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(54) **METHODS FOR PRODUCING CORROSION  
RESISTANT ELECTRODEPOSITED NICKEL  
COATINGS**

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(57) **ABSTRACT**

Embodiments of the present methods deposit smooth, semi-bright nickel coatings from a nickel bath at room temperature, with relatively high concentrations (between about 5 and about 10%) of an organic modifier (such as butanol) under acidic conditions and using a modified pulse potential. The methods for electrodepositing nickel coatings result in nickel coatings that have improved internal structure and corrosion resistance.

FIG. 1A

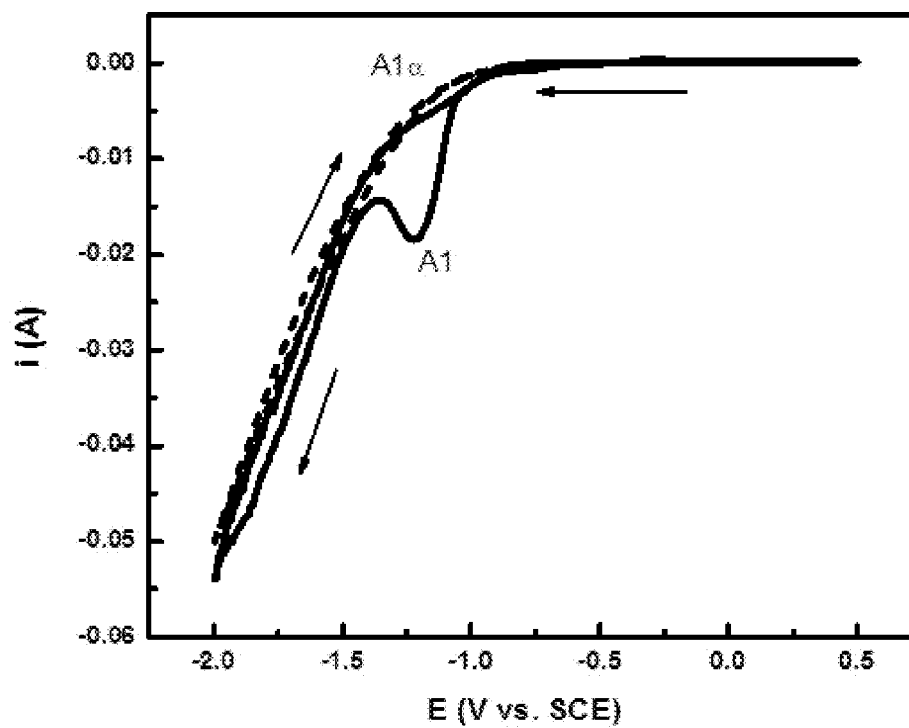


FIG. 1B

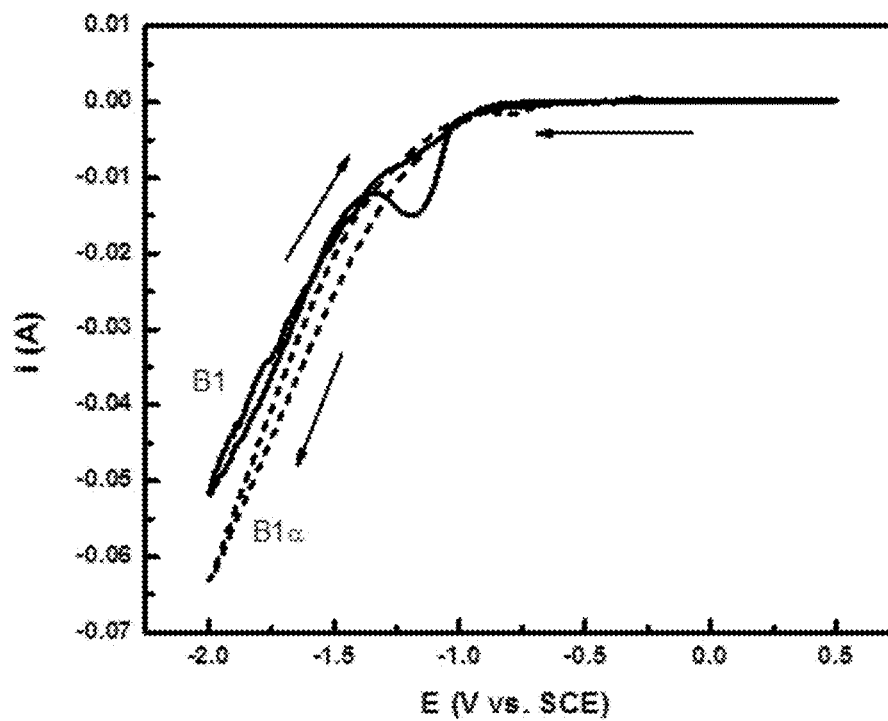


FIG. 1C

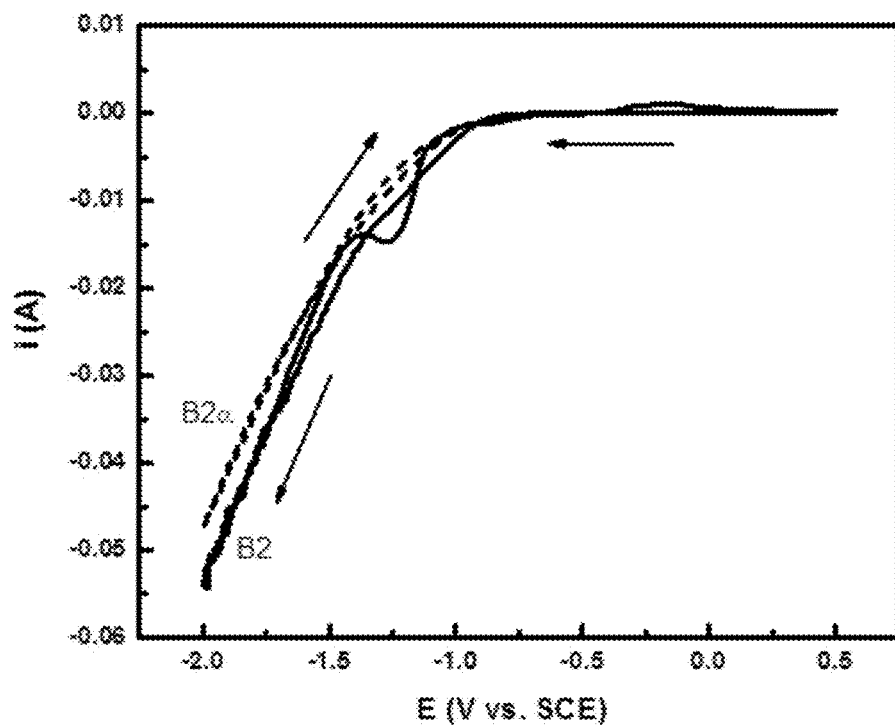


FIG. 2

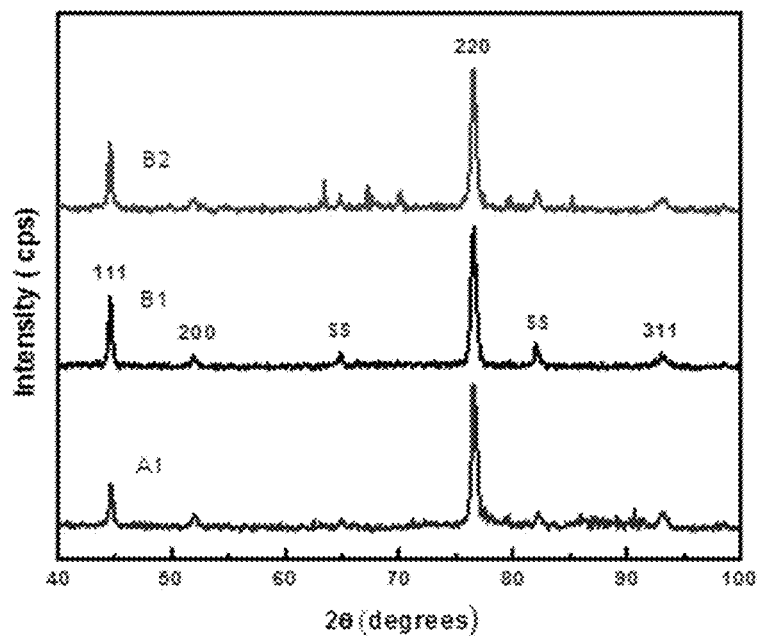


FIG. 3A

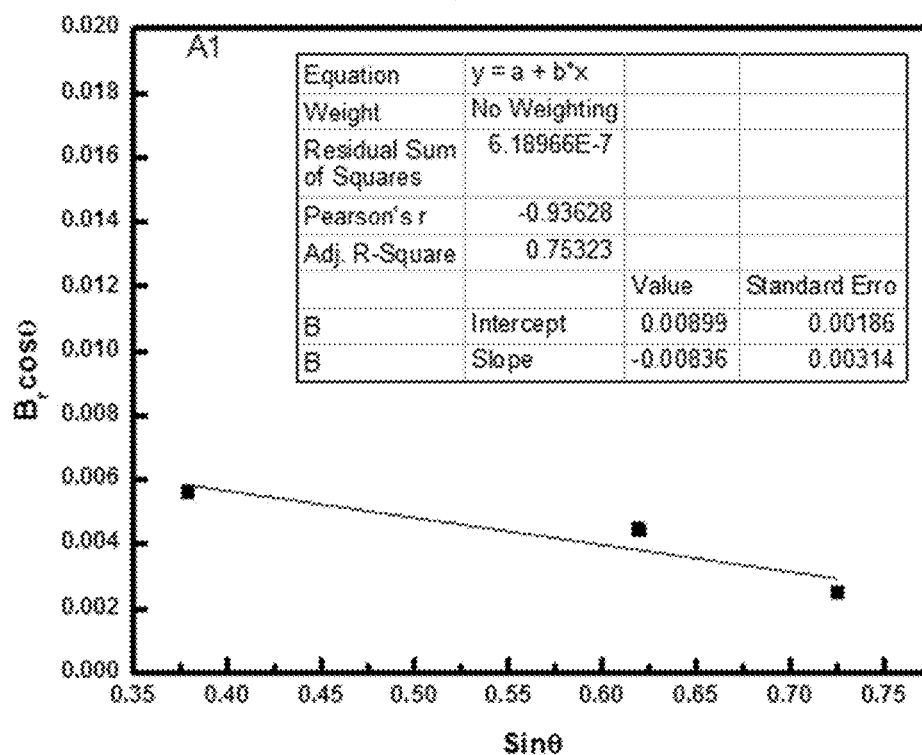


FIG. 3B

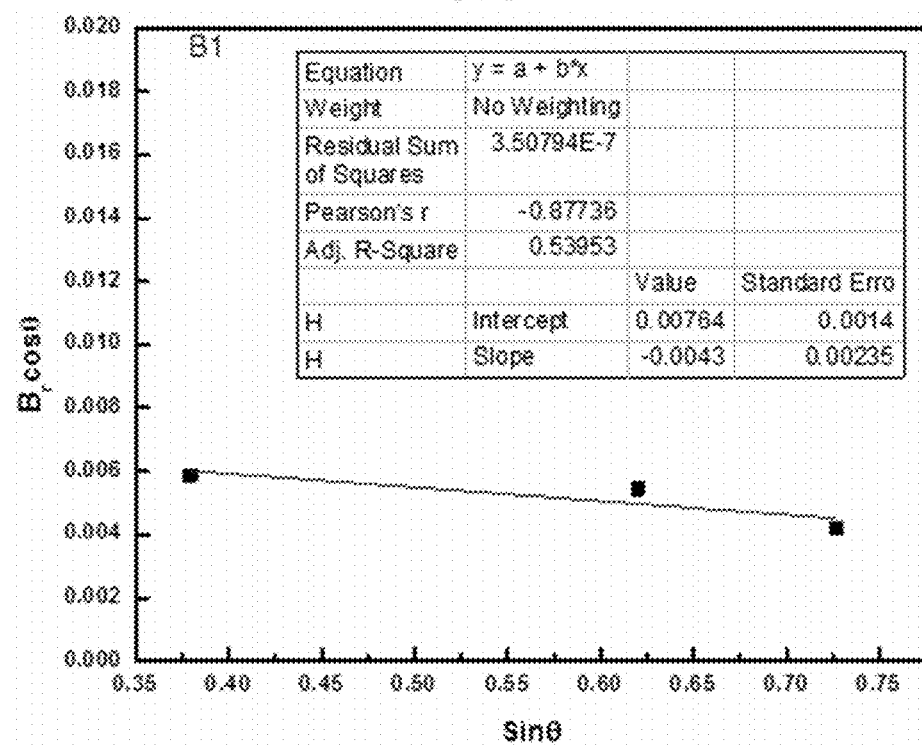


FIG. 3C

