



- (51) International Patent Classification:
C25D 5/34 (2006.01)
- (21) International Application Number:
PCT/US2015/010855
- (22) International Filing Date:
9 January 2015 (09.01.2015)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
61/927,637 15 January 2014 (15.01.2014) US
- (71) Applicant: **THE BOARD OF TRUSTEES OF THE LE-
LAND STANFORD JUNIOR UNIVERSITY** [US/US];
3000 El Camino Real, Building Five, Third Floor, Palo
Alto, CA 94306 (US).
- (72) Inventor: **FARVID, Ali, A.**; 3299 Waverly Street, Palo
Alto, CA 94306 (US).
- (74) Agents: **JACOBS, Ron** et al.; 550 S California Avenue,
Suite 300, Palo Alto, CA 94306 (US).
- (81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,

[Continued on next page]

- (54) Title: A METHOD FOR PLATING FINE GRAIN COPPER DEPOSIT ON METAL SUBSTRATE

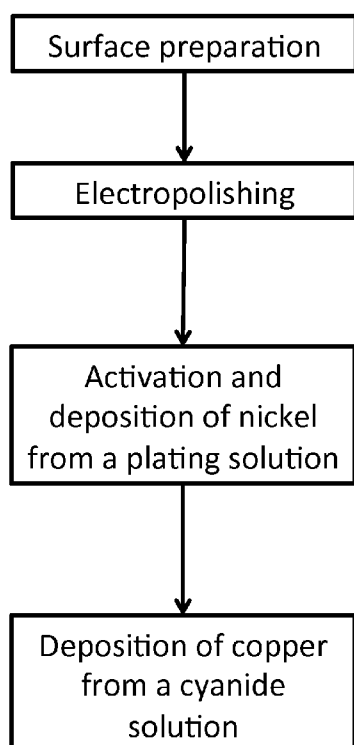


FIG. 1

(57) Abstract: A method of depositing an oxygen-free electronic copper layer on a metal substrate is provided that includes cleaning a substrate surface, electropolishing the substrate surface activating the substrate surface, depositing nickel on the substrate; and depositing copper on the substrate using a cyanide copper strike bath and a cyanide copper plate bath, where a periodic pulse and a reverse periodic pulse current is applied using a pulse periodic reverse current power supply, where the deposited oxygen-free copper comprises a fine-grained, equiaxed structure having a uniform surface geometry and less than 10% thickness variation across all surfaces.

WO 2015/108784 A1



LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, **Published:**

SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, — *with international search report (Art. 21(3))*
GW, KM, ML, MR, NE, SN, TD, TG).

A METHOD FOR PLATING FINE GRAIN COPPER DEPOSIT ON METAL SUBSTRATE

FIELD OF THE INVENTION

5 The current invention relates generally to metal deposition. More specifically, the invention relates to a method of forming an adherent oxygen-free electronic (OFE) copper plated layer on a metal substrate.

BACKGROUND OF THE INVENTION

10 Copper and its alloys are being used very widely in the electronics industry on account of the unique properties that these materials present to the user. For brazing and vacuum device applications, impurity level, grain size, and porosity are critical parameters that must be stringently controlled. Copper deposited from an electrolytic plating solution act as thermal expansion barriers by absorbing the stress produced when metals with different
15 thermal expansion coefficients undergo temperature changes. Most vacuum devices are made of stainless steel, which needs to be copper plated or brazed together for different reasons and applications. The mechanical properties of electroplated copper vary widely depending on factors such as solution composition, current density, temperature, impurities and addition agents. What is needed is method of forming an adherent oxygen-free
20 electronic (OFE) copper plated layer over non-ferrous metals, and ferrous metals such as stainless steel, for brazing and vacuum applications and operations.

