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[Continued on next page]

(54) Title: ELECTRODEPOSITION OF Al-Ni ALLOYS AND Al/Ni MULTILAYER STRUCTURES



FIG. 1A

(57) Abstract: A method for electrodepositing aluminum and nickel using a single electrolyte solution includes forming a mixture comprising nickel chloride and an organic halide, adding aluminum chloride to the electrolyte solution in an amount at which the mixture becomes an acidic electrolyte solution, providing a working electrode and a counter electrode in the acidic electrolyte solution, and applying a waveform to the counter electrode using cyclic voltammetry to cause aluminum and nickel ions to be deposited on the working electrode.



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ELECTRODEPOSITION OF Al-Ni ALLOYS AND Al/Ni MULTILAYER STRUCTURES

5 Cross-Reference to Related Application

This application claims priority to co-pending U.S. Provisional Application Serial Number 62/199,464, filed July 31, 2015, which is hereby incorporated by reference herein in its entirety.

10 Background

Alloys comprising aluminum (Al) and one or more transition metals (TMs) exhibit excellent physical and mechanical properties. Among the various transition metals with which Al can be alloyed, nickel (Ni) is particularly interesting because Al-Ni alloys exhibit excellent corrosion resistance, high temperature oxidation
15 resistance, high strength, good ductility, and magnetic pertinence. In addition to Al-Ni alloys, Al/Ni multilayer structures that comprise alternate layers of Al and Ni are of interest because such structures also exhibit many desirable properties, including easy ignition, self-sustaining exothermic synthesis after reaction, high local temperatures upon propagation (around 1000°C), and zero emission.

Various processing techniques have been used to synthesize Al-Ni alloys and Al/Ni multilayer structures, including physical vapor deposition (PVD), plasma-assisted chemical vapor deposition (PACVD), hot pressing, and electromagnetic stirring. Not included in this list, however, is electrodeposition. The reason for this is that it is difficult to form Al-Ni alloys and Al/Ni multilayer structures through electrodeposition using a single electrolyte solution. Conventionally, electrodeposition of Ni is performed using an aqueous solution at or near room temperature, while electrodeposition of Al is typically performed using a molten salt electrolyte at high temperature (e.g., $\sim 1000^{\circ}\text{C}$). It is unfortunate that a suitable electrodeposition technique has not been developed for these metal systems because electrodeposition is more economical and easier to scale as compared to the other techniques that have been used. In addition, electrodeposition enables one to easily control the composition and phase of the deposit through adjustment of the deposition parameters, including electrolyte composition, agitation, temperature, and current/potential.

In view of the above discussion, it can be appreciated that it would be desirable to be able to form Al-Ni alloys and/or Al/Ni multilayer structures through electrodeposition.

Brief Description of the Drawings

The present disclosure may be better understood with reference to the following figures. Matching reference numerals designate corresponding parts throughout the figures, which are not necessarily drawn to scale.

Figs 1A-1C are photographs of (A) a 2:1 AlCl_3 :EMIM electrolyte under agitation, (B) a bright orange AlCl_3 -EMIM- NiCl_2 suspension, and (C) AlCl_3 -EMIM-

NiCl₂ with undissolved NiCl₂ at the bottom.

Figs. 2A and 2B are photographs of (A) a basic NiCl₂-EMIM-AlCl₃ solution and (B) and acidic AlCl₃-EMIM-NiCl₂ solution.

Fig. 3 is a graph showing cyclic voltammograms on W electrodes measured with scan rate of 20 mV/s with a step size of 2 mV in AlCl₃-EMIM compared with AlCl₃-EMIM containing 0.026 mol L⁻¹ NiCl₂.

Fig. 4 is a graph showing a comparison of cyclic voltammograms on W electrodes in AlCl₃-EMIM, AlCl₃-EMIM containing 0.024 mol L⁻¹ NiCl₂, AlCl₃-EMIM containing 0.026 mol L⁻¹ NiCl₂, and AlCl₃-EMIM containing 0.1 mol L⁻¹ NiCl₂ measured with scan rate of 20 mV/s with a step size of 2 mV.

Fig. 5 is a graph showing cyclic voltammograms on W electrodes measured with scan rate of 20 mV/s with a step size of 2 mV in AlCl₃-EMIM compared with AlCl₃-EMIM containing 0.026 mol L⁻¹ NiCl₂.

Fig. 6 is a graph showing a comparison of cyclic voltammograms on Cu electrodes in AlCl₃-EMIM, AlCl₃-EMIM containing 0.024 mol L⁻¹ NiCl₂, AlCl₃-EMIM containing 0.026 mol L⁻¹ NiCl₂, and AlCl₃-EMIM containing 0.1 mol L⁻¹ NiCl₂ measured with scan rate of 20 mV/s with a step size of 2 mV.

Fig. 7 is a photograph showing multiple electrodeposited samples (Samples 1-9).

Figs. 8A-8F are scanning electron microscope (SEM) images of (A) Sample 1, (B) Sample 2, (C) Sample 3, (D) Sample 5, (E) pure Al deposit at -0.3 V in 1.5:1 M AlCl₃-EMIM containing 0.026 M NiCl₂, and (F) pure Ni deposit at 0.4 V in 1.5:1 M AlCl₃-EMIM containing 0.1 M NiCl₂.

Fig. 9 is a SEM image of a focused ion beam (FIB) cross-section of Ni/Al bilayer sample.

Fig. 10 is a flow diagram of an embodiment of a method for electrodepositing aluminum and nickel using a single electrolyte solution.

Detailed Description

5 As described above, it would be desirable to be able to form aluminum-nickel (Al-Ni) alloys and/or aluminum/nickel (Al/Ni) multilayer structures through electrodeposition. Disclosed herein are methods for forming such alloys and structures through electrodeposition using a single electrolyte solution. In some embodiments, Al-Ni alloys are electrodeposited at room temperature using an electrolyte comprising a solution of aluminum chloride (AlCl_3), nickel chloride (NiCl_2), and an organic halide. In some embodiments, Al/Ni multilayer structures are formed by first depositing Ni and then depositing Al on the nickel using a single electrolyte solution comprising AlCl_3 , NiCl_2 , and a an organic halide. In some embodiments, the organic halide can be selected from the group consisting of 1-ethyl-3-
10 methylimidazolium chloride (EMIM), N-[n-Butyl] pyridinium chloride (BPC), and trimethylphenylammonium chloride (TMPAC).
15

In the following disclosure, various specific embodiments are described. It is to be understood that those embodiments are example implementations of the disclosed inventions and that alternative embodiments are possible. All such
20 embodiments are intended to fall within the scope of this disclosure.