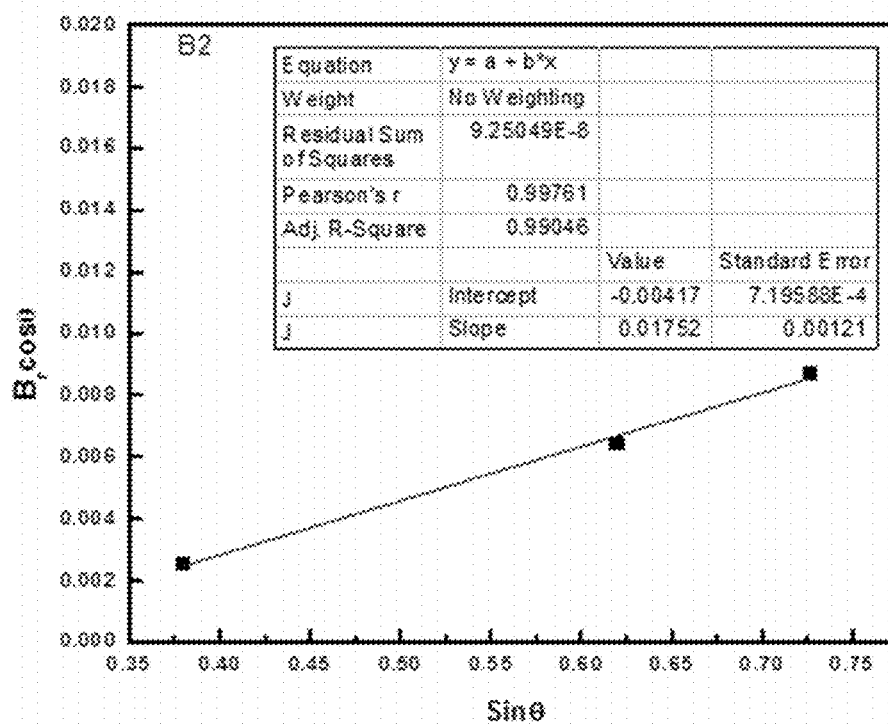


FIG. 4

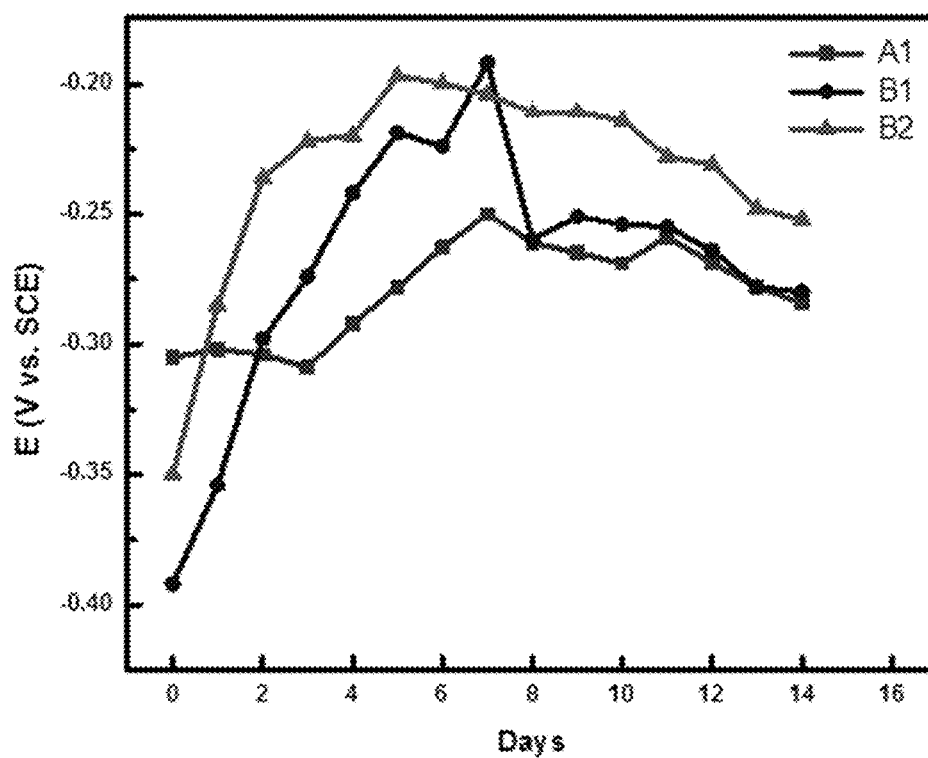


FIG. 5

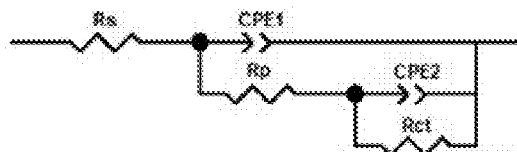


FIG. 6

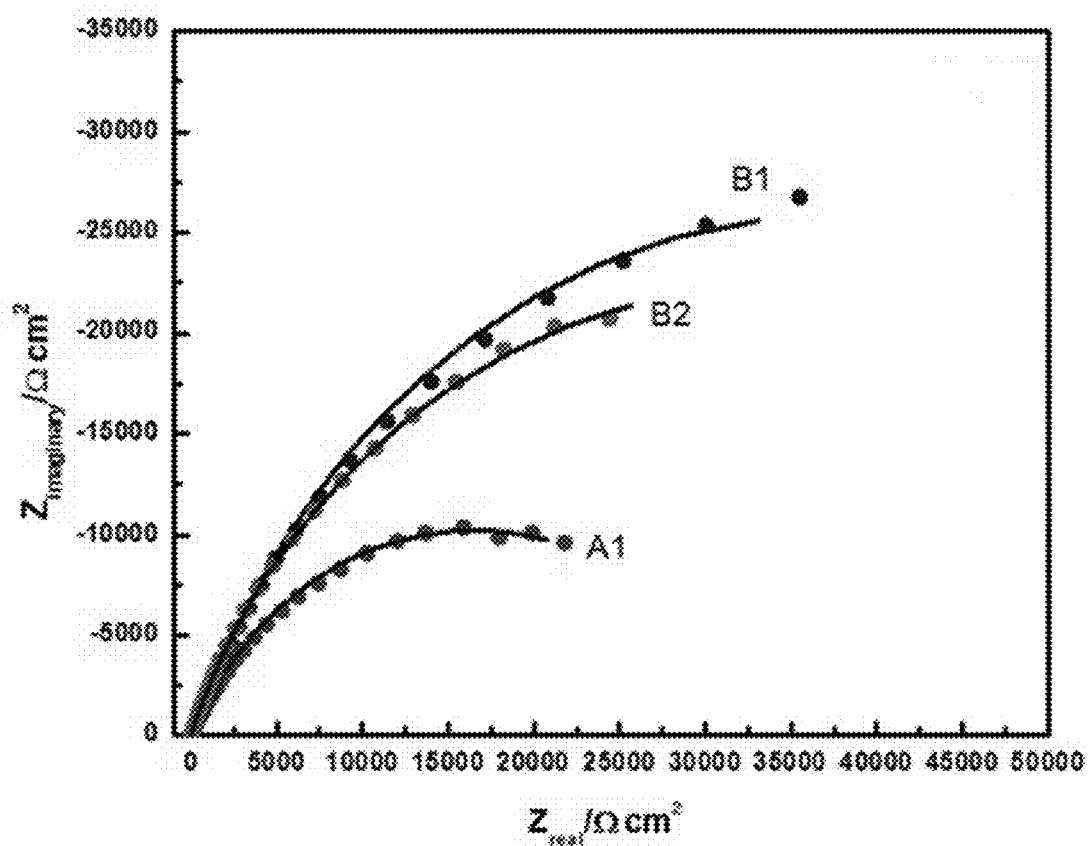


FIG. 7

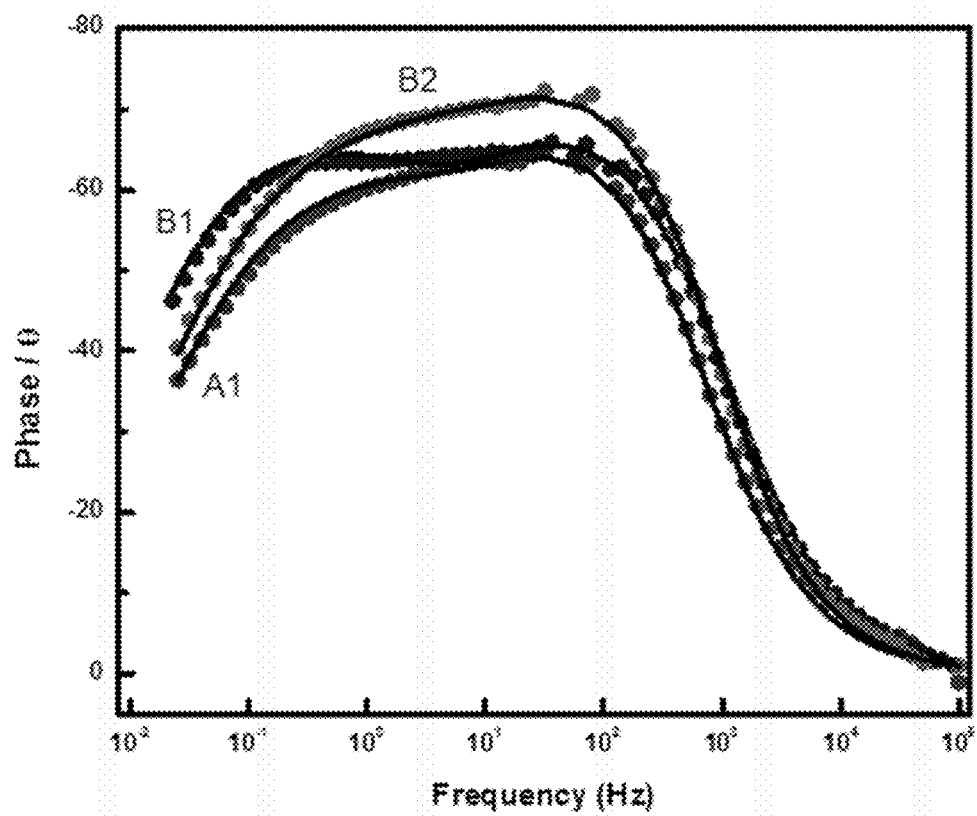


FIG. 8

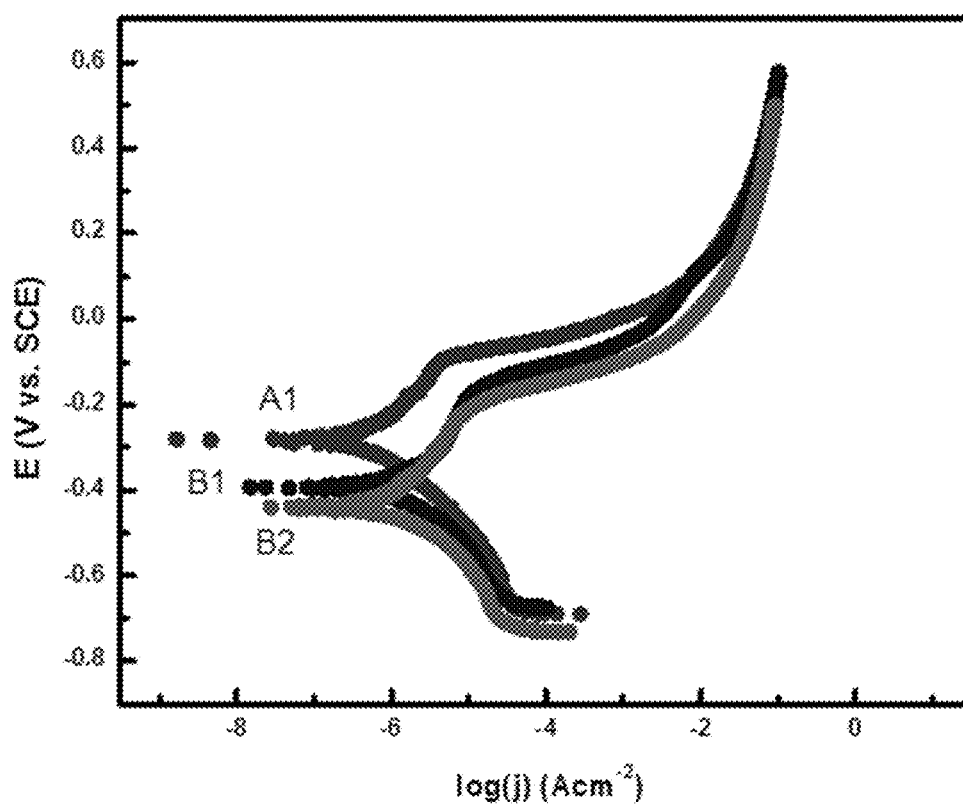
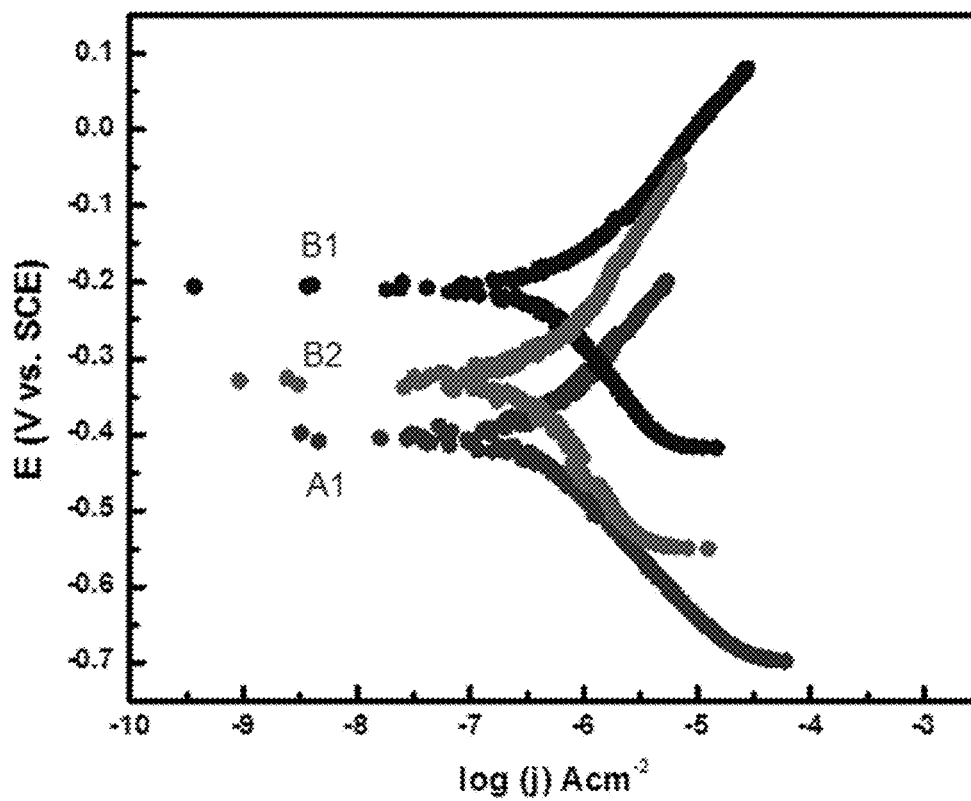


FIG. 9



## METHODS FOR PRODUCING CORROSION RESISTANT ELECTRODEPOSITED NICKEL COATINGS

[0001] This application claims priority to U.S. Provisional Patent Application Ser. No. 62/347,938, entitled "Methods for Producing Corrosion Resistant Electrodeposited Nickel Coatings," filed on Jun. 9, 2016, the entire content of which is hereby incorporated by reference.

### BACKGROUND

[0002] This disclosure pertains to electrodeposited nickel coatings and particularly to methods of producing electrodeposited nickel coatings having improved internal structure and corrosion resistance.