SUMMARY OF THE INVENTION

To address the needs in the art, a method of depositing an oxygen-free electronic copper layer on a metal substrate is provided that includes cleaning a surface of the substrate, electropolishing the substrate surface, activating the substrate surface, depositing nickel on the substrate, and depositing copper on the substrate using a cyanide copper strike bath and a cyanide copper plate bath, where a periodic pulse and a reverse periodic pulse current is applied using a pulse periodic reverse current power supply, where the deposited oxygen-free copper includes a fine-grained, equiaxed structure having a uniform surface geometry and less than 10% thickness variation across all surfaces.

According to one aspect of the invention, cleaning the substrate includes using a solvent degreaser, a detergent cleaner, a potassium permanganate solution dip, and a combined nitric acid and hydrofluoric acid dip. In one aspect, the solvent degreaser includes a liquid and vapor solvent degreaser capable of removing oil and soil from the substrate, where the vapor solvent includes a hot vapor degreaser with temperature in a range of 100 to 140°F and an ultrasonic cleaner.

In another aspect of the invention, the electropolishing includes using a phosphoric acid bath having a preset current density of 0.5 to 2 ampere per square inch of the substrate surface for a predetermined time.

In a further aspect of the invention, the activation of the substrate surface includes a two part process having an anodic treatment in a sulfuric acid comprising a concentration in a range of 10 to 50% by volume, and a cathodic treatment in a sulfuric acid comprising a concentration in a range of 10 to 50% by volume for a predetermined duration.

According to another aspect of the invention, the deposition of nickel includes a Watt nickel strike bath includes nickel chloride, hydrochloric acid and water having a current density of more than 40 amperes per square foot.

5

In yet another aspect of the invention, the cyanide copper strike bath includes Rochelle salt, copper cyanide and potassium cyanide with controlled free cyanide concentration in a solution with a temperature range from 120 to 150°F and a high current density between 30 to 60 ampere per square foot.

10

According to one aspect of the invention, the copper plate bath includes controlled free cyanide, potassium hydroxide and potassium carbonate concentrations at predetermined levels, where the copper bath further includes copper cyanide, potassium cyanide, potassium hydroxide, and potassium-sodium tartrate.

15

In a further aspect of the invention, the periodic pulse and reverse periodic pulse may each have durations ranging between 0 and 500 seconds.

In one aspect of the invention, the metal substrate includes a ferrous metal. In one aspect
20 the substrate includes titanium, copper-based alloys, nickel, cobalt, zinc, tungsten, or aluminum, where the copper-based alloys includes brass or Glidcop.

In yet another aspect of the invention, the metal includes a ferrous metal. In one aspect the substrate includes stainless steel or steel.

25

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram of the deposition process, according to one embodiment of the invention.

DETAILED DESCRIPTION

A method for application of an adherent oxygen-free electronic (OFE) copper plate to stainless steel or non-ferrous metal substrates in general is provided that includes surface preparation, electropolishing, activation and deposition of nickel from a plating solution and deposition of copper from a cyanide solution. The standard definition of oxygen-free electronic copper is 99.99% pure copper with 0.0005% oxygen content [American Society for Testing and Materials (ASTM) Unified Numbering System (UNS) database number C10100]. Non-ferrous metal substrates include, but are not limited to titanium, copper-based alloys (such as brass, Glidcop), nickel, cobalt, zinc, tungsten, and aluminum. In one embodiment, the surface preparation includes using a solvent degreaser, a detergent cleaner, a potassium permanganate solution dip, a nitric acid/hydrofluoric acid dip, electropolishing in a phosphoric acid solution, a two step activation process in sulfuric acid solutions and deposition of a nickel strike. The copper plating step includes using a cyanide copper strike and a cyanide copper plate with a pulse periodic reverse current power supply. The copper plated according to the current invention results in a fine-grained, equiaxed structure with no voids during heat treatment to 1000°C, that has a uniform surface geometry and less than 10% thickness variation across all surfaces.

