu sublayers was composed of $CuSO_4.5H_2O$ 250g/L, H_2SO_4 70 g without any additives.



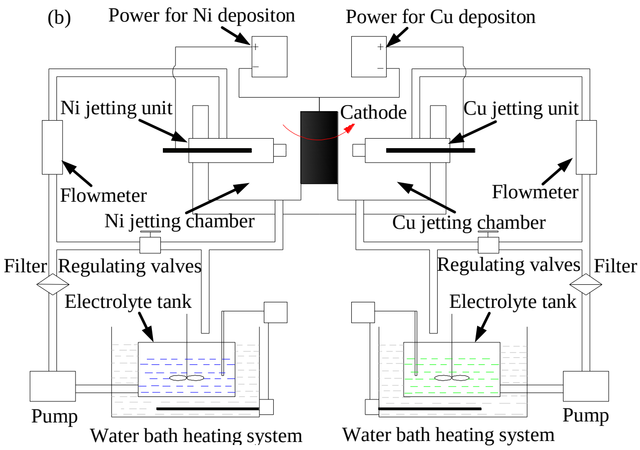


Figure 1. MJED system depicted by (a) physical photo and (b) schematic diagram.

Stainless steel sticks were used as cathodes. Spherical ceramic particles with diameter of Ø 1–2 mm were employed as the free particles. Deposit samples were prepared at 10 r/min rotational speed of the cathode. The current density for Ni electrodeposition ranges 60–140 A/dm^2, and the current density for Cu electrodeposition ranges 80–400 A/dm^2. Deposition process of PJED to produce multilayers is shown in fig. 2.

Deposit analysis. The cross-sectional morphology of deposits was characterized by JSM-7100F scanning electron microscope, and the surface roughness was measured by Mahr Perthometer M1 roughness tester. The microhardness of samples was measured with a HXS-1000A Vickers microhardness measuring device.

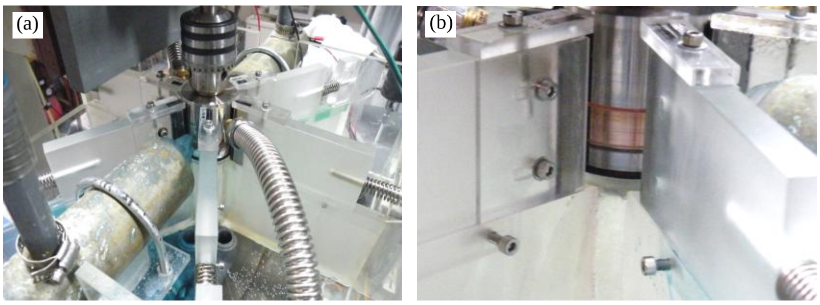


Figure. 2 Photos of (a) electrodeposition room and (b) multilayer during MJED.

3. RESULTS AND DISCUSSION

Fig. 3 illustrates some typical cross-sectional micrographs of Ni-Cu multilayers without and with real-time polishing of dynamical free particles during JED. All the multilayers with alternating white and black sublayers can be clearly observed, and each sublayer plays its own distinctive role in achieving preferred performances [10-12]. Relative dark bands represent etched Cu sublayers while bright ones represent the Ni sublayers [13]. Moreover, sublayers of Ni-Cu multilayers with real-time

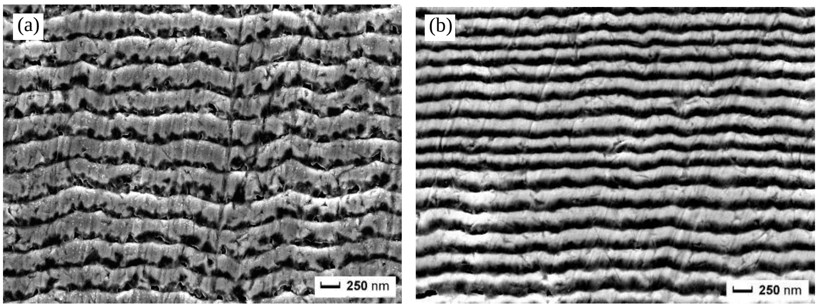


Figure 3. Cross-sectional micrographs of Ni-Cu multilayers by MJED (a) without and (b) with real-time polishing.

polishing were found to be thinner, regular and parallel to the substrate surface, which is different from those prepared without polishing. This can be attributed to the continuously movements and slightly polishing of dynamical free particles for deposit surface, which cleaned the surface and weakened the growth of surface protrusions [14-15].