Electrodeposition in non-aqueous room-temperature solutions or ionic liquids provides a cost-effective alternative to fabricating Al alloys and multilayer structures. As used herein, the term "multilayer structure" is used to describe any structure comprising multiple alternating layers of materials, including "bilayer" structures that
25 comprise two alternate layers of material and structures that comprise three or more

layers of alternating material. Room temperature ionic liquids synthesized by adding AlCl_3 to an organic halide provides useful and attractive characteristics, such as adjustable Lewis acidity, wide electrochemical window, aprotic nature, room-temperature stability, good conductivity, and low vapor pressure. AlCl_4^- and Al_2Cl_7^- unsaturated species are present in the electrolyte while the concentration of the latter increases with electrolyte acidity. The acid-base characteristic of this melt is represented by the reaction,



In AlCl_3 -EMIM electrolyte, Al electrodeposition can only be successful in an acidic solution because the formation of the electroactive Al_2Cl_7^- is formed only when the molar fraction of AlCl_3 becomes larger than 0.5. In basic AlCl_3 -EMIM solutions, the only electroactive specie is AlCl_4^- , whose reduction potential is more negative than the breakdown potential of the organic cation from the electrolyte. The electrochemically active Al_2Cl_7^- unsaturated ion reduces to Al at the cathode according to the following reaction,



For Al-Ni electrodeposition, AlCl_3 -EMIM- NiCl_2 of desired molarity is required. Previous studies suggest that NiCl_2 is difficult to dissolve in acidic AlCl_3 -BPC, while it is readily dissolved in basic melt. However, there have only been a few studies on the behavior of the dissolution of NiCl_2 in AlCl_3 -EMIM and its electrochemical properties. Described below is the electrochemistry of Al-Ni deposition, the

parameters that affect the alloy composition and microstructure, and synthesis and electrochemical properties of room-temperature electrolytes (molten salts) that can be used to produce electrodeposited Al-Ni alloys and Al/Ni multilayer structures. The electrolytes comprise an ionic solution including AlCl_3 , NiCl_2 , and an organic halide, such as AlCl_3 -EMIM- NiCl_2 .

Electrodeposition experiments were performed using a three-electrode setup inside an argon-filled glovebox (Mbraun Labstar, H_2O and $\text{O}_2 < 1$ ppm). A Gamry Reference 600 potentiostat was used for electrodeposition and cyclic voltammetry measurements. Acidic metal bases, including anhydrous aluminum chloride (AlCl_3 , 99.999%, Aldrich) and anhydrous nickel chloride (NiCl_2 , 99%, Alfa Aesar), were used as-received. 1-Ethyl-3-methylimidazolium chloride (EMIM, >98%, Lohitec) was heated at 60°C for 3 days under vacuum to remove excess moisture. Al plate (99.99%, Alfa Aesar) and Al wire (99.99%, Alfa Aesar) were used as the counter and reference electrodes, respectively, unless specified otherwise. Three different materials: copper (Cu) plate (99.99%, Online Metals, 25 x 15 x 1 mm), Al plate (99.99%, Alfa Aesar, 25 x 15 x 1 mm), and tungsten (W) wire (99.99%, Sigma Aldrich, 1 mm diameter) were employed as the working electrodes. The exposed areas of the Al and Cu working electrodes were limited to 2.25 cm² by covering the remainder of the areas with epoxy or electrochemical stop liquor. The Al electrodes were polished with 180-grit silicon carbide (SiC) paper and then dipped in an acid solution of 70% H_3PO_4 , 25% H_2SO_4 and 5% HNO_3 (by volume) for 10 minutes to remove the native oxides from the Al surface. The Cu electrodes were pretreated in an acid solution of 10% H_2SO_4 and 90% water (H_2O) (by volume) for 30 seconds. The W electrode was used as received. The deposited structures were characterized using scanning electron microscopy (SEM) (Hitachi SU-70) and energy-dispersive X-ray

spectroscopy (EDS) (EDAX-Phoenix). A cross-section of an Al/Ni bilayer was obtained by ion milling using focused ion beam microscopy (FIB) (FEI Quanta 200).

To study the dissolution behavior of NiCl_2 in AlCl_3 -EMIM, 0.01 M NiCl_2 was first directly added to a 2:1 molar ratio of AlCl_3 -EMIM electrolyte. After 24 hours of stirring, the clear electrolyte (Fig. 1A) turned into a bright orange suspension (Fig. 1B). Leaving the electrolyte unstirred for 24 hours caused the undissolved particles to settle at the bottom of the beaker (Fig. 1C). These observations reveal the low solubility of NiCl_2 in acidic chloroaluminate electrolyte. The NiCl_2 was readily dissolvable, however, in basic AlCl_3 -EMIM electrolyte. A desired amount of NiCl_2 was first added to EMIM. AlCl_3 was then slowly added to the mixture. AlCl_3 immediately reacts with EMIM leading to an acid-base reaction. This reaction is exothermic, accompanied by the release of white fumes. When the molar fraction of AlCl_3 (i.e. $[\text{AlCl}_3] / [\text{AlCl}_3] + [\text{EMIM}]$) is less than 0.5, the solution formed was basic which favors the dissolution of NiCl_2 . A clear green solution was observed, as shown in Fig. 2A. Increasing NiCl_2 from 0.026 to 0.1 M changes the solution color from green to blue. As soon as the molar fraction of AlCl_3 reaches 0.5, the solution turns brown as seen in Fig. 2B, indicating a shift from basic to acidic solution.

Further addition of AlCl_3 was performed to shift the reduction potential of Al to support its deposition. It was noticed that AlCl_3 was easily dissolved beyond 1:1 molar ratio of AlCl_3 :EMIM but could not reach 2:1 as excess AlCl_3 precipitated without dissolution. This can be understood by the fact that Ni_2^+ ions consume some of the EMIM anions making less available reactive anions for Al_3^+ cations. Thus, the molarity ratio of the AlCl_3 :EMIM was limited to 1.5:1 for all experiments. The resultant electrolyte (hereafter referred as NiCl_2 -EMIM- AlCl_3 electrolyte) was a clear brown solution and was used without further purification.

A voltage sweep starting from 2 V versus Al/Al_3^+ to -0.5 V and reversed back to 2 V was applied to determine the oxidation and reduction peaks suggesting dissolution and deposition of the respective metals or alloys, respectively. The peak shapes in the voltammograms depicted in Fig. 3 are consistent with those illustrated for AlCl_3 -EMIM and AlCl_3 -EMIM- NiCl_2 . A reduction wave C_1 and an oxidation peak A_1 with a peak potential at 0.44 V is observed in the voltammogram of AlCl_3 -EMIM, which is attributed to the bulk deposition and bulk stripping of Al, respectively. Al reduction started at -130 mV versus Al/Al_3^+ revealing the need of a relatively large nucleation overpotential. The electrolyte with 0.026 mol^{-1} shows additional peaks C_2 at 0.4 V attributed to the deposition of bulk Ni, as confirmed by EDS analysis. The constant cathodic peak ranging from -0.12 to 0.3 V can be attributed to the deposition of intermetallic Al-Ni alloys since this range corresponds to their deposition potential range, which is 0.08 to -0.2 V. Peaks A_2 and A_3 correspond to the relative stripping of Al-Ni intermetallic and bulk Ni, respectively. It can be clearly stated that the amount of NiCl_2 dissolved in the melt is in direct proportionality with the intensities of C_2 , A_2 , and A_3 peaks due to more Ni_2^+ ions available in the electrolyte, as shown in Fig. 4.