According to a further embodiment, by increasing or reducing the frequency and duty cycle of the pulse periodic reverse plating power supply, the level of the charge of the electrolyte layer is controlled, and the final electrical energy that participates in the absorption process

at the cathodic surface is controlled. The use of the reverse, forward and OFF time controls the boundary layer with the main target being the control over metal concentration variation at the cathodic surface. The duty cycle (ON/OFF ratio) of the power supply is integrated with the polarization control and with the effective average current of rate of deposition.

- 5 According to one embodiment, by decreasing the duty cycle finer grains are produced while maintaining the same plating time.

In a further embodiment, surface preparation includes using a liquid and vapor solvent degreaser to remove all oil and soil from the part or substrate, where the part or substrate is
10 placed into a hot vapor degreaser having ultrasonic agitation with a preset temperature in a range of 100 to 140°F and an ultrasound timer. Detergent cleaning using a potassium permanganate solution and nitric/HF dip are part of cleaning and descaling process.

The electropolish bath includes using a solution made up with phosphoric acid and a preset
15 current density of 0.5 to 2 Ampere per square inch of the substrate surface for a predetermined time.

In a further embodiment, the activation of a stainless steel substrate is a two-part process, which includes using anodic treatment in a sulfuric acid having a concentration of 10 to
20 50% by volume, followed by a cathodic treatment in a sulfuric acid having a concentration of 10 to 50% by volume for a preset time duration.

The deposition of the nickel is done using a Watt nickel strike that includes nickel chloride, hydrochloric acid and water with a current density of more than 40 amperes per square foot.

In a further embodiment of the invention, the cyanide copper strike includes Rochelle salt, potassium cyanide, and copper cyanide with a controlled free cyanide concentration in a solution with a temperature range from 120 to 150°F and a high current density between 30 to 60 ampere per square foot.

5

A cyanide copper strike bath is used to deposit a thin, adherent layer that can completely cover an active metal surface such as zinc or steel prior to further plating operations. Because of the bath's low plating efficiency, plating time, and thus the deposit's thickness, is often determined by the time needed to just obtain complete coverage.

10

The copper strike serves only as a protective layer for further plating, typically with copper or nickel. The low-metal and high-cyanide levels in the copper strike are responsible for the low efficiency, but these same properties ensure against a non-adhering immersion layer of copper that forms on the surface being plated. This formulation also produces the desired excellent covering and throwing powers.

15

The Rochelle salt bath is used for similar purposes. But, it may also be used to provide thicker deposits than can be obtained with cyanide strike baths, according to one embodiment.

20

In an embodiment, the cyanide copper plate bath electrolyte includes copper cyanide, potassium cyanide, potassium hydroxide and potassium-sodium tartrate. The cyanide copper plate bath comprises controlled free cyanide, potassium hydroxide, and potassium carbonate concentrations at predetermined levels to keep the plating process at optimum.

25

The copper cyanide forms a complex with the potassium cyanide in the plating solution,

which holds the copper metal in solution and provides the vehicle by which the copper metal is plated out. Free cyanide (the cyanide not combined with copper) is necessary to the success of cyanide copper plating. The free cyanide promotes anode corrosion and controls the bath performance. Low free cyanide permits higher cathode current densities, while high free cyanide improves brightness in the low-current areas. Free cyanide is essential in all cyanide copper plating solutions in order to obtain good corrosion of the copper anodes. If it is too low, the anodes polarize and become coated with an insulating film. The concentration of the free cyanide increases at higher temperatures, since lower complexes are formed and free cyanide is thereby liberated. Free cyanide concentration is determined by titrating a sample of the solution with silver nitrate at or below room temperature using potassium iodide as an indicator.

Potassium hydroxide enhances the solution electrical conductivity, the throwing power and the overall deposit brightness.

15

Potassium-sodium tartrate is used to form a temporary complex with copper by reacting with products of electrolysis produced in the anode film. Tartrate contributes to the plating solution operates with lower free cyanide and at higher current densities and efficiencies without impairing anode corrosion.

