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Electrodeposition of nano-structured nickel–21% tungsten alloy and evaluation of oxygen reduction reaction in a 1% sodium hydroxide solution

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Abstract

The nano-structured nickel–21 at.% tungsten alloys were electrodeposited onto the copper substrates from unstirred sulfate–citrate–chloride–bromide–sodium tungstate electrolyte at $60 \,^{\circ}$ C. The maximum particle sizes of the deposits, as estimated from the atomic force microscopy (AFM), and scanning electron microscopy (SEM), respectively were 125, 75, and 100 nm. The Tafel plot for oxygen reduction reaction in oxygenated unstirred 1% sodium hydroxide solution showed a Tafel slope of 130 mV/decade. There were minor variations in the limiting current density with a change in the particle size.

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1. Introduction

The applications of the electrodeposited metals and alloys are very well known and some of their applications can be found in corrosion protection, electronics, and catalysis. Hard microstructures are needed in the molding process for LIGA applications and this is where electrodeposited ductile and amorphous nickel-tungsten alloys are becoming important. Similarly, low-cost and efficient electrocatalysts are becoming important for the fuel cell electrodes. One of the major challenges in fuel cell electrocatalysis is to replace platinum by inexpensive non-noble metals. The nickel-tungsten alloy can be particularly attractive because of its low-cost and ease of synthesis. However, the studies on the electrocatalytic properties of the nickel-tungsten alloys are missing and such studies are important in probing new applications of electrodeposited nano-structured al-

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loys such as nickel-tungsten. Numerous attempts have been made to electrodeposit tungsten from various types of baths [1]. Much of the early literature has been reviewed by Holt and Kahlenberg [2]. It appeared that thin films of pure tungsten could be electrodeposited by electrolyzing different alkaline baths. However, this was proved incorrect because the deposits contained metallic iron as impurity [3]. A claim that pure tungsten can be electrodeposited from organic alkyl hydrocarbon polyamine [4] could not be confirmed. The electrodeposition of pure nickel from aqueous electrolytes has been known for sometime and nickel plating from sulfate-chlorideWatts type bath has been commercialized for long time [1]. The anomalous nature of electrodeposition of tungsten alloys with transition metals such as iron, nickel and cobalt is well known and the key features of anomalous codeposition are: high overpolarization, poor efficiencies, and low tungsten content in the alloy deposit even at high sodium tungstate concentrations in the electrolyte. Some significant electrolyte systems used in electrodeposition of nickel-tungsten alloys include the citrate baths [1,5,6], complex pyrophosphate baths [7], sulfamate baths

[8], and sulfate–citrate–chloride–bromide [9]. A recent study reports the pulse plating effects during the nickel–tungsten alloy electrodeposition [10,11] and suggest that pulse plating can improve surface roughness. The objective of the present study is to electrodeposit nano-structured nickel–tungsten alloy using direct current and pulse plating procedures and to investigate their electrocatalytic activity towards oxygen reduction reaction as a function of particle size as controlled by the plating current profile.

2. Experimental

2.1. Electrodeposition

The single metal and alloy deposition potentials for the electrodeposition of tungsten, nickel and nickel–tungsten alloy were determined from the current–potential curves in the citrate–chloride–bromide based solutions (Aldrich Chemical Company) containing separately (a) sodium tungstate, (b) nickel sulfate and (c) a mixture of sodium tungstate and nickel sulfate. The solution concentrations used in this study are listed below:

- 1. Common constituents: sodium citrate (0.4 M), ammonium chloride (0.5 M) and sodium bromide (0.15 M).
- 2. Tungsten deposition potentials: solution (1) + sodium tungstate dihydrate (0.14 M).
- 3. Nickel deposition potentials: solution (1) + nickel sulfate (0.06 M).
- 4. Ni–W alloy deposition potentials: solution (1) + sodium tungstate dihydrate (0.14 M) and nickel sulfate (0.06 M).

Unstirred solutions at $60 \,^{\circ}$ C were used for the deposition potential experiments as well alloy plating experiments. Etched 1 cm \times 1 cm copper foils were used as substrates. The etching of the copper substrate was carried out in order to improve the deposition and adhesion of the deposits.

The nickel-tungsten alloy electrodeposition was conducted using a dc current and pulse plating methods. The plating conditions are described in the legends in Fig. 2. A CHI Electrochemical Workstation (Model CHI 660A), having a wide variety of functional capabilities was used for the polarization, dc and pulse plating experiments. A saturated calomel electrode was used as a reference electrode and all the measured potentials are referred to the same scale.