[0003] Corrosion inhibitive coatings are one of the most common ways used to prevent undesirable corrosion to the base substrates of many materials. Nickel coatings are widely used to create protective coatings for marine engineering, aeronautical, and other general decorative applications. Nickel is valued for providing strong adhesion to stainless steels, good mechanical properties, and providing corrosion resistance for the underlying steel. Nanocrystalline nickel coatings, which have increased resistance to pitting corrosion, can be created by electrodeposition. In recent years, additional components (i.e. ceramics, metal oxides, polymers, etc.) have been added to nickel coatings to improve the protection mechanism of the coatings in corrosive environments. These composite metal coatings have been studied for their improved physical and corrosion resistant properties. The additional components chosen for inclusion into the coatings are often limited by their water solubility or flocculation properties in the electrochemical baths. Due to this, synthetic routes such as casting, accumulative roll bonding, and hot dip methods are often used, but at higher costs and often loss of control over the morphology.

[0004] Recently, a number of new electrolyte systems have been developed to lower the cost and widen the pH range for nickel deposition; however, the most common still in use are Watts type baths, which take advantage of the complexing effects of borate ions and its ability to cathodically shift hydrogen evolution. Boric acid has a long history as an additive for nickel electrodeposition and has been shown to provide a buffering effect at the electrode surface, decreasing the amount of hydrogen embrittlement in Ni coatings. Though the mechanism is not well understood, boric acid forms a weak complex with nickel in solution that is advantageous for deposition at low current densities, necessary for depositing nanocrystalline nickel.