Cyclic voltammetry with similar parameters was conducted on the Cu electrode to study the variations in the peak potentials for Al and Ni deposition shown in Fig. 5. Unlike inert W, Cu is electrochemically active, thus an anodic potential versus the aluminum reference electrode is observed until the first reduction peak, which represents constant dissolution of Cu in the electrolyte. The peak C_1 on the scan attributed to the reduction of Al reveals that the deposition of Al starts at -0.2 V, which deviated slightly from the C_1 on W. Consequently, the peak A_1 corresponds to the oxidation of bulk Al where Al is completely stripped away from the

substrate. The reduction peak C_3 at 0.5 V conforms to the deposition of Cu as it lies in proximity of the standard reduction potential of Cu. Cu undergoes oxidation represented by the A_4 peak at 1.5 V since the Cu electrode etched away at this potential. Minor oxidation and reduction peaks A_2 and C_2 are related to the underpotential stripping and deposition of Al on the Cu substrate. The reduction potential of Al-Ni intermetallics and bulk Ni did not vary significantly and were found to be 0 and 0.3 V respectively. Ni and Al-Ni peaks increase with the increasing amount of $NiCl_2$ dissolved in the melt, as shown in Fig. 6. The increase in the Ni peaks are counterbalanced by the evident decrease in the Al peaks owing to the reduced dissolution of $AlCl_3$ in the electrolyte.

A number of samples with different parameters were deposited to study the effect of deposition potentials, duty ratios, and frequencies on alloy composition, as shown in Fig. 7. The deposition parameters for each sample and their EDS results are tabulated in Table 1.

Table 1. Electrodeposition parameters and composition of deposits.

Sample	Amount of NiCl_2 in AlCl_3 -EMIM (M)	Substrate	Negative Potential (V)	Positive Potential (V)	Duty cycle ratio of negative to positive	Frequency f(Hz)	Deposit-ion(s)	Concentration (wt. %)		Concentration (at.%)	
								Al	Ni	Al	Ni
1	0.024	Cu	-0.3	0.15	9:1	1	3600	94.3	5.7	97.3	2.7
2	0.026	Cu	-0.5	0.4	4:1	1	3600	95.8	4.2	98.1	1.9
3	0.26	Cu	-0.3	0.15	1:1	1	7200	95.7	4.3	98	2
4	0.026	Cu	-0.3	0.15	1:1	0.5	7200	90.4	9.6	95.3	4.7
5	0.1	Cu	-0.3	0.15	1:1	1	7200	87.8	12.2	94	6
6	0.1	Cu	-0.3	0.15	9:11	1	7200	94.1	5.9	97.2	2.8
7	0.1	Electrode- posited Cu	-0.3	0.15	1:1	1	3600	68.2	31.8	82.3	17.7
8	0.026	Electrode- posited	-0.3		—	—	150	Pure Al			
9	0.026	Cu	0.4		—	—	375	Pure Ni			

Samples 3 and 5 were deposited using the same potential, duty cycle ratio, and frequency in AlCl_3 -EMIM containing 0.026 M and 0.1 M of NiCl_2 , respectively.

- 5 The Ni concentration increased nonlinearly from 2 to 6 at.% as the amount of NiCl_2 increased due to the availability of more Ni and fewer Al ions shown by their peaks in the CV. This non-linear proportionality with a much greater deviation can also be observed when comparing samples 1 and 6.

- 10 Samples 5 and 6 with duty ratios 1:1 and 9:1, respectively, were deposited in AlCl_3 -EMIM containing 0.1 M NiCl_2 using the same potentials. It was observed that the Al and Ni contents increased with increasing the time of the positive and negative cycles of the pulse, respectively. In Sample 5, the 9:1 ratio potential pulse spends most of the time in the negative cycle at -0.3 V responsible for depositing Al, while the positive pulse, which is just 1/10th of the total cycle, decreases the time for the
- 15 deposition of Ni and stripping of Al. On the contrary, in Sample 6, the 1:1 ratio

provides more time for Ni to be deposited. Also, since the reduction potential of Ni lies in close proximity of the oxidation potential of Al, Al stripping accompanies Ni deposition, resulting in lesser amount of Al in the mix.

The effect of frequency on the Al-Ni composition can be analyzed using Samples 3 and 4 deposited with frequencies 1 and 0.5 Hz with the same electrolyte, potential, and duty ratio. Decreasing the frequency by half resulted in almost twice the amount of Ni in the deposited alloy. With frequencies of 1 and 0.5 Hz, the deposition of Al and Ni takes place for 0.5 second and 1 second in each cycle, respectively. Since Ni deposition occurs via three-dimensional progressive nucleation, with more time for each cycle in the 0.5 Hz frequency, the current transient draws more current in 1 second as compared to that drawn in 2 cycles of 0.5 seconds in 1 Hz frequency. This increased current density on the Ni deposition cycle results in the increased Ni content.

Sample 7 was deposited on a smooth electrodeposited Cu substrate with the same potential, frequency, duty ratio, and electrolyte as Sample 5, which was deposited on a relatively rougher Cu substrate. Ni concentration was found to increase from 6 to 17.7 at.% using a smoother surface. The electrodeposited Cu substrate provides a much smoother surface with nano-scale roughness, which might favor metal nucleation resulting in better adherence of the Ni particles.

The SEM image of Sample 1 in Fig. 8A shows dense nodular structures consistent with previous studies. Sample 2 shows a columnar surface morphology with widely spread nodules, as shown in Fig. 8B. A close examination on the inset image of Fig. 8B reveals the presence of smaller nodules in the range of 10 to 15 μm with a cauliflower like appearance consistent with previous work. The cauliflower structure appears due to higher deposition rate with the increase of potential.

Samples 3 and 5 show coarse flake-like structures in Figs. 8C and 8D. A study suggests that the increase in the thickness of the deposit makes the surface of Al-Ni rougher. This was not found to be the case since Sample 7, deposited with the same parameters as Sample 5 but on smooth Cu substrate, also inhibited the flake structure. Also, this structure seems to be independent of the molarity of NiCl_2 in the melt since it was different for Sample 3. The formation of these flakes is not related to the potential used since Sample 1 uses the same potential but formed columnar structure. At the same time, it is not due to the frequency since Samples 1 and 2 have the same frequency. The only parameter that all of the flake structured deposits have in common is the duty ratio. These results indicate that the increased time for the Ni deposition and Al stripping in the positive cycle of the pulse affects the microstructure. Al deposits generally have nodular morphology but they have also been reported to form flake structures, while Ni deposits have been shown to have columnar cauliflower structures. The observed flake structures of the Al-Ni deposits appear to be a hybrid of the flake Al and cauliflower Ni. Dense and compact pure Al and Ni were also deposited having fine crystalline and nodular cauliflower microstructures, respectively.

Application of this system to Al/Ni bilayers was also tested and revealed useful results. A successful bilayer sample with Ni deposited on electrodeposited Cu with a pulse potential of 0 and 0.78 V for 800 seconds, and Al deposited at a constant -0.3 V for 150 seconds in AlCl_3 -EMIM containing 0.026 M NiCl_2 was prepared. The first cycle of the pulse potential waveform for the deposition of Ni was set to 0V. 0.78 V for the second cycle was chosen as the potential where the current becomes zero from voltammogram in Fig. 5. This waveform was selected to promote progressive nucleation of Ni in each cycle as opposed to a constant potential, which

imparts diffusion-controlled growth of Ni nuclei. A cross-section of the Ni/Al bilayer was milled using FIB imaging, as shown in Fig. 9. A clear color contrast between the darker Al and brighter Ni layers is observed. However, the difference in color contrast between Ni and Cu is not clearly visible since their atomic numbers differ only by 1. The known thickness of the electrodeposited Cu is 1 μm . From this, the thickness of Ni layer was estimated to be 1 μm while that of Al was 250 nm. The darker region beneath the electrodeposited Cu is the substrate.