20

Potassium carbonate is formed in solution due to the hydrolysis of free cyanide and the oxidation occurring at the anode. The carbonate exerts a strong buffer action at pH of 10.8 to 11.5 and facilitates pH control. It also reduces anode polarization. It is formed by oxidation of the cyanide radical at the surface of polarized anodes or insoluble anodic metal surfaces. Absorption of carbon dioxide from air by caustic alkali in the solution and by

25

hydrolysis of the cyanide are other sources of carbonates formed in the solution. An increase in the carbonate content is associated with a reduction in the maximum current for efficient copper deposition.

- 5 The oxidation of the cyanide should be avoided because it increases the cyanide consumption, causes a rapid buildup of carbonates, and complicates control of free cyanide. The efficiency of solution cannot be restored by precipitation of carbonate. According to the current invention, the concentration of the carbonate will be less than 100 g/l and a new bath will be made when concentration of carbonate reaches 100 g/l.

10

In a further embodiment, the anodes are high-purity, oxygen free copper bars.

- In a further embodiment of the invention, the power supply is a pulse periodic reverse power supply with a variable frequency and bipolar pulse waveform to enhance the quality
15 and copper distribution over all surfaces. The grain size is controlled without the use of additives by adjusting the duty cycle, where unwanted additives may co-deposit with copper and deteriorate brazing or vacuum application processes. Smaller grains reduce porosity and have higher tensile strength and hardness than larger grains. The tensile strength is inversely proportional to the square root of the grain size. Fine-grained deposits
20 have a higher hardness and usually higher ductility. Since fine-grained deposits pack together better, they have lower porosity and stress. This kind of copper deposit is very desirable in industries specially in brazing operations.

- The plating characteristic of the plating solution is improved by utilizing current
25 manipulation techniques as well as current interruption cycles. One of the advantages

gained by employing periodic current reversal or interrupted cycles is improved leveling. The degree of leveling is greatest using periodic current reversal, particularly with relatively long reversal cycles. Plating deposited according to the current invention shows a laminar structure, whereas plating using conventional direct current methods is columnar.

5 The leveling obtained with current interruption is less than with current reversal, but it is adequate for covering minor surface marks. The uniformity of distribution of the copper on irregularly shaped parts is also improved with current reversal operations, according to the current invention. The method according to the invention prevents excessive buildup of copper on high-current-density areas and yields saving in anode consumption. Current

10 interruption and periodic reverse (PR) are beneficial in high-efficiency processes, since they help provide brighter and smoother deposits. In one embodiment, the current interruption cycle is approximately 10 sec on and one sec off. In one embodiment the PR cycles require 10–60 sec direct current followed by 2–20 sec of reverse current. In the method of the present invention, current interruption mixed with periodic reversal

15 optimizes the copper plate quality. In the method of the present invention, some applications may achieve similar high quality with current interruption alone (i.e. when the reversal duration is set to zero duration).

Some exemplary processes for stainless steel substrates are described herein.

20 Step 1:

Vapor degrease a part or substrate using DuPont™ Vertrel® SDG at a temperature of 115°F, and using ultrasonic agitation for 6 minutes.

Step 2:

Alkaline cleaning is done using Enthone-OMI Corporation Enprep Q (527), at a concentration of 7 oz/gal, at a temperature of 150°F, for a duration of 5 minutes.

Step 3:

Rinse part or substrate with cold water for 1 minute.

5 Step 4:

Scale and oxide conditioner uses Diversey Wyandotte Diverscale 299 alkaline potassium permanganate solution, having a concentration of 20 oz/gal, at a temperature of 190°F, for a duration of 60 minutes.

Step 5:

10 Rinse with cold water for 1 minute.

Step 6:

Scale removal is done using Diversey Wyandotte Everite II having a concentration 50% by volume, at room temperature, for a duration of 30 seconds.

Step 7:

15 Rinse with cold water for 1 minute.

Step 8:

Stainless steel pickle is a mixture of nitric acid at a concentration of 11.5% by volume, hydrofluoric acid at a concentration of 13% by volume, and water balance at room temperature for a duration of 60 Seconds.

