Surface Technology White Papers
101 (1), 10-15 (January 2014)

3rd Quarterly Report
July-September, 2013
AESF Research Project #R-117

Electrodeposition of Ni-Fe-Mo-W Alloys

by
Prof. E.J. Podlaha-Murphy, Project Director,*
Professor of Chemical Engineering
Northeastern University
Boston, Massachusetts 02115

Editor's Note: This paper was submitted to NASF and AESF Foundation Research Board for the third project quarterly report for AESF Foundation Research Project R-117, July-September, 2013.

Introduction

This NASF-AESF Foundation research project addresses the induced codeposition of molybdenum and tungsten alloys with nickel and iron with a focus on developing a toolbox of plating conditions to deposit different combinations of Ni, Fe, Mo and W. The experimental approach utilizes electrodes with a controlled hydrodynamic environment, since it has been noted by the Project Director that the reduction mechanism can involve a coupled kinetic-mass transport behavior. The project was initiated in January 2013. A part of this work was also supported by the National Science Foundation, CHE-#0957448.

This third quarterly report follows the work of two of the three students in the lab that have participated in this project: undergraduate senior Matthew Silva, and graduate student Avinash Kola. They have been working on different aspects of the project to address the induced codeposition of molybdenum and tungsten alloys with nickel and iron with a focus on developing a toolbox of plating conditions to deposit different combinations of Ni, Fe, Mo and W. During the third quarter of the project, we have continued work focused on the effect of electrolyte temperature of NiFeMoW alloys, and the influence of adding thiourea to NiW alloys.

Sub-project #1
NiFeMoW and NiMoW deposition
Matthew Silva, Undergraduate student

In the previous quarter, the addition of iron to the Mo, W and Ni electrolyte resulted in a decrease of nickel and molybdate content, but more significantly it induced the codeposition of tungsten in a region where it was not codeposited when the iron ions were not present in the electrolyte. In an electrolyte containing 0.15M nickel sulfate, 0.1M sodium molybdate, 0.1M sodium tungstate, 0.375M sodium citrate, 1.0M boric acid and a pH of 7, and variable amounts of Fe ions, the surface structure changed considerably as depicted in Fig. 1 for deposits at 49.5 mA/cm^2. The electrode was a rotating cylinder electrode having a diameter of 0.6 cm and a rotation rate of 500 rpm. At iron sulfate concentrations greater than 0.1M, nodules formed on the deposits. Some of these nodules even had holes within them, indicating regions where gas bubbles adhered.

The current efficiency of this electrolyte has been found to be very low, on the order of 10%. The low current efficiency is attributed, in part to of the lack of ammonium species, such as ammonium hydroxide, that was not added in order to develop a more environmentally-friendly electrolyte.

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*Corresponding author:
Prof. E.J. Podlaha-Murphy
Professor of Chemical Engineering
Northeastern University
Boston, Massachusetts 02115
Phone: (617) 373-3796
E-mail: e.podlaha-murphy@neu.edu