Multilayers with a variety of compositionally modulated structure can be produced with MPJED by varying energized time, current density, nozzle size and so on of these jetting units. Fig. 4 shows the cross-sections of multilayers produced by MJED at different energized time of jetting units. For instance, the value t_{Ni}/t_{Cu}=5/10 for a energized time parameter of jetting units means that in the time of five cathode revolutions Ni jetting unit is energized, then in the time of next ten cathode revolution Ni jetting unit is energized. A multilayer structure with the thickness of Cu sublayers gradually increased can be clearly observed.

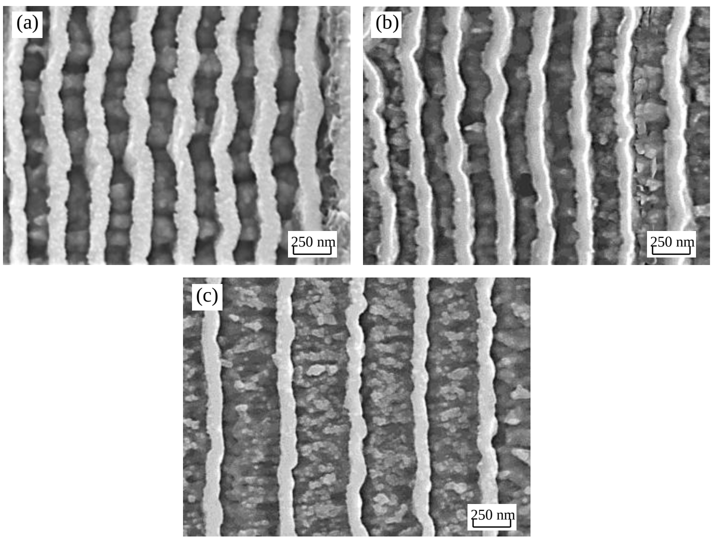


Figure 4. Cross-sectional micrographs of Ni-Cu multilayers by MJED with polishing at different t_{Ni}/t_{Cu} of (a) 8/8, (b) 8/14, (c) 8/20.

The cross-sectional micrographs of Ni-Cu multilayers produced at Ni sublayer deposition current density of 80 A/dm^2, and Cu sublayer deposition current densities of 160 A/dm^2, 240 A/dm^2

and 320 A/dm^2 respectively, are represented at the same magnification in Fig. 5. In this manner, multilayers with thickness of Cu sublayers gradually increased can also be produced.

The modulation wavelength of multilayers has received most attention mainly because this parameter is easy to vary and is known to influence the properties in a major way. The test results of microhardness are shown in Fig. 6. With a constant current density of 80 A/dm^2 for Ni sublayer deposition, Cu sublayer thickness increases with the increase of Cu deposition current density (see Fig. 6a), and Ni sublayer thickness increases similarly with a constant current density of 160 A/dm^2 for Cu sublayer deposition (see Fig. 6a), both of which lead to the change of the modulation wavelength of multilayers, and the sublayer thickness could be evaluated by deposition rates pre-measured in JED. Compared with the hardness of jet electrodeposited Ni (528 HV) and Cu (220 HV) produced under the same experimental conditions, Ni-Cu multilayers present an obvious strengthened hardness with the maximum value of 600 HV.

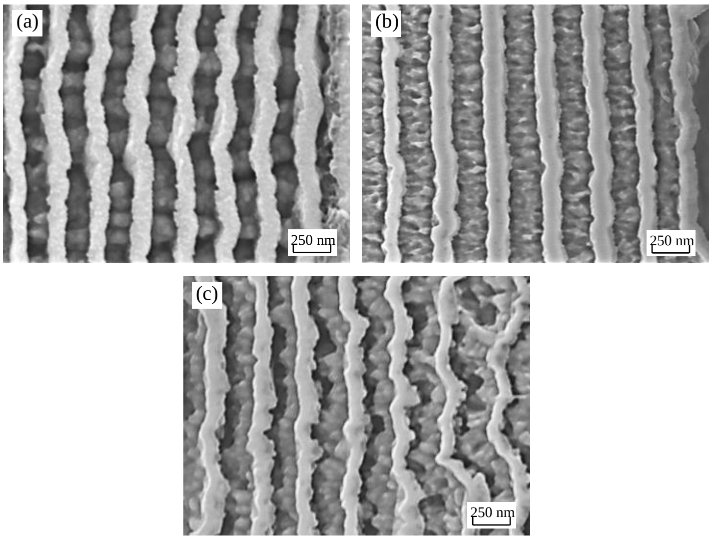


Figure 5. Cross-sectional micrographs of Ni-Cu multilayers by MJED with polishing at different current density of (a) 160 A/dm^2, (b) 240 A/dm^2, (c) 320 A/dm^2 when t_{Ni}/t_{Cu}=8/8.

