Electrodeposition of Mo-rich, MoNi Alloys from an Aqueous Electrolyte

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Abstract

Molybdenum alloys with nickel are well recognized for their superior corrosion resistance[1-3] and wear resistance[4-6] properties, and outstanding catalytic ability for the hydrogen evolution reaction.[7-12] The electrodeposition of these alloys is referred to as "induced codeposition";[13] molybdenum cannot be reduced alone from an aqueous solution, but can be fully reduced if codeposited with inducing elements, such as iron, nickel and cobalt, the iron-group metals. Similar behavior has also been observed with tungsten.[13-15] A consequence of this deposition behavior is that it is a challenge to achieve high Mo deposit concentration, due to the co-reduction of the iron-group ion, *e.g.*, Ni. Typically Mo content in alloys with nickel from aqueous electrolytes has been less than 50 wt %, with electrolytes containing ammonia.[16-24]

In this work, the molybdenum-nickel electrolyte, without ammonia, is re-examined as a path towards electrodepositing high Mo content alloys with nickel. Since molybdate reduction requires the co-deposition of an inducing element, such as nickel, in aqueous media, the ability to fabricate high molybdenum content alloys are a challenge.

Here, molybdenum-rich, MoNi alloys were successfully, deposited galvanostatically. Electrodeposition experiments were performed on vertically placed, stationary, working electrodes. The deposit composition was characterized by, X-ray fluorescence, XRF. Deposits having a composition ranging from 62-82 wt %, Figure 1, were realized, requiring high, cathodic, current densities greater than 200 mA/cm^2, although at extremely low current efficiency, less than 1 %. Increasing molybdate concentration in the electrolyte resulted in an increase Mo content in the alloys at a given current density. However increasing molybdate concentration in the electrolyte decreased deposits thickness, due to an enhancement of the side reaction. The partial current densities were also determined from the composition and thickness measurement according to Faraday's law. The partial current densities of Mo, Ni and side reactions are parallel, indicative of a coupled reaction mechanism. The deposit morphology was characterized by scanning electron microscope, SEM. Figure 2 shows that the MoNi alloys had a nodule morphology and contained micro-cracks. On the top of a nodule, nano structures were observed providing additional roughness. The catalytic property of the MoNi alloys were characterized in a sodium hydroxide electrolyte. Polarization was performed and exchange current density and Tafel slopes were quantified, Figure 3. The Tafel behavior is consistent with their hallmark feature as catalysts for electrolytic hydrogen evolution. The best catalysts were not those with the most Mo wt% but with a composition from 64 to 68 wt%.

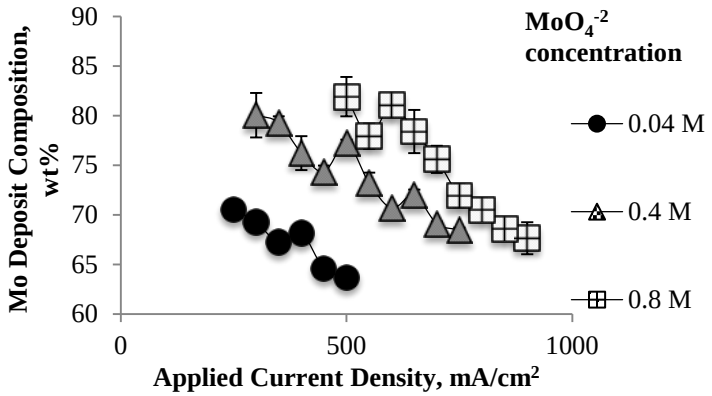

Figure 1. Galvanostatic MoNi electrodeposition on stationary Cu substrates deposit concentration.

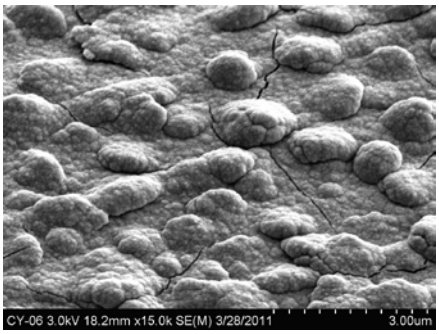

Figure 2. SEM of a sample with 76 wt% Mo content at15k X.

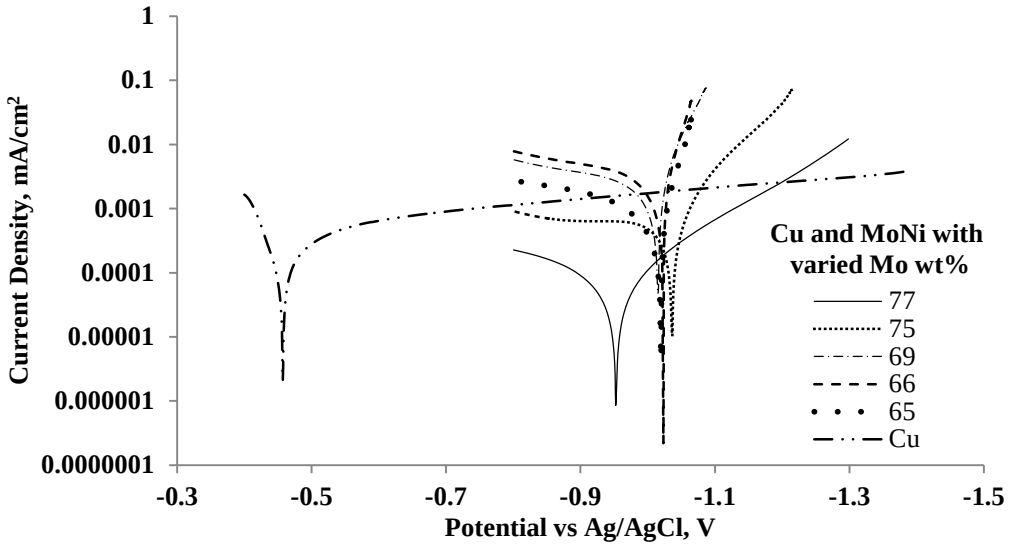

Figure 3. Catalytic behavior of MoNi electrodeposits (a) polarization curves.

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