As described in the foregoing discussion, electrodeposition of Al-Ni alloys and Al/Ni multilayer structures have been successfully demonstrated. Dissolution of NiCl_2 in an AlCl_3 -EMIM room-temperature melt was found to be favorable in basic electrolyte. A detailed study on the electrochemical properties of the electrolyte using cyclic voltammetry has been performed. The use of an electrochemically active Cu working electrode effects the electrochemistry of the electrolyte by dissolving Cu in the scan range of 1 to 2 V and introducing additional oxidation and reduction peaks pertaining to the stripping and deposition of Cu. The current density of Ni and Al oxidation and reduction peaks vary directly and indirectly to the amount of NiCl_2 dissolved in the AlCl_3 -EMIM electrolyte respectively. The concentration of Ni in the Al-Ni alloys increased with the increase in amount of NiCl_2 dissolved in the melt, increase in the time period of positive potential cycle, decrease in frequency, and decrease in surface roughness of the working electrode. The Al-Ni alloys typically showed nodular morphology with a cauliflower structure. Flake structures, which were independent of surface roughness, were found to develop for a 1:1 duty ratio. XRD on the Al-Ni alloys suggests the presence of supersaturated FCC crystalline solid solution of Al and Ni. A uniform Al/Ni bilayer was successfully deposited in 1.5:1 AlCl_3 -EMIM containing 0.026 M NiCl_2 . Deposition of Al on Ni was achieved.

Fig. 10 is a flow diagram of an embodiment of a method for electrodepositing Al and Ni (i.e., Al-Ni alloys or Al/Ni multilayer structures) using a single electrolyte solution that is consistent with the above-described electrodeposition methods. Beginning with block 10, a desired amount of NiCl_2 is first added to an organic halide to obtain a NiCl_2 -organic halide mixture. The amount of NiCl_2 that is added may depend on the nature of the alloy or multilayer structure that is to be formed. By way of example, the organic halide can comprise EMIM.

Referring next to block 12, AlCl_3 is added to the NiCl_2 -organic halide mixture to obtain an AlCl_3 -organic halide- NiCl_2 electrolyte solution. As described above, when the electrolyte solution contains small amounts of AlCl_3 , the electrolyte solution is basic. When the molar fraction of AlCl_3 reaches 0.5 or greater, however, the electrolyte solution becomes acidic, which facilitates electrodeposition of Al. Accordingly, the AlCl_3 is added in an amount sufficient to change the AlCl_3 -organic halide- NiCl_2 electrolyte solution from a basic electrolyte solution to an acidic electrolyte solution. Accordingly, AlCl_3 is added until the molar fraction of AlCl_3 within the solution is 0.5 or greater. In some embodiments, AlCl_3 is added to the electrolyte solution until a molar ratio of AlCl_3 :organic halide is 1.5:1. In some embodiments, the NiCl_3 is added to the electrolyte solution until a molar ratio of NiCl_3 : AlCl_3 -organic halide is 0.24 to 0.1.

With reference next to block 14, working, reference, and counter electrodes can be provided (immersed) in the acidic AlCl_3 -organic halide- NiCl_2 electrolyte solution and, with reference to block 16, a waveform is applied to the counter electrode using cyclic voltammetry to deposit Al and Ni on the working electrode. The various parameters of the cyclic voltammetry, such as the applied potential, the frequency, the duty cycle ratio, and time, can be selected depending upon the alloy

or multi-layer structure that is desired. Notably, however, the electrolyte solution need not be heated and, therefore, electrodeposition can be performed at room temperature.

CLAIMS

Claimed are:

1. A method for electrodepositing aluminum and nickel using a single electrolyte solution, the method comprising:
 - forming a mixture comprising nickel chloride and an organic halide;
 - adding aluminum chloride to the mixture in an amount at which the mixture becomes an acidic electrolyte solution;
 - providing a working electrode and a counter electrode in the acidic electrolyte solution; and
 - applying a waveform to the counter electrode using cyclic voltammetry to cause aluminum and nickel ions to be deposited on the working electrode.
2. The method of claim 1, wherein the organic halide comprises 1-ethyl-3-methylimidazolium chloride.
3. The method of claim 1, wherein the organic halide comprises N-[n-Butyl] pyridinium chloride.
4. The method of claim 1, wherein the organic halide comprises trimethylphenylammonium chloride.
5. The method of claim 1, wherein forming a mixture comprises forming a mixture comprising approximately 0.024 to 0.1 M of nickel chloride.
6. The method of claim 1, wherein adding aluminum chloride comprises

adding aluminum chloride in a molar ratio of aluminum chloride:organic halide that is no greater than 1.5:1

7. The method of claim 1, wherein providing a working electrode comprises providing an aluminum, copper, or tungsten electrode in the acidic electrolyte solution.

8. The method of claim 1, wherein applying a waveform comprises applying a waveform while the acidic electrolyte solution is at room temperature.

9. The method of claim 1, wherein applying a waveform comprises applying a potential of approximately -0.3 V to 0.4 V.

10. The method of claim 1, wherein applying a waveform comprises applying a waveform having a duty cycle ratio of approximately 1::1 to 9::1.

11. The method of claim 1, wherein applying a waveform comprises applying a waveform having a frequency of approximately 0.5 to 1 Hz.

12. The method of claim 1, wherein applying a waveform comprises applying the waveform for approximately 150 to 7200 seconds.