2.2. Morphology of the deposits

The morphology of the deposits was determined using the atomic force microscopy (AFM) and the scanning electron microscopy (SEM) techniques. The AFM on the deposits was performed using the Digital Instruments Nanoscope. The surfaces were scanned using tapping mode of scanning. A canonical probe (ultrasharp hyperboloid at the extreme tip used was silicon/doped n+ tip from nanosensor. The height of the tip was about 10 μ m. The cantilever had a spring constant of 40–75 N/m (resonating frequency: ~300 kHz). Identical scanning parameters were used for all the samples.

2.3. Oxygen reduction reaction

The electrocatalytic activities of the nickel-tungsten alloy electrodeposits were compared by examining the potential



Fig. 1. Current-potential curves for single metal and alloy plating. Composition: (1) sodium citrate (0.4 M), ammonium chloride (0.5 M) and sodium bromide (0.15 M). Curve (a): tungsten, solution composition (1) + sodium tungstate dihydrate (0.14 M); curve (b): nickel, solution composition (1) + nickel sulfate (0.06 M); curve (c): Ni–W alloy, solution composition (1) + sodium tungstate dihydrate and nickel sulfate (as for curves a and b).

versus logarithm current density relationships for the oxygen reduction reaction. The slow sweep polarization curves were obtained using a three electrode system consisting of the nickel–tungsten alloy working electrode, a saturated calomel reference electrode, and a platinum counter electrode. All the measured potentials are referred to the same reference electrode scale. An all-glass-three compartments, hollow cylindrical cell having a 150 ml volume working electrode compartment was used. Oxygen saturated, unstirred 1% NaOH solutions (pH at room temperature = 12.7) at room temperature (\sim 23 °C) were used for the slow sweep polarization experiments at scan rates of 0.004 and 0.05 mV/s.

3. Results and discussion

The current-potential curves for the deposition of tungsten, nickel and the nickel-tungsten are shown in Fig. 1. The deposition potentials, as estimated from the points of inflexion in these curves are: tungsten, -1.3 V (curve a); nickel, -1.25 V (curve b); nickel-tungsten alloy, -1.20 V (curve c). There is a 100 mV depolarization for the alloy deposition potential in comparison to that of tungsten, a metal that cannot be easily deposited from the aqueous solutions.

The atomic force micrographs (AFMs) of the direct current and pulse electrodeposited nickel-tungsten alloys are shown in Fig. 2. The morphology of the copper substrate was



Fig. 2. AFMs of electrodeposited Ni–21 at.% W alloy samples. Alloy plating solution composition see Fig. 1. Conditions: (a) dc current = 0.1 A/cm^2 ; (b) differential pulse voltammetry, initial E = 0.0 V, final E = -1.6 V, increment = 0.004 V, pulse width = 0.05 s, sampling width = 0.0167 s and pulse period = 0.1 s; (c) conditions as in (a), pulse period = 0.2 s, quiet time = 2 s, sensitivity = 0.1 A/V; (d) as in (a), pulse period = 0.5 s; (e) square wave voltammetry, initial E = -1.4 V, increment = 0.004 V, amplitude = 0.025 V and frequency = 15 Hz.

similar for all experiments and we observed that the predeposition morphology of the copper substrate did not have any significant effect on the deposited morphology. A banded structure with a maximum particle size of 100 nm can be seen for the sample that has been plated using a direct current of 100 mA/cm² for 300 s (Fig. 2a). On the other hand, use of a differential pulse produced deposits of different morphologies depending upon the pulse duration (conditions: initial E= 0.0 V, final E = -1.6 V, increment = 0.004 V, pulse width = 0.05 s and sampling width = 0.0167 s; variable = pulse duration). Deposits with a maximum particle size of 75 nm resulted for pulse durations of 0.1 and 0.2 s. On the other hand, 125 nm sized particles resulted for a pulse duration of 0.5 s. Again a banded structure resulted in this case. Application of square wave of 15 Hz (initial E = -1.2 V, final E = -1.4 V, increment = 0.004 V and amplitude = 0.025 V) gave rise to a columnar deposit having a maximum particle size of 100 nm.

The scanning electron micrographs (SEMs) of the direct current and pulse electrodeposited nickel–tungsten alloys are shown in Fig. 3. The energy dispersive scan showed that the tungsten content in the alloy is 21 at.%. The particle sizes approximately complement with those observed in the AFM images. In addition, the SEM image of the plated sample using a direct current of 100 mA for 300 s (Fig. 3a) shows the presence of distinct grain boundaries and of a second phase within the grains. These results are consistent with the previous studies [10,11] carried out under similar experimental conditions and suggest that the electrodeposition produces a Ni–W alloy on the copper substrate. Superimposition of differential pulse leads to possible dissolution of the second phase particles when the potential reaches a value of 0.0 V. Here again, the superimposition of 15 Hz results in a deposit having well rounded particles (Fig. 3b). Contrary to the AFM, the columnar structures are obvious and this may be due to the magnification of the SEMs.