Both in fig. 6a and 6b, the hardness increases gradually with the decreasing sublayer thickness, and further decreases when the modulation wavelength exceeds a critical value. Other studies have shown much the same pattern [16-17]. As it is expected, the polishing of free particles can significantly improve the hardness of deposits, and the highest value is about 650 HV, which may be obtained in a competitive balance between the polishing effect of particles and the growth of surface protrusions[18]. Fig. 7 shows the photo of a typical thicker multilayered deposit with smooth and bright appearance produced by MJED with polishing at current densities of 80 A/dm^2 for Ni deposition and 160 A/dm^2 for Cu deposition, and the thickness of the deposit obtained was about 1.2 mm. The multilayer is capable of folding into a variety of shapes with good flexibility compared with the pure Ni deposit.

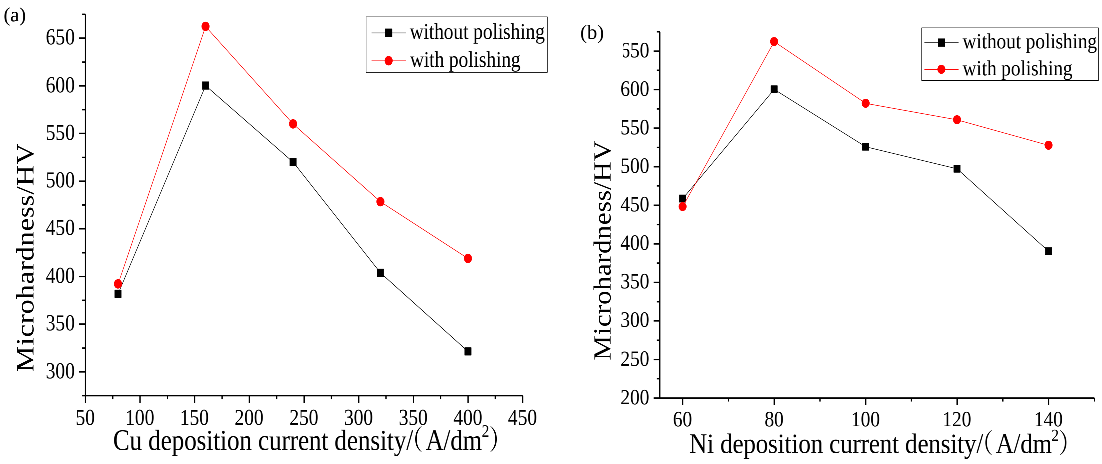


Figure. 6 Variation of microhardness of multilayers at different (a) Cu and (b) Ni deposition current density.

Thus, a new method for preparation of high-quality and large bulk of multilayers was developed. The deposit surface remained smooth and bright during MJED with polishing. Fig. 8 shows the test results of hardness and surface roughness measured along the multilayered deposit, both of which show small variations indicating a uniform structure.

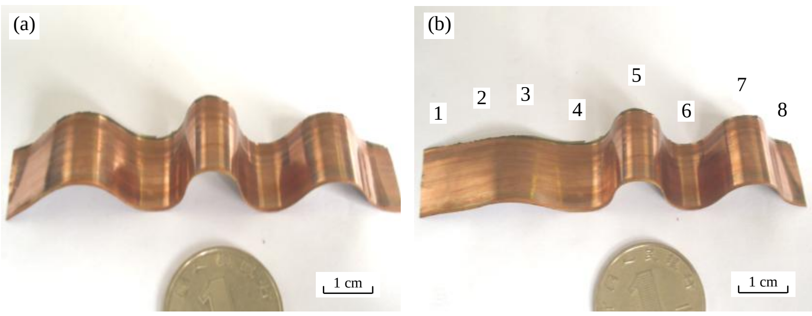


Figure 7. Photos of (a) and (b) folded thicker multilayered deposit prepared by MJED with polishing.