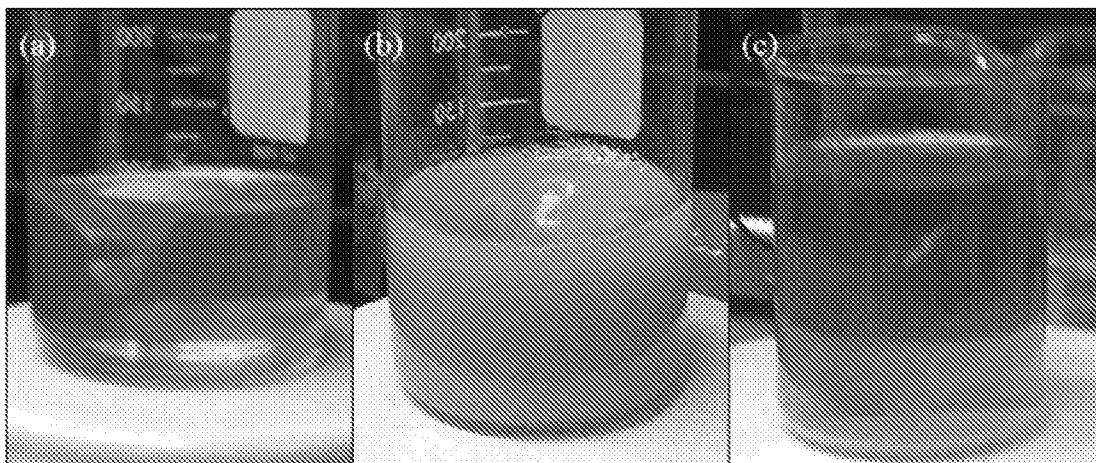
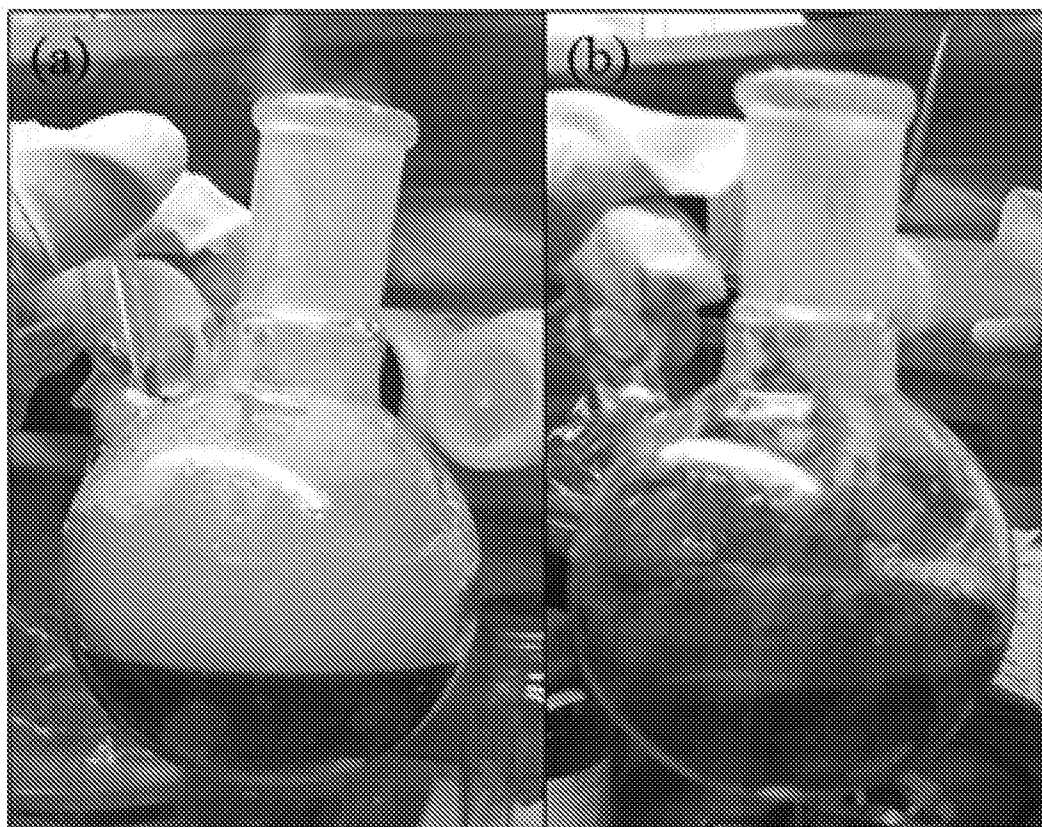
13. The method of claim 1, wherein applying a waveform comprises applying the waveform in a manner in which an aluminum-nickel alloy is deposited on the working electrode.

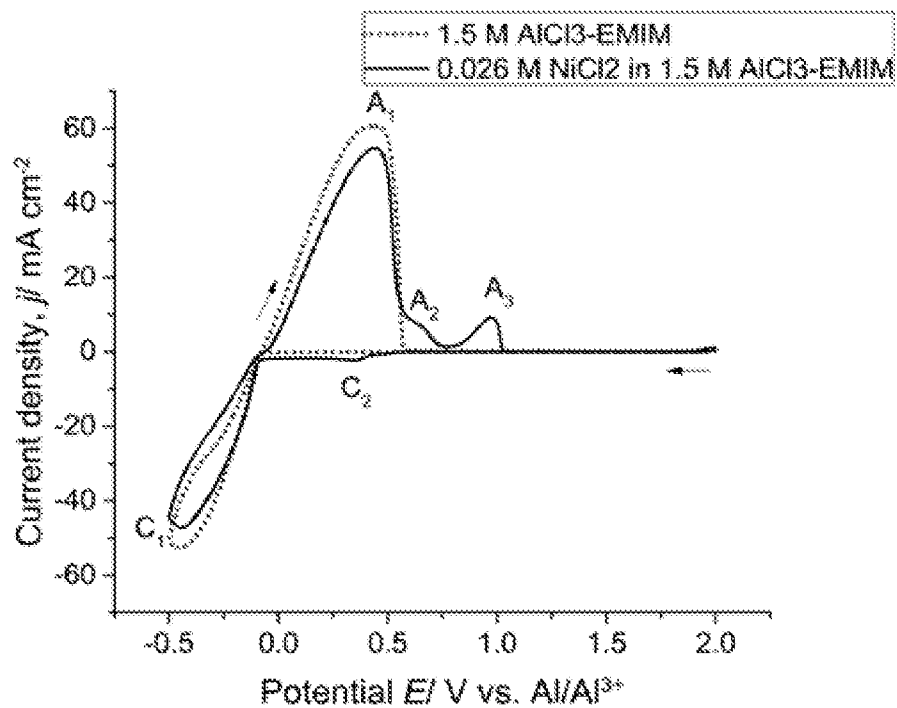
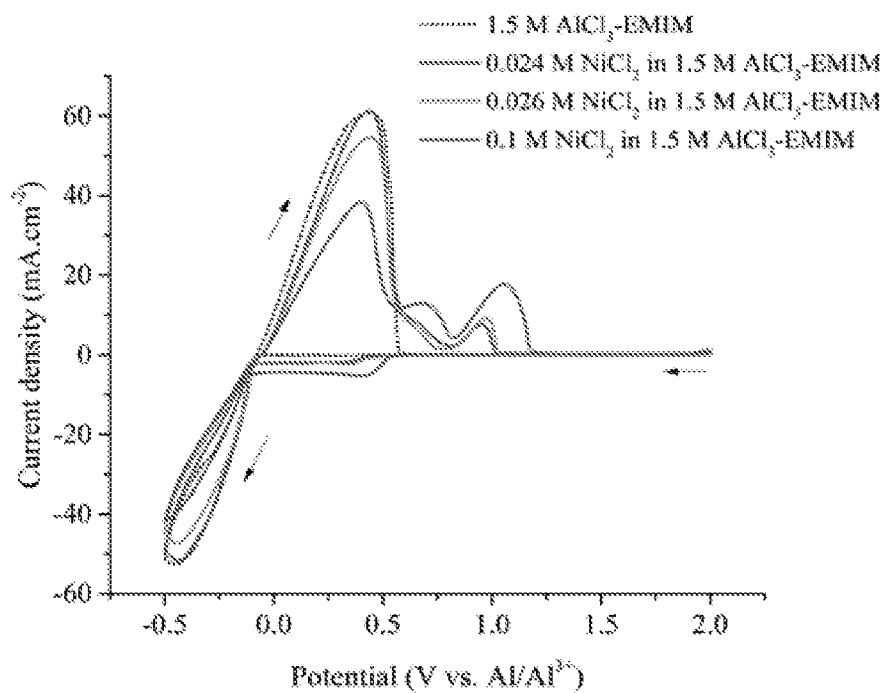
14. The method of claim 13, wherein the aluminum-nickel alloy comprises at least approximately 90% aluminum by weight percentage.

