Electrodeposition and Induced Codeposition Behavior of NiMoW Alloys

Shaopeng Sun
Department of Chemical Engineering
Northeastern University
Boston, MA, 02115

Introduction

NiMo and NiW alloys are of interest for their ability to catalyze hydrogen[1, 2], corrosion resistance [3, 4] and in the case of NiW for improved hardness [5]. The reduction of Mo and W is unique; they cannot be reduced alone by electrodeposition, but can be reduced when codeposited with iron elements, *e.g.*, Ni, defined as induced codeposition. Mechanisms of induced codeposition of W and Mo are still not well understood. Fukushima *et al.*[6] introduced a mechanism for molybdenum induced codeposition in 1979, which established an up limit of molybdenum content in the deposit, which has since been surpassed. A similar model was proposed by Chassaing *et al.* [7] drawing attention to a mixed oxide intermediate. Podlaha and Landolt [8] developed the model further to predict the coupled transport-kinetic interaction of Ni on Mo codeposition taking place from a mixed-metal intermediate. Eliaz and Gileadi [9] presented a mechanism to describe W codeposition with Ni, where tungsten was reduced from complexed species formed by tungstate, and the induced elements, such as Ni, with a complexing agent (*e.g.*, citrate).

In this work, the induced codeposition of Mo and W by Ni was examined from a citrate-boric acid electrolyte, without the typical ammonia addition, to fabricate ternary NiMoW alloy thin films. The alloys were galvanostatically electrodeposited onto rotating cylinder electrodes. The results are a first step towards understanding the coupled nature of Mo and W when codeposited with Ni.

Experimental

Electrodeposition was performed galvanostatically onto rotating cylinder electrodes (RCE). Electrolytes contained sodium tungstate, 0.075 M; sodium molybdate, 0 to 0.075 M; nickel sulfate, 0.1 M; sodium citrate, 0.375 M; boric acid, 1 M; and pH was adjusted by sodium hydroxide or sulfuric acid to 7. The working electrode was made of copper with a diameter of 1 cm and length of 1.2 cm. The reference electrode was a Ag/AgCl reference electrode. A dimensionally stable anode was used as the counter electrode. The applied current density was varied from 50 to 450 mA/cm^2. To explore the effect of mass transfer on the deposit composition and deposition rate, different rotation rates were applied, from 517 to 3748 rpm. All the deposits were analyzed by X-ray flourorescence (XRF) for the compositoin and thickness. According to Faraday's law, the partial current densities were calculated and the current efficiency was obtained.

Results and Discussion

The composition of the resulting deposits fabricated from electrolytes containing tungstate and molybdate of the same electrolyte concentration, 0.075 M, does not reflect the concentration ratio in the electrolyte. The molybdenum content in the deposit was, 63 wt%, far more than the tungsten deposit concentration, which was less than 5 wt%. It was also observed that the composition of deposits was relatively insensititive to changes in the applied current density from 50 to 450 mA/cm^2. When the molybdate concentration was reduced to 0.005 M, the ratio of concentration of tungstate to molybdate in the electrolyte reached as high as 25. Comparing to the previous electrolyte, this ratio is only 1. The content of molybdenum was only close to tungsten at low applied current densities and even much higher at high applied densities. When molybdate was completely taken out, it was observed that the tungsten content hit a maxinum at 50 mA/cm^2, then kept decreasing with an increase in the applied current density.

The changes in the deposit composition are reflecting the changes in the partial current densities. The molybdenum partial current densities show that adding more molybdate into the electrolyte didn't lead to an increase of molybdenum partial current density, but a decrease. It is also observed that more molybdate inhibited the reduction of tungsten and nickel. These changes may be attributed to the side reaction. Its adsorbed intermediate decreased the available area for the reduction of molybdenum, tungsten and nickel.

Conclusions

Electrodeposited alloys of NiMoW were for the first time deposited from an ammonia-free electrolyte. There is a preferential deposition of Mo over W. The partial current densities of the metal reduction reactions are decreased with added molybdate and this inhibition may be due to adsorbed hydrogen blocking the electrode.

Acknowledgement

The author acknowledges financial support from the National Science Foundation and for help by Mr. Robert Eagan in making rotating cylinder electrodes.

Reference:

[1] R. Schulz, J.Y. Huot, M.L. Trudeau, L. Dignard-Bailey, Z.H. Yan, S. Jin, A. Lamarre, E. Ghali, N.A. Van, J. Mater. Res. 9 (1994) 2998-3008.
[2] E. Navarro-Flores, Z. Chong, S. Omanovic, J. Mol. Catal. A: Chem. 226 (2005).
[3] P. Prioteasa, F. Golgovici, G. Sbircea, L. Anicai, T. Visan, Rev. Chim. (Bucharest, Rom.) 61 (2010) 1046-1053.
[4] M. Zemanova, R. Kurinec, V. Jorik, M. Kadleciova, Chem. Pap. 66 (2012) 492-501.
[5] Z. Ghaferi, K. Raeissi, M.A. Golozar, A. Saatchi, S. Kabi, Iran. J. Mater. Sci. Eng. 7 (2010) 16-24.
[6] H. Fukushima, T. Akiyama, S. Akagi, K. Higashi, Trans. Jpn. Inst. Met. 20 (1979) 358-364.
[7] E. Chassaing, K. Vu Quang, R. Wiart, Journal of Applied Electrochemistry 19 (1989) 839-844.
[8] E.J. Podlaha, D. Landolt, journal of electrochemistry society 143 (1996) 893.
[9] N. Eliaz, E. Gileadi, ECS Trans. 2 (2007) 337-349.