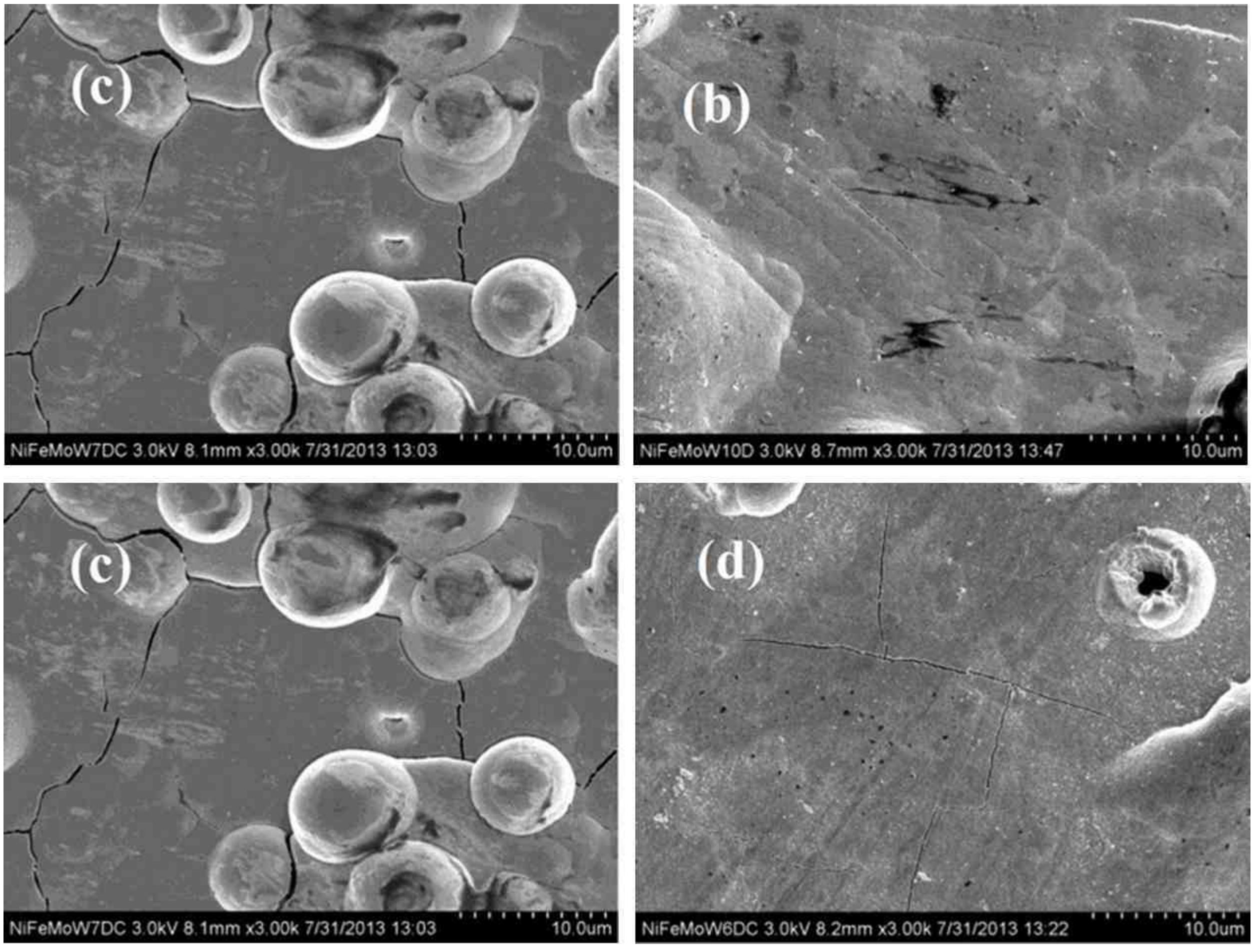

Figure 1 - SEM micrographs of the surface of deposits from an electrolyte containing Ni, Mo and W and variable amounts of Fe ions: (a) 0, (b) 0.05M, (c) 0.1M and (d) 0.15M, at 49.5 mA/cm^2.

The literature shows that ammonium species in general, significantly improve the current efficiency, although with an accompanying decrease in molybdenum and tungsten content in the deposit.[1] It was observed in our studies that when the amount of sodium molybdate was decreased, the current efficiency improved. To access the range where the current efficiency was improved, a rotating Hull cell was employed. The composition was measured using x-ray fluorescence, scanned along the electrode surface. Figure 2 shows the composition results using a different electrolyte without the iron present and with a lower amount of sodium molybdate in the electrolyte: 0.15M nickel sulfate, 0.005M sodium molybdate, 0.075M sodium tungstate, pH 7.0, with an applied average current density of 16.5 mA/cm^2.

