



Microstructure and composition of pulse plated Re–Ni alloys on a rotating cylinder electrode



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ABSTRACT

The effect of pulse electrodeposition parameters on the composition and microstructure of Ni–Re alloys were studied on a rotating cylinder electrode. Ni–Re alloys were deposited from a citrate bath where the nickel-to-rhenium ratio was 45:1. The composition of the deposited alloy was monitored by energy dispersive spectroscopy (EDS) and compared to a single component transport-based model describing the pulse limiting current of perrhenate. At long pulse times and high duty cycles, the partial current density of rhenium is predicted by the model, and rhenium inclusion into the alloy can therefore be described as being completely transport controlled. At shorter pulse times and low duty cycles, rhenium deposits under mixed or activation control. The morphology of the surface and cross-section were studied by SEM. The oxidation states and phases were studied by XPS and XRD, respectively, and discussed in view of the pulse parameters. By examining the effect of pulse parameters on composition and microstructure, we can deduce the practical range of pulse parameters for use in Ni–Re alloy film synthesis from dilute perrhenate electrolytes.

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1. Introduction

Nickel–Rhenium alloys are unique materials due to their favorable mechanical and chemical properties [1]. They are exploited in various industries such as aerospace, aircraft, nuclear, electrical and catalysis. It was found that co-deposition of rhenium with iron-group metals (Fe, Ni, Co) can dramatically improve the efficiency and quality of the deposit compared to direct rhenium deposition from aqueous solutions [2–4]. Rhenium exhibits induced co-deposition with iron-group metals. The mechanism, composition, and microstructure of Ni–Re alloys have been studied by our group under a variety of d.c. conditions [5–7]. In brief, iron-group metals act as mediators in the reduction of the perrhenate ion. After the iron-group metal ion is electrochemically reduced on the surface, it can act as the reducing agent for the perrhenate ion to a lower valence oxide or to the metal atom.

Application of a pulsed current, however, can allow for current densities, Faradaic efficiencies, compositions, and microstructures that are unattainable with d.c. plating [8,9]. Pulse plating has widely been used to increase the uniformity, adhesion, and speed of electrodeposition as well as to generate unique morphologies.

There are only a few papers in the literature that discuss the pulse plating of rhenium [10]. We therefore wish to contribute to the fundamental knowledge of the formation of Ni–Re alloys in view of the unique transport parameters attainable under rotation, and the influence of a pulsing current.

Pulse plating plays a critical role in the mass transport of ions that exist in dilute concentrations. Application of a pulsed current modifies the transient concentration gradient profile of the diffusion layer by allowing for regeneration of depleted ions from the bulk during the relaxation time. This creates a steeper concentration gradient and allows for higher partial current densities within a certain range of pulse parameters. If, however, the concentration of the metal ion is large enough, its concentration profile will be insensitive to the pulse parameters and will always resemble the profile in the bulk.

Several groups have developed analytical models describing the effect of pulse plating variables on the electrodeposition of a single metal [11–13]. Most of these models assume diffusion control of metal ion and attempt to calculate the transient concentration profile as a function of pulse parameters. The influence of pulse parameters on alloy deposition is more complicated. To simplify the description of pulse parameters on the Ni–Re alloys, the metal concentrations in the electrolyte were selected such that only rhenium is mass-transport controlled and sensitive to the changing pulse parameters. The concentration of nickel in the diffusion layer

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is large enough that its deposition is activation controlled and insensitive to pulse parameters.

Such systems have been studied by several authors to describe Ni–Zn [14,15], Ni–Co [16,17] and Ni–Mo [18] alloys, to name a few, but a general knowledge of pulse plated Ni–Re alloys is lacking.

Landolt et al. have published extensively on the importance of understanding how mass transport contributes to pulse plated alloy deposits [9,19,20]. In particular, their work utilized a single component transient mass transport model by Viswanathan et al. [21] to describe the effect of pulse parameters on the pulsating diffusion layer of Mo adjacent to the electrode. They found good agreement between the model and experimental data over a large window (4 orders of magnitude) of pulse times at intermediate (0.4–0.6) duty cycles, implying that molybdenum is controlled entirely by mass transport over a majority of the range of pulse parameters studied. We took a similar approach in order to describe the role of mass transport in Ni–Re alloy formation in order to determine the practical range of pulse parameters in view of composition and microstructural changes.

2. Experimental

Ni–Re coatings were prepared using a rotating cylinder electrode (RCE). The turbulent conditions present at the surface were used to control the transport of material to and from the electrode. Accurate control of electrolyte convection assisted in isolating transport limitations from activation limitations at various pulsing conditions. Our substrates were bulk copper cylinders that were machined with an outer diameter of 1 cm and a surface area of 3.14 cm². Prior to each experiment, the copper cylinders were mechanically ground with P600, P800, and P1000 abrasives, then sonicated for 15 min in acetone, followed by an additional 15 min in DI water. It was later observed that the adhesion of the Ni–Re film was greatly improved by pretreating the substrate for 2 min in 1:2 HCl:H₂O; however, such pretreatment did not affect the composition or morphology of the coating. Pulse plating was conducted using a Bio-Logic VSP potentiostat/galvanostat controlled by EC-Lab software. The reference electrode was Ag/AgCl(Sat). The counter electrode was a concentric ring of platinum mesh (size 52) affixed 1 cm away from the working electrode cylinder to allow for a uniform primary current distribution. The height of the counter electrode was 0.2 cm larger than the copper cylinder in order to make alignment easier.