Fig. 4 shows the logarithm current density versus potential curves for the oxygen reduction reaction at electrodeposited Ni–21 at.% W alloy in unstirred, oxygenated 1% sodium hydroxide solution at room temperature (\sim 23 °C). These curves were obtained at a scan rate: 0.05 mV/s. It can be seen that the currents in the potential -0.2 to -0.4 V for the dc current plated sample having a maximum particle size = 125 nm (curve 1) are lower than those for the differential



Fig. 3. SEMs of electrodeposited Ni-21 at.% W alloy samples. Conditions as in Fig. 2: (a) Direct current for 300 s, (b) pulse deposition.



Fig. 4. Logarithm current density vs. potential curves for oxygen reduction reaction at electrodeposited Ni–21 at.% W alloy in unstirred, oxygenated 1% sodium hydroxide solution at room temperature ($\sim 23 \,^{\circ}$ C). Scan rate: 0.05 mV/s. Conditions—curve 1: dc current plated sample, maximum particle size = 125 nm; curve 2: differential pulse plated sample using conditions stated in Fig. 2b, maximum particle size = 75 nm; curve 3: square wave plated sample using the conditions stated in Fig. 2e, maximum particle size = 100 nm.

pulse plated (curve 2) or square wave plated samples (curve 3) having the maximum particle sizes of 75 and 100 nm, respectively. On the other hand, there are only minor differences in the current densities in the limiting current region. Marginal differences in the limiting current densities as a function of particle size for differently electrodeposited the nickel–tungsten alloy can be attributed to the narrow differences in the maximum particle sizes, i.e., 125 nm for dc plated sample versus 75 nm for differential pulse plated sample. Despite the differences in the particle size, the over-all surface area differences, based on a range of particle sizes for the given samples may be marginal, thereby producing marginal changes in the electrochemical effects for the oxygen reduction reaction.

Fig. 5 shows the logarithmic current density versus potential curves for oxygen reduction at differential pulse plated Ni–21 at.% W alloy sample in unstirred, oxygenated 1% sodium hydroxide solution at room temperature (\sim 23 °C). A linear relationship is obtained with a Tafel slope of 130 mV/decade and is suggestive of a rate-determining first



Fig. 5. Logarithm current density vs. potential curves for oxygen reduction reaction at a scan rate of 0.04 mV/s on Ni–21 at.% W alloy electrodeposited using dc current.

electron transfer step [11,12]. On the basis of the present evidence we think that the dissocialize adsorption of oxygen is the most likely pathway for oxygen reduction consistent with previous studies [11,12] on metal surfaces. In order to be reduced the oxygen molecule has to reach on the surface of the electrode and interact with the electrode surface, and this is very much dependent on the electrode/electrolyte interface. The interaction of these species with the electrode surface may determine the effectiveness of the catalyst for oxygen reduction. Unlike noble metals/electrolyte interface in which H₂O molecules are adsorbed by weak interactions with the metal surface, the oxide covered metal/electrolyte interface consists of a hydroxyl Ted surface. This is because when a metal oxide comes in contact with the water, the metal ions on the surface get coordinately saturated by binding OH⁻ and this in turn hydroxylates the surface [13,14]. The metal atoms in this hydroxylated surface are chemically bonded to OH^- or O^{2-} . For oxygen reduction to occur on this surface, O₂ has to displace these groups from the surface before reaching the surface of the oxide. Oxygen is a non-polar molecule and therefore the probability of O_2 to replace chemically bonded OH^- or O^{2-} is negligible. Therefore, the first step probably involves an outer sphere electron transfer to form a superoxide ion, which is polar in nature and hence can find its way to reach metal sites for subsequent reaction. We also observed only minor variations in the Tafel slopes and the limiting current density with a change in the particle size of the electrodeposits. This result is important since the corrosion rates in oxygen containing alkaline solutions are proportional to the limiting current densities for oxygen diffusion [8]. In this particular study, there were only minor changes in the limiting current densities for oxygen reduction for the deposits having the particle sizes between 75 and 125 nm, thereby meaning that the corrosion rates do not vary substantially when the particle size differences are marginal.

4. Conclusions

Electrodeposition of nickel–21 at.% tungsten alloys was possible from the citrate–bromide electrolyte. Variation in the direct and pulse plating parameters and use of differential pulse voltammetry and square wave voltammetry resulted in the electrodeposits with particle sizes from 75 to 125 nm. A linear relationship is obtained with a Tafel slope of 130 mV/decade was observed for the oxygen reduction reaction at the electrodeposits in unstirred, oxygen saturated, 1% sodium hydroxide solution at room temperature and is suggestive of a rate-determining first electron transfer step. There were marginal variations in the limiting current densities for the oxygen reduction as the particle size decreased from 125 to 75 nm suggesting that the corrosion rates do not vary substantially when the particle size differences are marginal.

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