An interesting result is found at the low current density end of the Hull cell (Fig. 2(a)). Even with sodium tungstate in the electrolyte, the deposit contains only NiMo, (Fig. 2(b)), and while the ratio of molybdate to nickel ions is 0.005:0.15, there is a much larger amount of molybdenum in the deposit. In Fig. 2(a), an estimate of the dimensionless local current density is provided along the electrode length (i/i_{avg}). With a measure of local thickness and knowing the local current density, the current efficiency can be estimated locally as shown in Fig. 2(c). Interestingly, the current efficiency (Fig. 2(c)) is significantly improved at the low current density region where tungstate does not codeposit into the alloy. As the tungstate is reduced and found in the deposit at higher current densities, the current efficiency falls. However, the deposit composition has a relatively constant value over a wide range of current densities (40-80 mA/cm^2) suggesting parallel partial current densities and hence good throwing power.

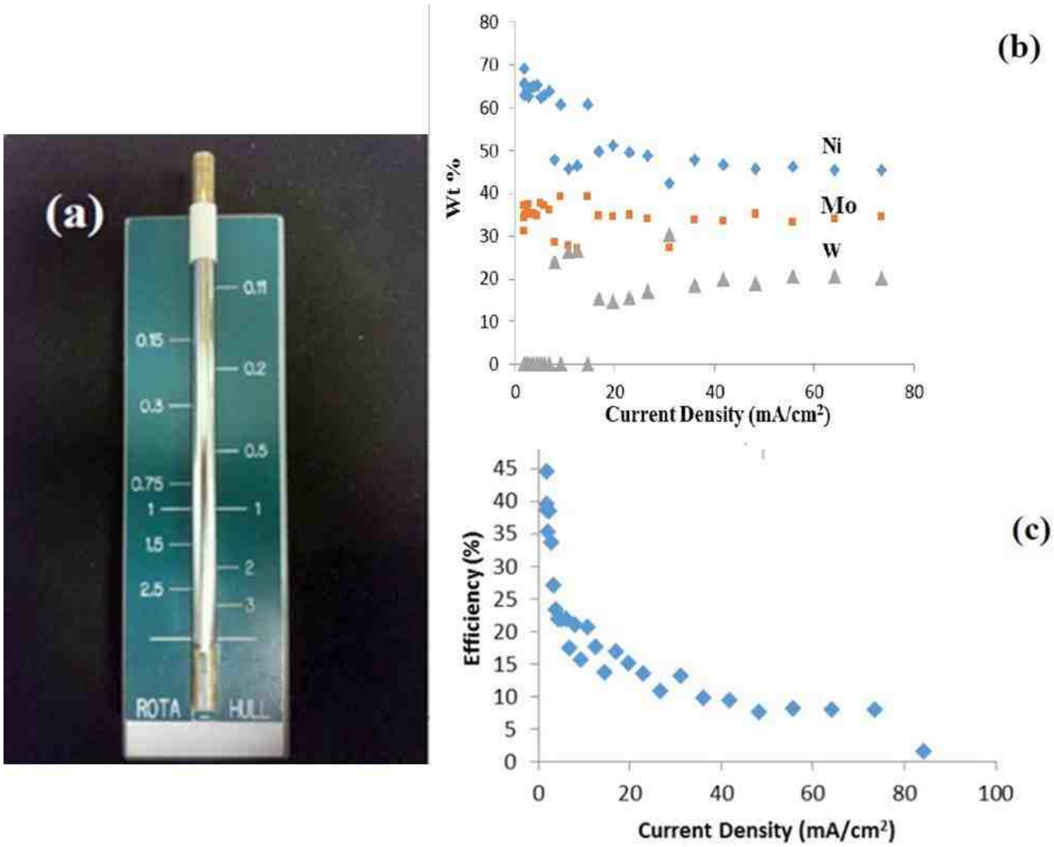

Figure 2 - Rotating Hull cell study of an electrolyte containing Ni, Mo and W at 500 rpm, at an average current density of 16.5 mA/cm^2: (a) electrode and a scale representing a primary current distribution local current density estimate, (b) composition and (c) efficiency.