[0005] Addition of organic solvents can also have advantageous effects on the mechanisms of crystal growth and morphology, but the resultant corrosion inhibition of these nickel coatings has not been tested. There are some instances in literature of aqueous-organic systems used to deposit metal coatings. Previously, N,N-dimethylformamide (DMF) was successfully used as an organic modifier to control microstructure, current efficiency, and hardness for nickel electrodeposits. More recently, nickel based alloys and nanocomposite coatings electrodeposited in pure DMF were examined as aprotic solvent baths to deposit metals that typically can't undergo deposition in aqueous systems.

Microcracking is often observed in these systems due to internal strain from the growth mechanism caused by large amounts of DMF.

[0006] Aliphatic alcohols have also been used as modifiers to generate fine grained nickel electrodeposits. The addition of unsaturated alcohols such as 2-butyne-1,4-diol and propargylic alcohol into a nickel electroplating bath were shown to induce inhibited growth modes on nickel crystallization during electrodeposition but it wasn't shown to control isolated or polycrystalline growth planes. The effects of n-propyl, allylic, and propargylic alcohol were also studied and it was found that these aliphatic alcohols caused a cathodic shift in the reduction potential of nickel as well as an inhibitory effect on the current efficiency in Watts type baths. It was seen that as unsaturation of the molecule increased, the reduction potential shifted more cathodically. It was also shown that both cis and trans 1,4-butenediol completely inhibited discharge of nickel above a concentration of 25 mM. Oxygen containing species, like these diols, containing unsaturated bonds will adsorb parallel to the electrode surface to be hydrogenated, which is beneficial but potentially decreases the natural efficiency of borate species for removing adsorbed hydrogen at the electrode surface. This adsorption affinity also limits the amount of additive that can be added into the plating solution. Even though increasing unsaturation helps dehydrogenate the electrode surface, the alcohol will strongly adsorb and can shut down the reaction if the concentration is too high. Typically, no more than 50 mmol (~0.05%) of the unsaturated alcohol additive can be added to the plating solution.

[0007] Electrodeposition of composite materials for use as corrosion inhibitive coatings containing nanoparticle size dopants is a growing field of research, but so far, is limited to purely aqueous systems. Therefore, it is important to explore new organic additives for plating solutions that can produce a wide variety of composite coatings at low temperatures, with small grain size and low strain. This aqueous-organic bath system can help stabilize nanoparticles of very low solubility during the electrodeposition of nickel coatings.

### SUMMARY

[0008] The present disclosure relates generally to methods for electrodepositing nickel coatings that have improved internal structure and corrosion resistance. The present methods deposit smooth, semi-bright nickel coatings from a nickel bath at room temperature, with relatively high concentrations (between about 5 and about 10% by volume) of an organic modifier (such as butanol) under acidic conditions and using a modified pulse potential. Butanol (BuOH) has terminal alcohols and no unsaturated bonds, with a nonpolar chain that can act as a pseudo surfactant, potentially stabilizing non-hydrophilic nanoparticles. The important role borate plays in complexing with nickel and facilitating the reduction process can be inhibited by mono or polyunsaturated diol compounds, known to complex with borate in solution.

[0009] A series of embodiments of nickel coatings deposited from baths containing BuOH demonstrated improved reduction potential, growth inhibition, strain, and corrosion resistance to chloride attack. The exemplary coatings were nanocrystalline with particle sizes between 16-35 nm as calculated from Williamson-Hall analysis. No cracking of the films was observed in the scanning electron microscopy

images, even as the percentage of butanol increased, which is typically observed in other aqueous-organic baths. The corrosion resistance of the nickel coatings in a 3.5% sodium chloride solution was the best for coatings deposited from a plating solution containing 5 and 10% butanol.  $E_{corr}$  was shifted from  $-0.405$  V for the nickel coating from the additive free bath to  $-0.234$  V for the nickel coating from the 5% butanol solution. EIS results indicated a 100% improvement in the corrosion resistance for the nickel coatings from the butanol solution. Higher percentages of organic modifiers in the aqueous plating bath help open up the use of non-electroactive components to produce new composite coatings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1A shows a cyclic voltammetry study at a scan rate of 10 mV/s for bath solution samples containing no butanol and without nickel (A1 $\alpha$ ) and with nickel (A1).

[0011] FIG. 1B shows a cyclic voltammetry study at a scan rate of 10 mV/s for bath solution samples containing 5% butanol and without nickel (B1 $\alpha$ ) and with nickel (B1).

[0012] FIG. 1C shows a cyclic voltammetry study at a scan rate of 10 mV/s for bath solution samples containing 10% butanol and without nickel (B2 $\alpha$ ) and with nickel (B2).

[0013] FIG. 2 shows X-ray diffraction patterns of each nickel coating A1, B1, and B2.

[0014] FIG. 3A shows a Williamson-Hall plot for nickel coating A1.

[0015] FIG. 3B shows a Williamson-Hall plot for nickel coating B1.

[0016] FIG. 3C shows a Williamson-Hall plot for nickel coating B2.

[0017] FIG. 4 shows OCP versus time for each nickel coating immersed in 3.5% NaCl solution for 14 days.

[0018] FIG. 5 shows an equivalent circuit model for a nickel coating layer with a thin passive oxide layer displaying some micropores within the coating.

[0019] FIG. 6 shows Nyquist plots and fittings for nickel coatings (a) A1, (b) B1, and (c) B2, using the circuit displayed in the inset. Black lines are the fitting curves and the dots represent the data from the EIS experiment.

[0020] FIG. 7 shows Bode phase angle plots for nickel coating samples. Black lines are the fitting curves and the dots represent the data from the EIS experiment.

[0021] FIG. 8 shows potentiodynamic polarization curves for fresh coatings in 3.5% NaCl.

[0022] FIG. 9 shows Tafel polarization curves for each coating in 3.5% NaCl after 14 days immersion in 3.5% NaCl.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0023] Generally, the present disclosure relates to electrodeposited nickel coatings having improved properties such as corrosion resistance. In preferred embodiments, the nickel coatings are electrodeposited using an aqueous organic bath containing about 5% to about 10% of an organic modifier such as butanol. The aqueous organic bath preferably contains sodium borate and is preferably adjusted to an acidic pH level, preferably having a pH of about 2.5 to about 3.5. The coatings display minimal strain and nanocrystalline particle size using a pulse potential deposition at room temperature. After 14 days immersion in 3.5% NaCl,

coatings that were deposited using an aqueous organic bath containing 5% or 10% BuOH had an improved resistance to corrosion showing ~100% increase in the  $R_{ct}$  value (73672  $\Omega\text{cm}^2$ ) over a coating deposited without using the BuOH modifier. Linear polarization displayed an anodic shift of  $E_{corr}$  for coatings deposited using the organic modifier, due to the development of a thicker passive oxide layer.

[0024] The present methods for electrodeposition of nickel coatings using an aqueous organic bath containing an organic modifier such as butanol produce additional advantages as well. Applied overpotential is lower than other deposition methods to form coatings, needing only a 0.5-1.0 A/dm<sup>2</sup> current density, which is 50 to 1000% lower than commercial all-sulfate plating baths used. This lower overpotential decreases the amount of hydrogen evolution that occurs during the plating process. Coatings are formed at ambient temperatures. Typical commercial techniques commonly require temperatures of 40-70° C., thus no equipment for elevating and maintaining the heat of the bath is required. Butanol addition has only minor effects on the conductivity of baths and doesn't shut down the deposition process. Common additives such as 1,4-butanediol, 1,4-butenediol, 1,4-butyndiol, allylic alcohol, and propargylic, are known to decrease the deposition process at additions as high as 50 mM. Morphology of coatings show predominant (220) preferred orientation with only slight (5-15%) (111) and (311) character, with some controllability through the addition of butanol. Addition of butanol also decreases the grain size of nickel coatings, which decreases susceptibility to pitting corrosion. Addition of butanol also does not increase internal strain within the coatings, whereas additives tested before, i.e. DMF, have microcracking problems. Finally, passive oxide formation is thicker than coatings not formed in the presence of butanol. Values for charge transfer resistance via electrochemical impedance spectroscopy testing were doubled by the addition of butanol, compared to the modified all-sulfate bath without addition of butanol.