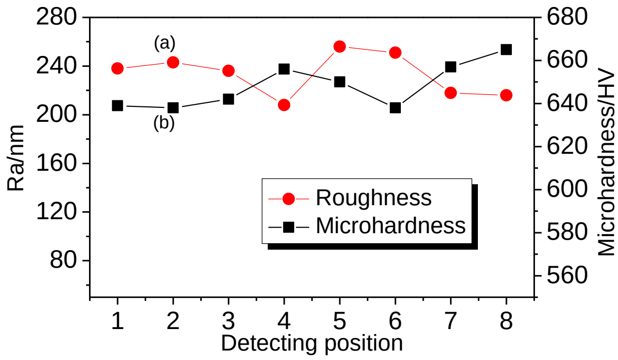


Figure 8. Distributing graph of (a) surface roughness and (b) microhardness of the thicker rmultilayered deposit.

4. CONCLUSION

Multilayers can be produced by MJED, and the technique offer excellent control of the structure, composition and sublayer thickness of the multilayers. It is evident that the polishing of the particles can significantly smoothen the deposit surface during MJED in real time. The regularity and microhardness of multilayers improved significantly compared with that without polishing. And a thicker multilayer deposit up to 1.2 mm was experimentally produced with mirror-like surface and excellent hardness uniformity.

ACKNOWLEDGEMENTS
Authors acknowledge financial support from the Academic Program Development of Jiangsu Higher Education Institutions of China (Grant No. SZBF2011-6-B35), the Specialized Research Fund for the Doctoral Program of Higher Education of China (Grant No. 20120095120019), the National Natural Science Foundation of China (Grant No. 51105204), and the State Key Laboratory of Coal Resources and Safe Mining, CUMT(SKLCRSM12X08).

References

1. I. Bakonyi, L. Péter, *Prog. Mater Sci*. 55 (2010) 107–245.
2. I. Kazeminezhad, W. Schwarzacher, *J. Magn. Magn. Mater*. 240 (2002) 467–468.
3. S. K. Ghosh, S. Singh, S. Basu, *Mater. Chem. Phys*.120 (2010) 199–205.
4. A. S. M. Haseeb，J. P. Celis, J. R. Roos. *J. Electrochem. Soc*. 141(1994) 230-237.
5. N. Rajasekaran, S. Mohan, *Corros. Sci*. 51 (2009) 2139-2143.
6. C. Richard, *J. Electrochem. Soc*. 192 (1982) 2424-2432.
7. G. F. Wang，L. D. Shen, Y. H. Huang, *Int. J. Electrochem. Sci*. 7 (2012) 10818-10824.
8. C. Bocking, Trans. *Inst. Met. Finish*. 69 (1991) 119-127.
9. D. Thiemig, J. B. Talbot, A. Bund, *J. Electrochem. Soc*. 154 (2007) 510-515.
10. H. C. Barshilia, K. S. Rajam. *Surf. Coat. Technol*, 155 (2002) 195-202.
11. B. P. Shu, L. Liu, Y. D. Deng, C. Zhong, Y. T. Wu, B. Shen, W. B. Hu, *Mater. Lett*. 89 (2012) 223–225.
12. D. Rafaja, C. Schimpf, V. Klemm, G. Schreiber, I. Bakonyi, L. Péter. *Acta Mater*. 57 (2009) 3211–3222.
13. A Tokarz, P. Wieczorek, T. Fraczek, Z. Nitkiewicz, *Phys. Status Solidi C*. 5 (2008) 3526-3529.
14. Z. W. Zhu, D. Zhu, N. S. Qu, *Mater. Sci. Eng. A*. 528 (2011) 7461–7464.
15. S. Shivareddy, S. E. Bae, S. R. Brankovic, *Electrochem. Solid-State Lett*. 11 (2008) 13-17.
16. H. E. Fanity, M. Bouanani ,H. Lassri, F. Cherkaoui, H. Ouhamane, A. Dinia, A. Berrada, *Ann. Chim. - Sci. Mat*. 24 (1999) 505-508.
17. N. Sato, Y. Kaneko, S. Hashimoto, *J. Japan Inst. Metals*. 73 (2009) 234-237.
18. Z. W. Zhu, D. Zhu, N. S. Qu, K. Wang, J. M. Yang, *Int. J. Adv. Manuf. Technol*. 39 (2008) 1164–1170.