Sub-project #2

Effect of thiourea concentration on NiW deposition

Avinash Kola, Graduate student

We examined the effect of thiourea concentration on NiW deposition from a citrate electrolyte without ammonium ions. The NiW citrate electrolyte contained 0.5M nickel sulfate, 0.15M sodium tungstate, 0.5M trisodium citrate and varying concentrations of thiourea (0.065M, 0.325M and 0.650M) at pH 2.0. A conventional Hull cell was employed with air agitation (3 L/min). The average applied current density was 10 mA/cm^2, with copper as the substrate. The composition was measured using x-ray fluorescence. Figure 3 shows images of the NiW deposits obtained from the Hull cell. When thiourea was not present the deposit appeared light-gray in color with a reflective surface. The deposit appearance tended to get darker and rougher with increasing thiourea concentrations. In Fig. 3(a) without thiourea, no deposit was obtained for the lower current densities, but with the addition of small amounts of thiourea a deposit was obtained at the lower current densities (Figs. 3(b-d)), indicating a change in the current-potential behavior that may be due to a change in reacting species, such as a Ni-thiourea complex.

The composition analysis of the deposits with varying amounts of thiourea is shown in Fig. 4. The curves for nickel (Fig. 4(a)) and tungsten (Fig. 4(b)) show little effect of current density on the composition. However, with increasing concentration of thiourea, a higher amount of nickel is obtained. This trend is more noticeable at higher current densities. Nickel forms stable complexes with citrate and thiourea, and using the stability constants of various Ni, W citrate complexes,[1,2] the dominant complex species present in the electrolyte was determined. A summary of chemical equilibria reactions is shown in Table 1. Figure 5 shows the amounts of three dominant species of nickel ions in the electrolyte: an uncomplexed Ni^{+2}, a nickel-citrate complex $NiHCit_2$, and a nickel thiourea complex in the electrolyte. The largest nickel species is the one complexed with citrate, and the addition of thiourea does not significantly change that dominance. However, the role of the thiourea helps to complex the free, Ni^{+2} ions to form the Ni-Tu complex. Another interesting observation is the reduction in the tungsten content in the deposit. This may be attributed to the loss of the free Ni^{+2} species that helps to induced tungsten codeposition and/or the adsorption of thiourea. We are currently examining this effect.