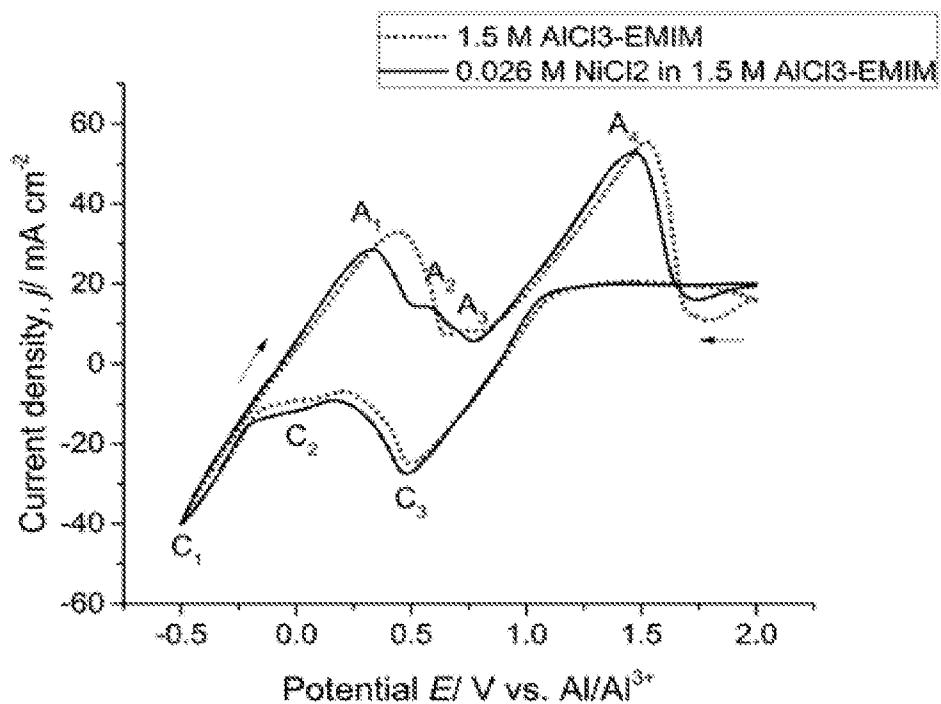
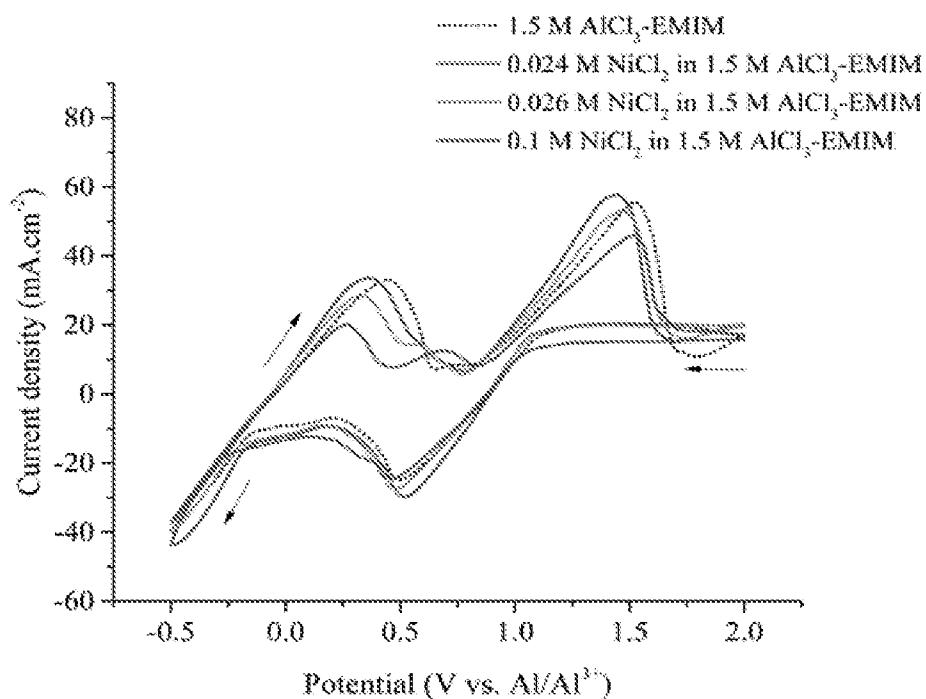
15. An aluminum-nickel alloy formed using the method of claim 14.

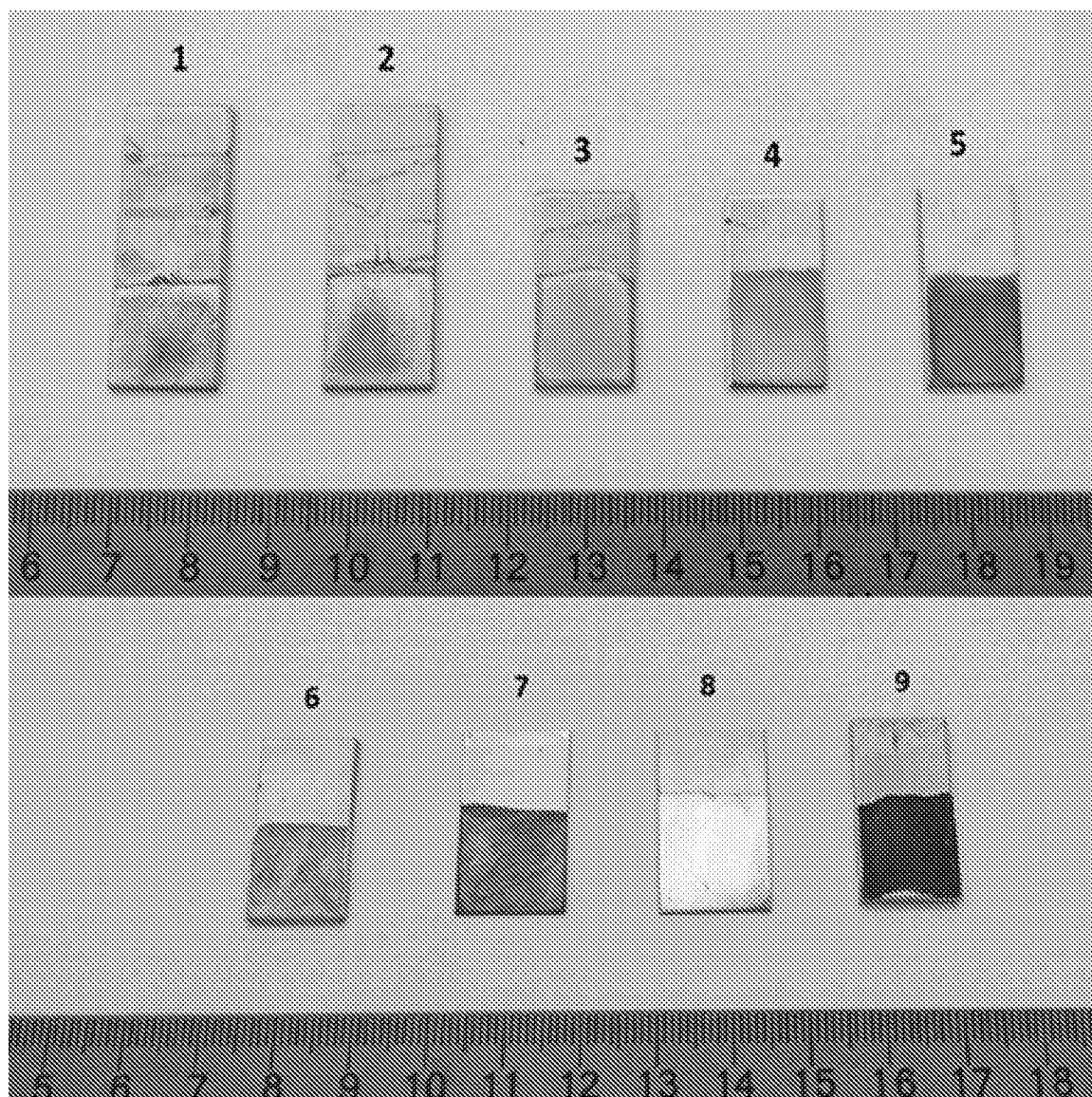
16. The method of claim 1, wherein applying a waveform comprises applying the waveform in a manner in which a multilayer structure is formed having alternating layers of aluminum and nickel.