#### Example 1. Electrodeposition of Nickel Coatings

[0025] Materials. All reagents were analytical grade and were used as received with no further processing. Nickel coatings were electrodeposited from solutions containing 26.29 g/L NiSO<sub>4</sub>·6H<sub>2</sub>O (Alpha Aesar), 57.21 g/L Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O (Fisher) and butanol (Mallinckrodt), adjusted to pH 3.0 $\pm$ 0.05 using 5.0 M H<sub>2</sub>SO<sub>4</sub> (EM Scientific). By using the sodium borate and adjusting the pH to acidic levels, sodium cations can initially increase conductivity of the solution and also maintain higher conductivity throughout the deposition, as Ni<sup>+2</sup> is deposited from solution. The solvent composition of the plating baths was designated as A1 (no BuOH addition), B1 (5% of BuOH added), and B2 (10% BuOH added).

[0026] Electrodeposition. An EG&G PAR potentiostat/galvanostat model 273A was used for all depositions. Nitrogen was bubbled in all solutions prior and during electrodeposition. The electrode substrates were 10 mm stainless steel 430 disks (Ted Pella), attached to copper leads with conducting silver based epoxy and coated in resin epoxy to expose only one face. The stainless steel working electrodes were prepared by polishing with 320 to 1200 grit SiC pads, followed by a final polish with 0.30  $\mu\text{m}$  alumina. Electrodes were submerged in 5 M H<sub>2</sub>SO<sub>4</sub> for 120 s, rinsed with DI H<sub>2</sub>O, and dried just prior to deposition and cyclic voltammetry studies. Electrodeposition for all nickel coatings was

carried out by a modified pulse loop consisting of  $-1.08$  V for  $10$  s followed by  $-0.6$  V for  $4$  s, scanning at  $100$  mV/s between steps, until a total charge of  $\sim 40.0$  coulombs was reached. The resulting coatings were  $\sim 6$   $\mu\text{m}$  thick for all these experimental parameters.

**[0027]** Reduction potential of Ni and the effect of BuOH. A Thermo Orion 550A conductivity meter with a Thermo Orion 013005A platinum black four cell conductivity probe was used to measure the conductivity of the plating baths. Cyclic voltammetry (CV), open circuit potential immersion testing (OCP), Tafel polarization, and electrochemical impedance spectroscopy (EIS) studies were performed with a PAR Parstat 4000 potentiostat (Ametek). Cyclic voltammetry of the solutions was carried out in a three electrode cell system, composed of a stainless steel (SS) working electrode, chromel counter electrode, and a saturated calomel (SCE) reference electrode. Potentiodynamic polarization, EIS, and OCP were all performed in a solution of  $3.5\%$  sodium chloride diluted with deionized water. The EIS was scanned from  $10^5$  Hz to  $25$  mHz with a perturbation amplitude of  $10$  mV. Potentiodynamic polarization scans were run from  $\pm 250$  mV at a scan rate of  $1$  mV/s.

**[0028]** Cyclic voltammetry was performed for each of the plating bath systems to determine the effects of BuOH on the reduction potential at pH  $3 \pm 0.05$ . Each solution was scanned between  $0.5$  V and  $-2.0$  V, starting from OCP, at a scan rate of  $10$  mV/s. The reduction and oxidation potentials of each bath are presented in Table 1 below.

TABLE 1

| $E_{pc}$ , $E_{pa}$ , $i_{pc}$ , and $i_{pa}$ for each sample measured from cyclic voltammetry at a scan rate of $10$ mV/s. |              |               |              |               |
|-----------------------------------------------------------------------------------------------------------------------------|--------------|---------------|--------------|---------------|
| Sample                                                                                                                      | $E_{pc}$ (V) | $i_{pc}$ (mA) | $E_{pa}$ (V) | $i_{pa}$ (mA) |
| A1                                                                                                                          | $-1.22$      | $18.4$        | $-0.300$     | $0.484$       |
| B1                                                                                                                          | $-1.33$      | $15.0$        | $-0.300$     | $0.465$       |
| B2                                                                                                                          | $-1.27$      | $14.7$        | $-0.287$     | $0.853$       |

**[0029]** Cyclic voltammograms for each sample bath are displayed with and without the presence of nickel in FIG. 1. Electrolyte bath systems containing no nickel are shown with a designations and were performed to subtract any capacitive effects of BuOH on the scan. The addition of BuOH in B1 ( $5\%$ ) and B2 ( $10\%$ ) shifted the reduction potential of nickel to slightly more cathodic potentials around  $-1.25$  V. This is consistent with findings that aliphatic alcohols do cause a cathodic shift in the reduction potential of nickel. The current slightly decreased as BuOH percentage increased, due to a larger amount of adsorption onto the electrode surface, limiting the active area for nucleation. Hydrogen evolution in the cathodic region was considerable but expected at such large negative potentials, but the characteristic suppression, due to the presence of borate, was evident in this system. There was a small anodic peak on the reverse scan at  $\sim -0.30$  V, which was due to the nickel metal oxidizing to nickel oxide on the surface. Anodic peak current,  $i_{pa}$ , in all solutions was minimal, and the organic modifier appeared to have little effect on the anodic potential,  $E_{pa}$ , and  $i_{pa}$  in that direction.

**[0030]** Deposition conditions. A modified pulse reverse deposition provides more uniform coatings of nickel and the upper and lower potentials were chosen after analyzing CV studies. An upper deposition potential of  $-1.08$  V was selected, to minimize hydrogen evolution at the electrode surface but still provide a large enough overpotential to deposit nickel from solution. Deposition of A1 (no organic modifier) was used as a benchmark to test the deposition

quality for cathodic potentials between  $-1.0$  V to  $-1.2$  V. It was found that  $-1.08$  V produced good quality and uniform nickel coatings with minimal hydrogen evolution. The lower potential of  $-0.6$  V was determined experimentally and selected as the potential where zero current flow was observed. A running scan rate of  $100$  mV/s between these potentials was selected because it produced more uniform deposits versus a square wave potential step method. The pulse deposition was cycled until  $\sim 40$  C of charge was obtained to provide full coverage of the substrate. The thickness of the coatings was measured using a profilometer and averaged  $6.30 \pm 0.11$   $\mu\text{m}$  for this amount of charge. The coating thicknesses did not vary with the addition of butanol to the solution. Even though the conductivity of the plating solution was slightly lowered with the organic addition, it was still high enough to allow good plating of the nickel;  $A1 = 26.53 \pm 0.57$ ,  $B1 = 23.01 \pm 0.64$ , and  $B2 = 21.46 \pm 0.57$  mS/cm. The appearance of all coatings (with and without butanol) was similar and semi-bright in appearance.

#### Example 2. Characterization

**[0031]** Techniques. Coating morphology was characterized by an Environmental FEI Quanta 200 scanning electron microscope. Powder x-ray diffraction was used to measure crystallinity and composition of the coatings using a Siemens D-500 X-ray diffractometer. Scans were run from  $30$ - $100$  degrees  $2\theta$  at a  $1$  sec dwell time and  $0.05^\circ$  step size, using CuK $\alpha$  radiation with the tube set to  $35$  kV and  $24$  mA. Coating thickness was measured using a Veeco Dektak 8 stylus profilometer.