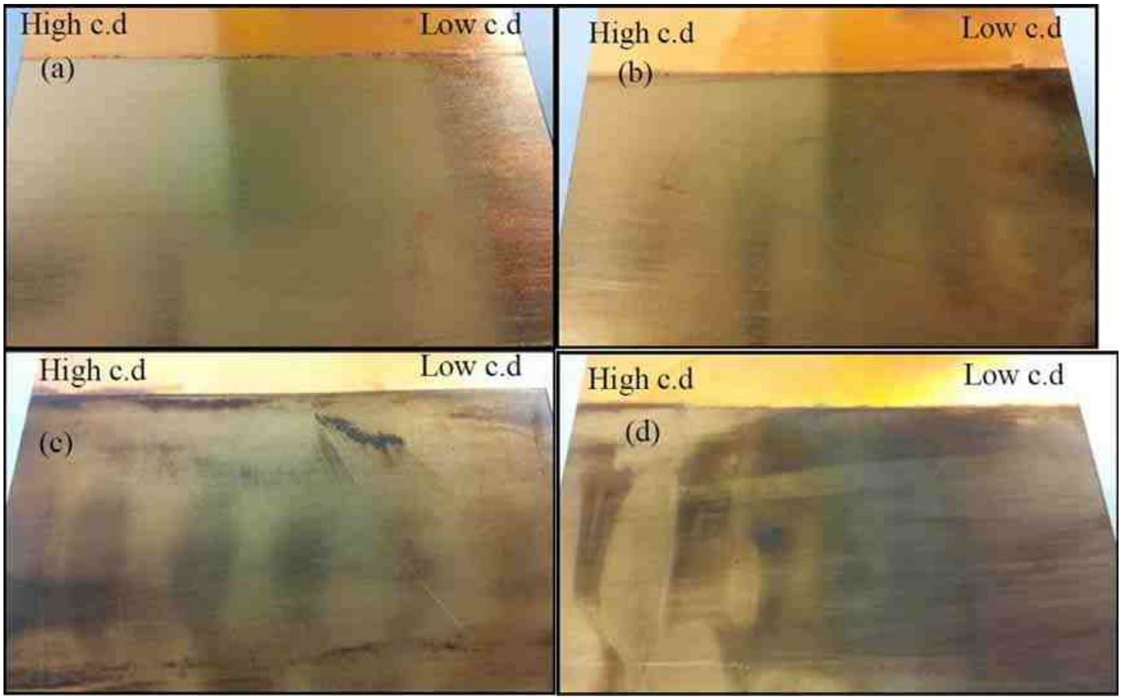

Figure 3 - NiW deposition on a Hull cell, low CD to high CD (L-R) with: (a) no thiourea, (b) 0.065M thiourea (c) 0.325M thiourea and (d) 0.625M thiourea.

Table 1 - Equilibrium data used to calculate species in the electrolyte.

$Ni^{+2} + Cit^{-3} \rightarrow [NiCit]^{-}$	Log K = 5.35
$Ni^{+2} + H^{+} + Cit^{-3} \rightarrow [NiHCit]$	Log K =9.13
$Ni^{+2} + H^{+} + Cit^{-3} \rightarrow [NiHCit_2]^{-3}$	Log K = 13.5
$Ni^{+2} + 2Cit^{-3} \rightarrow [NiCit_2]^{-4}$	Log K = 8.11
$Wo_4^{-2} + HCit^{-3} + H^{+} \rightarrow [Wo_4HCitH]^{-4}$	Log K = 10.2
$Wo_4^{-2} + HCit^{-3} + 2H^{+} \rightarrow [Wo_4HCitH]^{-3}$	Log K = 17.03
$Wo_4^{-2} + HCit^{-3} + 3H^{+} \rightarrow [Wo_4HCitH]^{-2}$	Log K =21.67

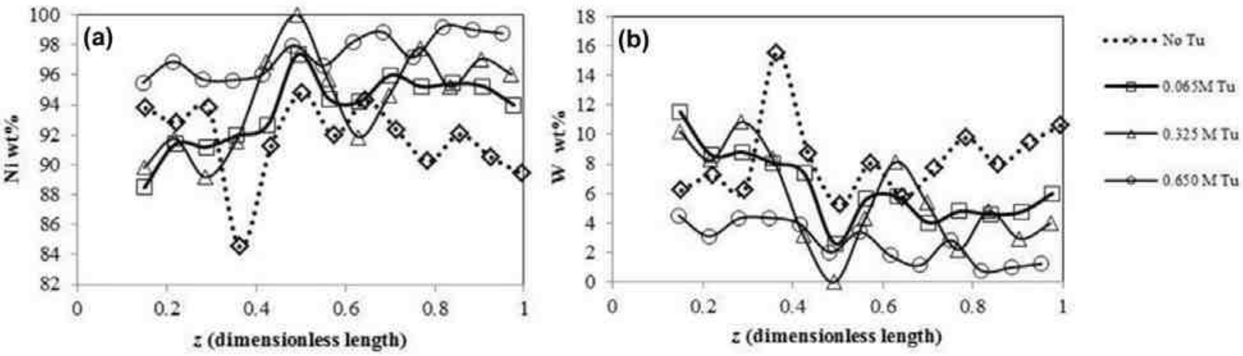

Figure 4 - Deposit composition along the Hull cell length (a) wt% Ni and (b) wt% W with variable amounts of thiourea in the electrolyte.