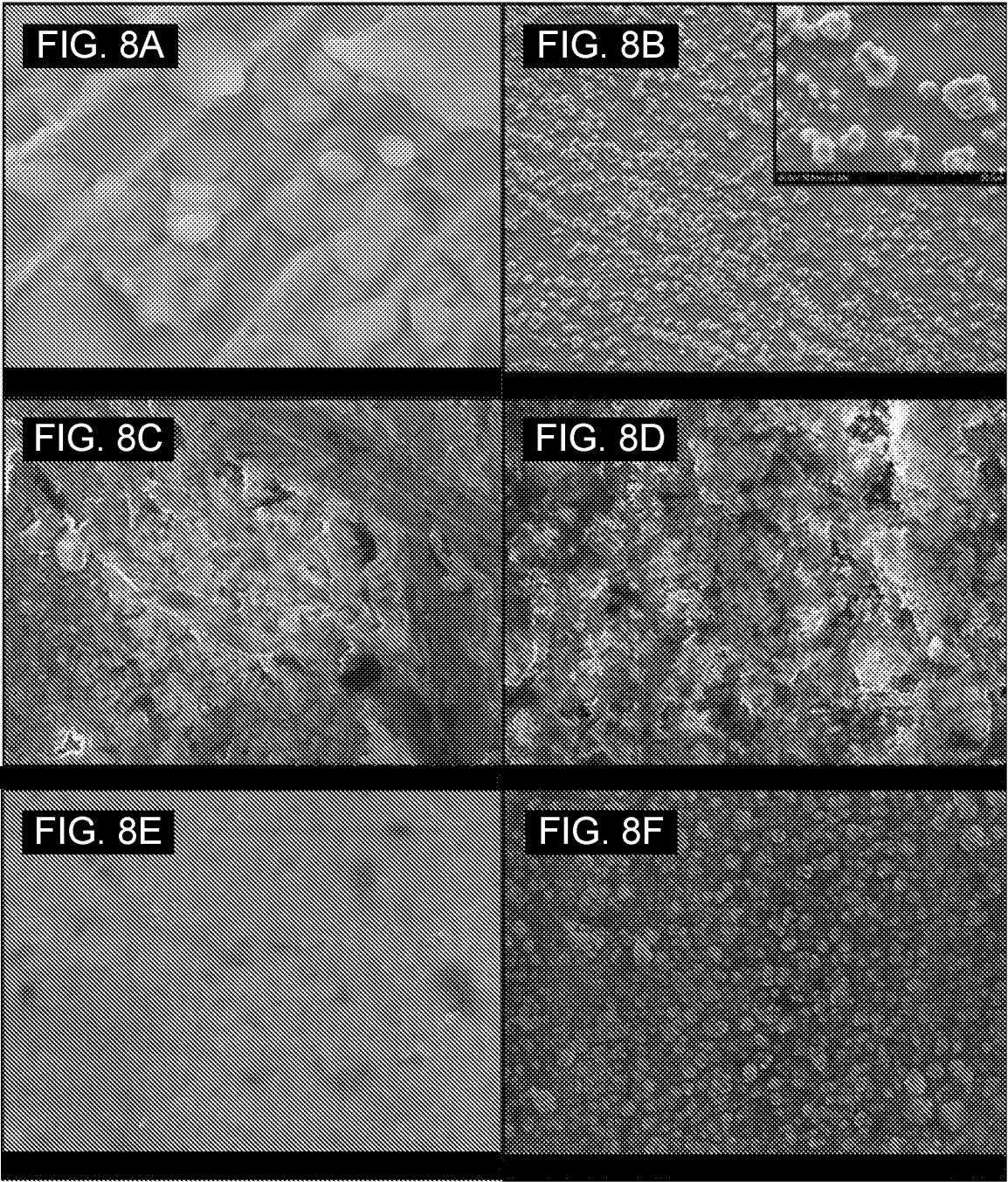
17. An aluminum/nickel multilayer structure formed using the method of claim 16.