20 Step 9:

Rinse with cold water for 1 minute.

Step 10:

Stainless steel electropolish is done using a mixture of 25% by volume of ElectroGlo 300 (ElectroGlo, Inc.) and 75% by volume phosphoric acid (85%) at a temperature of 140°F with agitation for a duration of 3 minutes, while subject to 8 Volts using anodic current.

5 Step 11:

Rinse with cold water for 2 minute until all chemicals are removed.

Step 12:

The anodic treatment is done using sulfuric acid having a concentration of 25% by volume, at room temperature, while subject to 6 Volts anodic (reverse) current for a duration of one
10 minute, using lead anodes and agitation.

Step 13:

Rinse with cold water for 1 minute.

Step 14:

Cathodic treatment includes using sulfuric acid having a concentration of 30% by volume
15 at room temperature, using cathodic (direct) current at 6 Volts for a duration of one minute from lead anodes under agitation, where the solution in step 12 is not used.

Step 15:

Rinse with cold water for 1 minute.

Step 16:

20 Nickel strike is done using nickel chloride having a nickel concentration as nickel metal of 7 to 8 oz/gal, hydrochloric acid having a concentration of 12 to 16 Fl.oz/Gal, using water balance at room temperature for 6 minutes, while subject to 40 to 60 Amperes per square

foot from a rolled depolarized nickel anode at a current density of 40 to 60 Amperes per square foot, while using agitation.

Step 17:

Rinse with cold water for 1 minute.

5 Step 18:

Copper strike is done using potassium copper cyanide having a concentration of 5 to 6 oz/gal, potassium cyanide having a free potassium cyanide concentration of 2 oz/gal, sodium-potassium tartrate having a concentration of 7 to 8 oz/gal at a temperature of 110°F for a duration of two minutes, while subjecting it to 40 Amperes per square foot using an
10 OFE copper anode, while subject to moderate agitation and 1 micron continuous filtration.

Step 19:

Transfer to copper plating bath without rinsing.

Step 20:

Copper plate is done using copper cyanide having a concentration of 7 to 9 oz/gal,
15 potassium cyanide having a concentration of free cyanide of 2 oz/gal, potassium hydroxide having a concentration of 2-3 oz/gal, and potassium-sodium tartrate, 4 H₂O, having a concentration of 6 oz/gal, at a temperature of 140°F for a duration that achieves the desired thickness using OFE copper (bagged) anodes subject to moderate agitation and 1 micron continuous filtration, with free cyanide having a concentration of 2 oz/gal, potassium
20 hydroxide having a concentration of 2.2 oz/gal, potassium carbonate having a maximum concentration of 100 g/l, and using pulse periodic reverse with a direct plating time having a duration of 30 seconds, OFF for 5 seconds, and ON for 25 seconds, where the reverse plating time has a duration of 8 seconds, OFF for 2 second, and ON for 6 seconds, with a

forward current density of 20 Amperes per square foot, and a reverse current density of 30 Amperes per square foot.

Step 21:

Rinse with cold water for 2 minute.

5 Step 22:

Copper electropolish is done using a mixture of 25% by volume of ElectroGlo 200 (ElectroGlo Inc.) and 75% by volume phosphoric acid (85%) at a temperature of 90°F, subject to agitation for a duration of 3 minutes and 8 Volts using anodic (reverse).

Step 23:

10 Rinse with cold water for 2 minute until all chemicals are removed.

Step 24:

Rinse with DI cold water for 2 minute.

Step 25:

15 Copper anti-tarnish is done using Rohm & Haas Advantage 2000 OXYBAN 60 having a concentration of 1% by volume at room temperature for a duration of 3 minutes, under agitation.

Step 26:

Rinse with cold water for 1 minute.