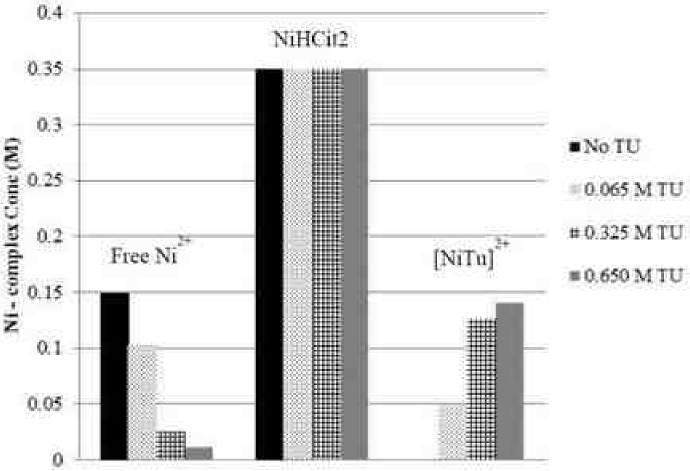

Figure 5 - Distribution of free Ni^{+2}, $NiHCit_2$ and Ni-thiourea (Ni-Tu) complex species for varying amounts of thiourea.

Overall summary

Two students participated in the NASF/AESF research this quarter, continuing deposition of NiFeMoW and NiMoW deposition with an aim to improve current efficiency, and the effect of thiourea on NiW electrodeposition. The contribution by Matthew Silva, a former undergraduate at Northeastern University continued with SEM and compositional analysis on rotating cylinder electrodes. Graduate student Avinash Kola continued work in NiW looking at different aspects of the project: the effect of additives, with thiourea.

Matthew Silva continued to build upon the large body of work on the effect of iron on NiMoW deposition, reported in the second quarter. New SEM analyses have shown that the iron addition has an effect on the deposit morphology, promoting a more nodular deposit with low current efficiency ~10%.

One aim of our work is to improve efficiency without the addition of ammonia, for a more environmentally sound electrolyte. A step toward that direction resulted in reducing the amount of molybdate in the electrolyte, maintaining a pH as high as possible without metal ion precipitation, while retaining the molybdate content in the deposit over 20 wt%. A NiMoW electrolyte with a current efficiency of over 40% was reported with high Mo deposit concentration, despite its lower quantity in the electrolyte (compared to nickel). At higher current densities, tungsten was more readily codeposited and was also coupled to a lower current efficiency.

Graduate student Avinash Kola targeted a study to investigate the NiW system with thiourea using a conventional Hull cell. Thiourea affected the deposit composition of NiW slightly but greatly affected the deposit morphology. The changes in composition were attributed to the different complexing species of nickel generated with the thiourea addition.

References

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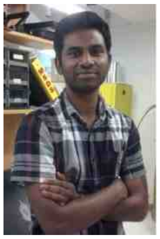
2. T.A. Green, A.E. Russell & S. Roy, *J. Electrochem. Soc*., 145 (3), 875 (1998).

About the authors

Dr. Elizabeth Podlaha-Murphy is a Professor of Chemical Engineering at Northeastern University, Boston, MA. She has been active in electrodeposition for more than 20 years and currently leads efforts in the understanding of reaction mechanisms and kinetic-transport behavior governing electrodeposition. She received her Ph.D. in 1992 from Columbia University, New York, NY and a B.S./M.S. from the University of Connecticut, Storrs, CT.

Matthew Silva is a recent B.S. graduate from the Department of Chemical Engineering, Northeastern University. He completed a co-op position at Xtalic Inc. working in the area of NiW plating. He plans to attend graduate school.



Avinash Kola is a current graduate student in the Department of Chemical Engineering at Northeastern University. He received his B.S. from Jawaharlal Nehru Technological University, India in 2006 and a M.S. from Louisiana Tech, Ruston, LA in 2010.