**[0032]** X-ray diffraction (XRD). The effects of the addition of BuOH on the crystal orientation of nickel were investigated with powder XRD and the results are shown in FIG. 2. There are two predominate peaks observed for each nickel coating, the (111) and (220) reflections. Those orientations are characteristic for face centered cubic (fcc) nickel, although the XRD patterns showed preferred orientation (220) for the coatings. This mixed phase is a result of a lower reduction potential of  $-1.08$  V applied during the deposition of the coatings. It has been found that a lower overpotential can cause a preference for [110] growth planes when there is low current density, or in the presence of wetting or brightening agents. Samples B1 and B2, containing butanol, also display (220) preferred growth but slightly more (111) character, again consistent with the observed cathodic reduction potential shift of nickel. To better understand the influence of how organic addition influences the preferred orientation of the coatings, the relative peak intensities were analyzed by determining the relative texture coefficients of the peaks ((111), (200), (220), and (311)) present in the XRD patterns.

**[0033]** Additionally, due to the polycrystalline nature of the coatings, determining which orientation is more beneficial for corrosion resistance was of interest as well. The influence of each can be represented by calculating the relative texture coefficient ( $RTC_{hkl}$ ) for each orientation and comparing it with the corrosion resistance of the films. Eq. [1] shows how this was performed,

$$RTC_{hkl} = \frac{I_{p,hkl} / I_{p,hkl}^0}{\sum I_{p,hkl} / I_{p,hkl}^0} * 100\% \quad [1]$$

where  $I_{p,jkl}$  is the intensity of the peak for each sample at (111), (200), (220), and (311) reflections and  $I_{p,jkl}^o$  is the intensity of those reflections for the nickel standard reference (PDF#00-004-0850). The standard provides a random orientation pattern to compare against any preferred orientation found in the samples. Results are listed in Table 2 below.

TABLE 2

| Relative texture coefficients for (111), (200), (220), and (311) growth planes for each sample as measured with XRD. |                    |                    |                    |                    |
|----------------------------------------------------------------------------------------------------------------------|--------------------|--------------------|--------------------|--------------------|
| Sample                                                                                                               | RTC <sub>111</sub> | RTC <sub>200</sub> | RTC <sub>220</sub> | RTC <sub>311</sub> |
| A1                                                                                                                   | 5.26               | 4.85               | 72.32              | 17.66              |
| B1                                                                                                                   | 8.09               | 4.32               | 71.84              | 15.74              |
| B2                                                                                                                   | 7.80               | 4.27               | 72.66              | 15.26              |

**[0034]** Sample A1 has a relative texture coefficient of 72.32 for the predominant (220) reflection, 5.26 for (111), 4.85 for (200), and 17.66 for (311). Samples B1 and B2 display RTC values for (220) similar to that of A1, at 71.84 and 72.66, respectively, which is also consistent with the cathodic shift in nickel reduction potential. There is a noticeable increase in (111) and decrease in (311) coefficients for B1 and B2.

**[0035]** Organic addition into the coating bath can lead to microcracking and internal strain in nickel electrodeposits, so Williamson-Hall analysis was performed. A correction for instrumental broadening was done using a Si powder 325 mesh (Alpha Aesar) sample which matched the PDF#00-027-1402 file. The particle size and strain were calculated by solving for the full width at half maximum (FWHM) of the nickel peaks for reflections (111), (220), and (311) using Eq. [2].

$$B_r^2 = B_o^2 - B_i^2 \quad [2]$$

where  $B_r$  equals the corrected FWHM of each peak,  $B_o$  is the observed FWHM of the nickel film peaks, and  $B_i$  is the instrumental broadening value calculated from a 325 mesh silicon powder standard. Lattice strain and particle size (shown in Table 3 below) was found by plotting  $B_r \cos \theta$  vs.  $\sin \theta$  (FIG. 3) for the corrected nickel peaks. The strain for each coating was minimal, most likely due to the presence of borate and absence of allylic groups on the organic modifier. The low strain values are promising results for these nickel coatings deposited using the aqueous/organic baths. Particle size was in the nanometer range from ~16 to 35 nm, which is predicted from the addition of a borate electrolyte, the addition of organic modifier, and a pulse reverse deposition.

TABLE 3

| Strain and particle size of each sample as determined from Williamson-Hall analysis of the x-ray diffraction data |                   |                    |
|-------------------------------------------------------------------------------------------------------------------|-------------------|--------------------|
| Sample                                                                                                            | Strain ( $\eta$ ) | Particle Size (nm) |
| A1                                                                                                                | 0.0083            | 16.09              |
| B1                                                                                                                | 0.0043            | 19.05              |
| B2                                                                                                                | 0.0175            | 34.48              |

**[0036]** Surface morphology. All samples were examined with scanning electron microscopy (SEM) after electrodeposition. For the freshly deposited samples, a uniform coating across the surface with smooth fine grained deposit and no microcracking was observed for the nickel coating, which matches the minimal strain present in the deposits as indicated by XRD. All samples were nanocrystalline, as determined with XRD, and similar in morphology. The presence of (220) geometry appears as pyramidal structures, but due to the mixed (111) and (220) orientations, the surface is comprised of a hybrid geometrical appearance for all the samples. Samples B1 and B2 appear to have smaller grains than that of A1.

### Example 3. Corrosion Studies

**[0037]** Open Circuit Potential (OCP) Immersion Studies. After electrodeposition, the coatings were submerged in a 3.5% NaCl solution to simulate corrosion and the OCP was monitored for 14 days prior to Tafel polarization and EIS analysis. The immersion study results can be seen in FIG. 4. All samples showed anodic shifts in OCP, due to the formation of an oxide layer, providing barrier protection, and evidence of generalized corrosion on the surface was observed for all samples. Sample B2 maintained the most anodic OCP at -0.252 V. After 14 days, each sample was analyzed by linear polarization to determine  $E_{corr}$  and  $i_{corr}$  values. Each samples was immersed in fresh NaCl (3.5%) for 1 hour, until a stable OCP was reached prior to analysis.

**[0038]** Electrochemical impedance spectroscopy. Electrochemical impedance (EIS) was run to better understand how BuOH addition affects the corrosion resistance of the electrodeposited nickel coatings after a 14 day soak. ZView software was used to model the EIS results and calculate the equivalent circuit values of each circuit element. Each sample was normalized to a 1.0 cm<sup>2</sup> area and modeled successfully. The equivalent circuit model shown in the inset FIG. 5, contains 5 elements; 3 resistors and 2 constant phase elements, which model non-ideal capacitors. The circuit models a nickel coating layer with a thin passive oxide layer displaying some micropores within the coating. The oxide layer will have formed after the immersion time, but would be thin compared to the nickel coating. For this circuit,  $R_s$  represents the resistance of the 3.5% NaCl solution,  $CPE_f$  represents the capacitance of the passive coating where  $\alpha_1$  is a coefficient between 0 and 1, 1 being ideal, representing the behavioral deviation from an ideal capacitor.  $R_p$  represents the resistance of the electrochemical reaction between the solution and the nickel coating, both on the surface and within the micropores.  $CPE_{dl}$  and  $\alpha_2$  represent the double layer capacitance between the electrolyte and the coating interface at the bottom of the pores.  $R_{ct}$  is the charge transfer resistance, which is related to the corrosion resistance. This circuit model matches other measurements for nickel coatings on steels. The calculated values for the circuit elements are listed in Table 4 below.