The electrode rotation speed was controlled by a Pine analytical rotator. All experiments were conducted at 400 rpm except for the determination of the apparent diffusion coefficient of the perrhenate species. The electrolyte for every experiment contained 450 mM nickel (II) sulfamate, and 10 mM ammonium perrhenate. The citric acid concentration was 225 mM, except in experiments conducted to determine the effect of the nickel-to-citrate ratio. Linear sweep voltammetry at various rotation speeds confirm that nickel deposition is activation controlled under all experimental conditions. Previous work by our group, albeit in more dilute nickel electrolytes, have shown that a nickel-to-citrate ratio of 2:1 yielded the highest Faradaic efficiency in d.c. plating. The initial pH of the electrolyte was adjusted to 5.0 ± 0.1 with sodium hydroxide. A charge of 10 C cm⁻² was passed for each experiment, leading to a coating thickness between 2.5 and 2.9 μm. The on-time current density (j_p) was -40 mA cm⁻². It has been reported that continuous current densities above -50 mA cm⁻² can lead to spongy deposits which can reduce the Re-content of the deposit in half [22]. The off-time (j'_p) current density was -0.05 mA cm⁻² in order to ensure that no oxidation current was passed during the off-time. The duty cycle ($\theta = t_{on}/(t_{on} + t_{off})$) was set to 0.4, 0.6, or 0.8. The pulse period ranged from 10 ms to 20 s. All experiments were

conducted in a 100 mL jacketed cell, filled to 62 mL and connected to a heated bath recirculator. The electrolyte was kept at (70 ± 1) °C for all experiments. Prior to each experiment, the electrolyte was purged for 30 min with nitrogen. Nitrogen was passed above the solution during the experiment to prevent the dissolution of oxygen during electrodeposition.

The Faradaic efficiency was calculated by comparing the charge passed during the experiment with the mass gained and the composition of the coating. The composition was determined by energy dispersive spectroscopy (EDS) using a liquid-nitrogen cooled Oxford Si detector attached to an environmental scanning electron microscope (ESEM) operated in high vacuum mode (Quanta 200 FEG from FEI). The ESEM was also used for morphological characterization of the deposits. Each sample was characterized in at least 7 locations to ensure uniformity in composition. The error bars compound the standard deviation of 3 samples with the instrumental error of EDS analysis (generally ±0.8 wt.%).

The composition, thickness, and morphology of the cross-section for several samples were analyzed by first cold-mounting the cylinder with a two-part epoxy from Struers and grinding the mount with P600 abrasive until the center of the sample was reached (to avoid edge effects). The sample was then polished down to ¼ μm using a polishing cloth and Buehler DIAPERM colloidal diamond suspensions.

X-ray diffraction (XRD) data were collected using Cu K α radiation. To accommodate the cylindrical shape of our electrode, XRD was done at a grazing incidence of 6° and was not moved during the experiment; only the position of the detector was changed. X-ray photoelectron spectroscopy (XPS) measurements were performed in UHV using a 5600 Multi-Techniques System (PHI, USA). The samples were irradiated with an Al K α monochromatic source at a takeoff angle of 60°, and the electrons were analyzed by a spherical capacitor analyzer with a slit aperture of 0.8 mm. The C1 peak at 285 eV was taken as the energy reference for all measured peaks and samples. A charge neutralizer was used for charge compensation due to carbon accumulation on the surface of some samples.

3. Results and discussion

3.1. Electrochemical analysis

By controlling the electrode rotation speed and electrolyte composition, we were able to determine the limiting control mechanism (mass transport, activation, or mixed) of rhenium deposition into Ni–Re alloys under pulsing conditions. We report the effect of the total pulse time ($\tau_{pp} = t_{on} + t_{off}$) and duty cycle ($\theta = t_{on}/(t_{on} + t_{off})$) on the composition, microstructure and morphology of Ni–Re deposits from an electrolyte where the d.c. deposition of rhenium and nickel are transport and activation controlled, respectively. Under such conditions, it is possible to model the effect of pulse parameters on the partial current density of rhenium, j_{Re} , using a single component transport model. The use of such a model first requires the diffusion coefficient of the relevant electroactive species. Since the exact nature of the electroactive rhenium species is not precisely known, we can only determine the “apparent” diffusion coefficient of perrhenate. In a recent paper [23], we used Raman spectroscopy to observe how the perrhenate exhibits weak ionic interactions with the [NiCit]⁻ complex during alloy deposition.

Ni–Re alloys were plated at a constant (d.c.) current density (-40 mA cm⁻²) at various rotation speeds. Fig. 1 shows a Levich plot for the partial current density of rhenium from the nickel-rich citrate electrolyte described above. It is clear that there are two regions of rhenium control. In the transport controlled region, j_{Re}

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