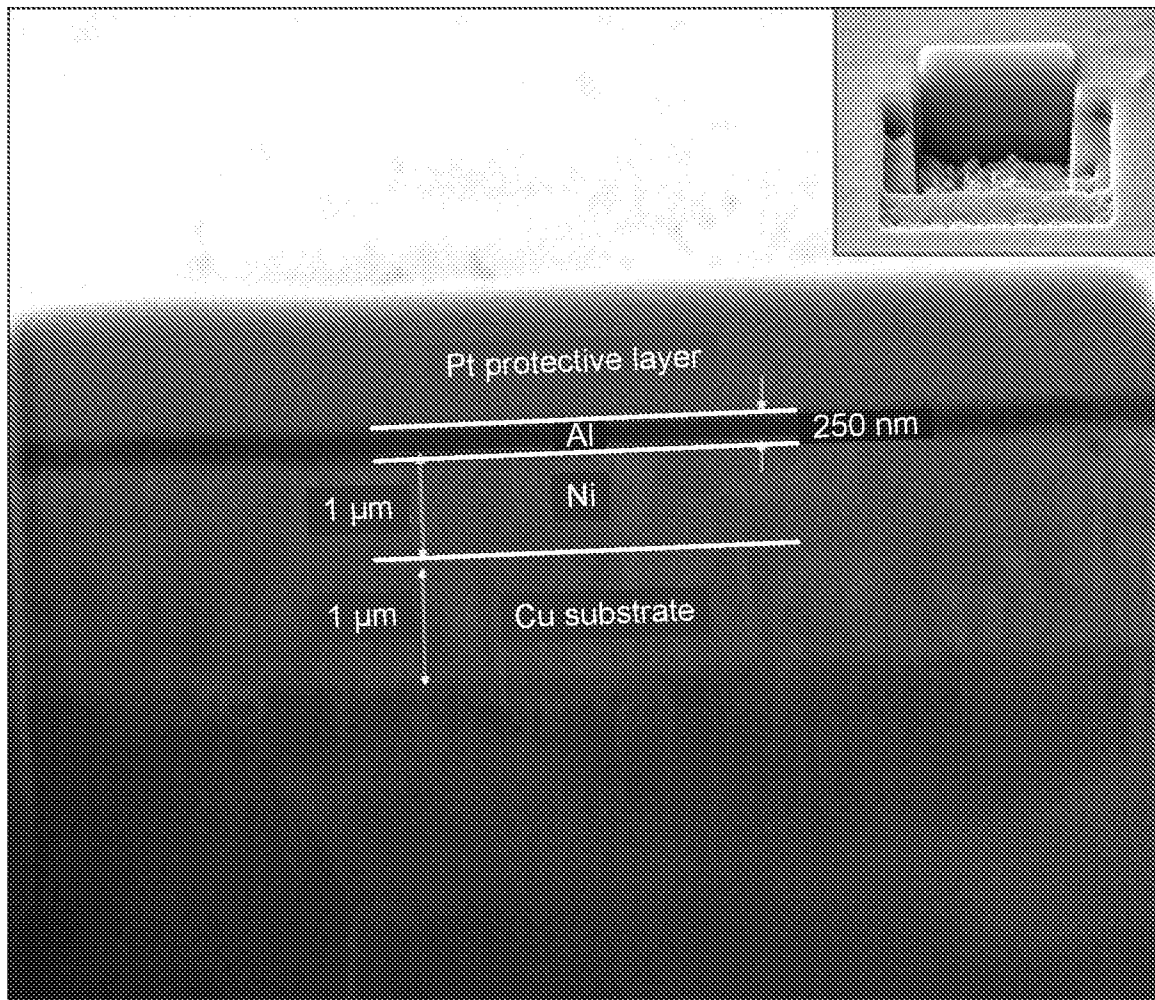
**FIG. 1A****FIG. 1B****FIG. 1C****FIG. 2A****FIG. 2B**

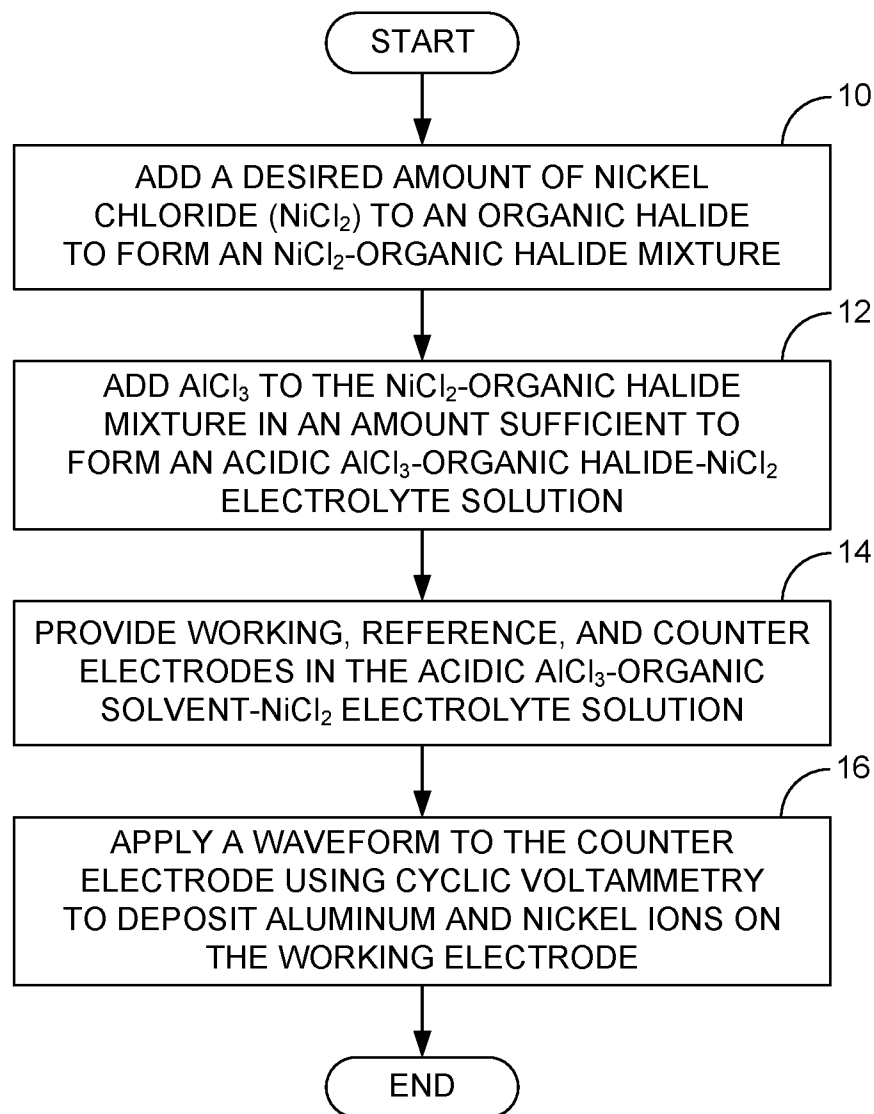
**FIG. 3****FIG. 4**

**FIG. 5****FIG. 6**

**FIG. 7**



**FIG. 9**

**FIG. 10**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/44689

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C25D 3/44, C25D 3/02, C25D 3/04 (2016.01)

CPC - F05D 2300/121, C25D 3/562, C25D 7/008

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - C25D 3/44, C25D 3/02, C25D 3/04 (2016.01)

CPC - F05D 2300/121, C25D 3/562, C25D 7/008

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Patents and non-patent literature (classification, keyword; search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatBase, Google Scholar (non-patent literature), Google Patents; search terms: electrodeposition, aluminum, nickel, aluminum-nickel, alloy, chloride, organic halide, acidic, waveform, cyclic voltammetry

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Waqar. "Exploration of Electrodeposition of Aluminum-Nickel Alloys and Multilayers in Organic Chloroaluminate Ionic Liquids." Graduate Theses and Dissertations, 2014. Download available since 9 July 2015 (09.07.2015), entire document	1-17
A	US 2014/0374263 A1 (Cai et al.) 25 December 2014 (25.12.2014), entire document, especially abstract, para [0008], [0010], [0012], [0013], [0035]	1-17
A	US 2011/0083967 A1 (Ruan et al.) 14 April 2011 (14.04.2011), entire document, especially abstract, para [0018], [0034], [0085], [0086], [0088]	1-17
A	US 2012/0118745 A1 (Bao) 17 May 2012 (17.05.2012), entire document	1-17
A	US 2006/0272949 A1 (Detor et al.) 7 December 2006 (07.12.2006), entire document	1-17

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

9 September 2016

Date of mailing of the international search report

20 OCT 2016

Name and mailing address of the ISA/US

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