TABLE 4

| Calculated circuit elements generated using ZView software from the EIS data. |                    |                               |            |                         |                               |            |                            |
|-------------------------------------------------------------------------------|--------------------|-------------------------------|------------|-------------------------|-------------------------------|------------|----------------------------|
| Sample                                                                        | $R_s$ ( $\Omega$ ) | $CPE_{dl}$ ( $\mu Fcm^{-2}$ ) | $\alpha_1$ | $R_p$ ( $\Omega cm^2$ ) | $CPE_{dl}$ ( $\mu Fcm^{-2}$ ) | $\alpha_2$ | $R_{ct}$ ( $\Omega cm^2$ ) |
| A1                                                                            | 12.99              | 75.3                          | 0.826      | 945                     | 81.6                          | 0.625      | 32653                      |
| B1                                                                            | 10.13              | 73.2                          | 0.813      | 1662                    | 50.8                          | 0.718      | 73672                      |
| B2                                                                            | 10.58              | 49.3                          | 0.869      | 1656                    | 38.3                          | 0.610      | 69290                      |

**[0039]** The Nyquist and Bode plots for EIS are shown in FIGS. 6 and 7, respectively. Nyquist plots and fittings for each sample show a distinct single semicircle pattern (FIG. 6). Values for  $R_s$  range between 10 to 13 $\Omega$ , shown in Table 4, displaying a reliable fit for each sample.  $R_p$  increases slightly for B1 and B2 over A1, indicating an increase in the passive film resistance. B1 and B2 display larger capacitive loop diameters, giving larger  $R_{ct}$  values compared to A1, and a higher resistance to corrosion. This increase is most likely due to the smaller grain sizes of the deposits. Sample B1 displays the highest  $R_{ct}$  value at 73,672  $\Omega cm^2$ , nearly double the value for A1. Increasing the percentage of BuOH to 10%, in B2, leads to a slight drop in  $R_{ct}$ , but only negligible decreases in  $R_p$ . It is apparent that when butanol is present during deposition, it modifies the deposition of nickel, possibly by stabilizing the NiOH colloid, slowing the rate of deposition and decreasing the grain size of the deposited nickel. Due to this, corrosion is slower, and the passive layer forms more quickly for these films.

**[0040]** Bode phase angle plots (FIG. 7) were studied to determine how the phase angle values model the capacitive effects and corrosion resistant behavior of the coatings. All coatings tested displayed a broad phase angle maximum, characteristic of the two time constants, which is consistent with the circuit model and fitting. This suggests that there are two capacitive responses, first for the interface of the nickel coating to the substrate and the other represents the response due to diffusion of solution through an outer passive-oxide layer that is formed. This is displayed as a second maxima in the lower frequency regions for all samples. All coatings approach 0° in the high frequency region, and the phase angle maximum occurred between 30-50 Hz, for every coating except for sample B1, which occurred at 2 Hz. In the lower frequency range, sample A1 shows the lowest value, followed by B2 and B1. B1 sustains a higher phase angle value through the lower regions, indicating the most capacitive behavior, indicative of a smaller particle size and surface charge. B1 and B2 phase angles are closer to 90° than A1, indicating a more stable passive film.

**[0041]** Potentiodynamic polarization measurements. Potentiodynamic polarization scans from -0.25 V to 1.0 V were run on fresh coatings in order to measure their resistance to corrosion in the active region of the scan, where the dominant reaction is oxidation of nickel (FIG. 8). The passive region formed for the fresh coatings is minimal compared to the soaked coatings, but allows a measure of how thick a passive layer can be formed for the different coatings. Fresh coatings deposited from the solutions containing BuOH, had rest potentials ( $E_{corr}$ ) cathodic to A1, and a higher  $\beta_a$  slope, indicating an ability to form an oxide layer more readily. The breakdown potential ( $E_{bd}$ ) was located after the passive region, where there is a large onset of current, indicating failure of the coating due to pitting or crevice corrosion reaching the steel substrate. By measuring

the difference between the rest potential and breakdown potential, the resistance of the passive layer to breakdown can be measured for each coating. Samples B1 and B2 displayed the largest difference in the active region (100 and 50 mV wider than A1, respectively), showing that the smaller grain size helps with the onset of oxide layer formation more quickly. Addition of BuOH in the plating bath improved the initial oxide layer formation for the nickel coating, and fits the EIS results.

**[0042]** Linear polarization was carried out for the coatings after soaking for 14 days in a 3.5% NaCl solution. Coatings were immersed in a fresh 3.5% NaCl solution and scanned  $\pm 250$  mV from OCP in both directions at a scan rate of 1 mV/s. The  $E_{corr}$  and estimated  $i_{corr}$  values were measured by locating the intersection point of the extrapolated linear sections of the anodic ( $\beta_a$ ) and cathodic ( $\beta_c$ ) portions of the scan. The results are listed in Table 5 below and shown in FIG. 9 for each coating.

TABLE 5

| $E_{corr}$ and $i_{corr}$ corrosion values for the nickel coatings calculated from linear polarization measurements. |                        |                           |                   |                   |
|----------------------------------------------------------------------------------------------------------------------|------------------------|---------------------------|-------------------|-------------------|
| Sample                                                                                                               | $E_{corr}$ (V vs. SCE) | $i_{corr}$ (Acm $^{-2}$ ) | $\beta_a$ (V/dec) | $\beta_c$ (V/dec) |
| A1                                                                                                                   | -0.405                 | $1.99 \times 10^{-7}$     | 0.185             | 0.393             |
| B1                                                                                                                   | -0.234                 | $3.35 \times 10^{-7}$     | 0.190             | 0.195             |
| B2                                                                                                                   | -0.343                 | $2.14 \times 10^{-7}$     | 0.241             | 0.191             |

**[0043]** All sample sets containing the organic modifier (B) displayed better passivation than sample A1, which can be seen by the slope of  $\beta_a$  and the  $E_{corr}$  values for B1 and B2 were shifted anodically from the A1 values. The slope of this linear region represents a passivity due to a thicker oxide layer. The  $i_{corr}$  values were all in the same range of  $10^{-7}$  Acm $^{-2}$ , with A1 displaying the lowest corrosion current of  $\sim 2 \times 10^{-7}$  Acm $^{-2}$ . The anodic slopes of  $\beta_a$ , describe the onset of passivation and the rate at which a passive oxide layer forms. The corrosion studies show again that there is an improvement in corrosion resistance when additions of BuOH are added to the plating bath.

What is claimed is:

1. A method for electrodepositing nickel coatings, comprising:

preparing an aqueous bath comprising nickel and about 5% to about 10% by volume of an organic modifier, wherein the aqueous bath has an acidic pH;  
submerging electrode substrates in the aqueous bath; and  
using modified pulse reverse deposition to electrodeposit the nickel coatings on the substrates.

2. The method of claim 1, wherein the organic modifier is butanol.

3. The method of claim 1, wherein the acidic pH is about 2.5 to about 3.5.

4. The method of claim 1, wherein the aqueous bath further comprises sodium borate.

5. The method of claim 1, wherein all steps are carried out at room temperature.

6. An electrodeposited nickel coating prepared by the method of claim 1.

7. A method for electrodepositing nickel coatings, comprising:

preparing an aqueous bath comprising nickel, sodium borate, and about 5% to about 10% by volume of butanol, wherein the aqueous bath has pH of about 2.5 to about 3.5;

submerging electrode substrates in the aqueous bath; and using modified pulse reverse deposition to electrodeposit the nickel coatings on the substrates, wherein all steps are carried out at room temperature.

8. An electrodeposited nickel coating prepared by the method of claim 7.

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