Step 27:

20 Rinse with cold DI water for 2 minute. (Minimum resistivity 1,000,000 ohms cm)

Step 28:

Rinse with cold DI water for one minute. (Minimum resistivity 1,000,000 ohms cm)

Step 29:

Immerse in analytical reagent isopropyl alcohol for dewatering.

Step 30:

5 Dry with dry nitrogen blast.

Step 31:

Wrap and protect plated part.

In summary, the current invention provides a method of plating copper on a metal substrate,
10 where the copper is oxygen free (high purity), fine grain, and has excellent adhesion. The
oxygen free aspect is achieved by the selection of the materials for the chemical bath. It is
critical to minimize the species types by choosing the appropriate electrolyte type chemistry
and avoiding additives such as organic impurities and addition agents. Organic impurities
cause degradation of copper plating baths and together with addition agents that degrade
15 the deposition quality via co-depositing organic materials in the copper plated layer. One
of the principal reasons for using oxygen free copper in critical applications is its low
oxygen content and its contaminant freedom from hydrogen embrittlement. Organic
impurities and addition agents will not result in an OFE copper plated layer.

20 The fine grain aspect is accomplished via pulse and reverse pulse processing. Without the
use of addition agents, cyanide electrolytes produces harder coating than acid baths.
Hardness of the electrodeposit is generally associated with fine grain. Leveling has a
significant effect on the appearance of the copper coating. The high concentration

potassium cyanide electrolytes produce excellent leveling when interrupted current or periodic reversal is used during plating. The combination of cyanide electrolytes and pulse/reverse pulse processing achieves levelling without additives. The pulse plating allows much faster plating without surface burning, produces finer grain deposits and
5 increases throwing power and distribution.

The improved adhesion property is accomplished by proper surface preparation of the substrate. Different substrates have different surface preparation processes. Substrates that can be used include, but are not limited to, stainless steel, titanium, copper-based alloys
10 (such as brass, Glidcop), steel, nickel, cobalt, zinc, tungsten and aluminum.

The present invention has now been described in accordance with several exemplary embodiments, which are intended to be illustrative in all aspects, rather than restrictive. Thus, the present invention is capable of many variations in detailed implementation, which
15 may be derived from the description contained herein by a person of ordinary skill in the art. For example, for non-stainless steel substrates steps 4 through 6 can be replaced with an appropriate cleaning steps. The current density in steps 10, 16 and 18 may be adjusted based on geometry of substrate.

20 All such variations are considered to be within the scope and spirit of the present invention as defined by the following claims and their legal equivalents.

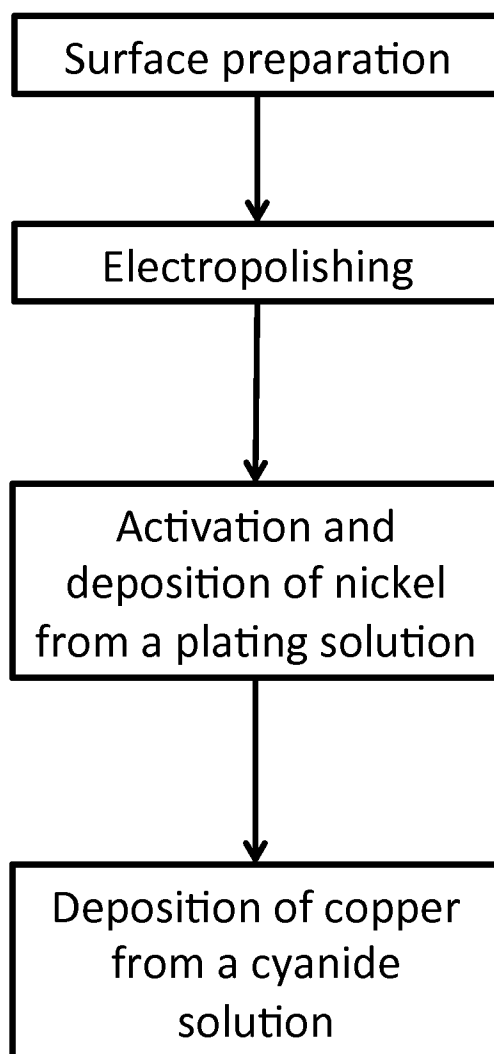
CLAIMS

What is claimed:

1. A method of depositing an oxygen-free electronic copper layer on a metal substrate, comprising:
 - a. cleaning a surface of a substrate;
 - b. electropolishing said substrate surface;
 - c. activating said substrate surface;
 - d. depositing nickel on said substrate; and
 - e. depositing copper on said substrate using a cyanide copper strike bath and a cyanide copper plate bath, wherein a periodic pulse and a reverse periodic pulse current is applied using a pulse periodic reverse current power supply, wherein said deposited oxygen-free copper comprises a fine-grained, equiaxed structure having a uniform surface geometry and less than 10% thickness variation across all surfaces.
2. The method according to claim 1, wherein said cleaning said substrate comprises using a solvent degreaser, a detergent cleaner, a potassium permanganate solution dip, and a combined nitric acid and hydrofluoric acid dip.
3. The method according to claim 2, wherein said solvent degreaser comprises a liquid and vapor solvent degreaser capable of removing oil and soil from said substrate, wherein said vapor solvent comprises a hot vapor degreaser with temperature in a range of 100 to 140°F and an ultrasonic cleaner.

4. The method according to claim 1, wherein said electropolishing comprises using a phosphoric acid bath having a preset current density of 0.5 to 2 ampere per square inch of said substrate surface for a predetermined time.
5. The method according to claim 1, wherein said activation of said substrate surface comprises a two part process having an anodic treatment in a sulfuric acid comprising a concentration in a range of 10 to 50% by volume, and a cathodic treatment in a sulfuric acid comprising a concentration in a range of 10 to 50% by volume for a predetermined duration.
6. The method according to claim 1, wherein said deposition of nickel comprises a Watt nickel strike bath comprises nickel chloride, hydrochloric acid and water having a current density of more than 40 amperes per square foot.
7. The method according to claim 1, wherein said cyanide copper strike bath comprises Rochelle salt, copper cyanide and potassium cyanide with controlled free cyanide concentration in a solution with a temperature range from 120 to 150°F and a high current density between 30 to 60 ampere per square foot.
8. The method according to claim 1, wherein said copper plate bath comprises controlled free cyanide, potassium hydroxide and potassium carbonate concentrations at predetermined levels, wherein said copper bath further comprises copper cyanide, potassium cyanide, potassium hydroxide, and potassium-sodium tartrate.

9. The method according to claim 1, wherein said periodic pulse and reverse periodic pulse may each have durations ranging between 0 and 500 seconds.
- 5 10. The method according to claim 1, wherein said metal substrate comprises a ferrous metal.
11. The method according to claim 10, wherein said substrate comprises titanium, copper-based alloys, nickel, cobalt, zinc, tungsten, or aluminum, wherein said
10 copper-based alloys comprises brass or Glidcop.
12. The method according to claim 1, wherein said metal comprises a ferrous metal.
13. The method according to claim 12, wherein said substrate comprises stainless
15 steel or steel.

**FIG. 1**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/010855

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - C25D 5/34 (2015.01) CPC - C25D 5/34 (2015.01) 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 5/34, 5/36 (2015.01) CPC - C25D 5/34, 5/36 (2015.01) (keyword delimited) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC - 205/205 (keyword delimited) Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Orbit, Google Patents, Google, Google Scholar Search terms used: metal degrease electropolish activate steel copper nickel plating oxygen free cyanide strike baths pulse reverse Rochelle				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
Y	US 8,152,985 B2 (MACARY) 10 April 2012 (10.04.2012) entire document	1-3, 5-13		
Y	US 6,709,564 B1 (TENCH et al) 23 March 2004 (23.03.2004) entire document	1-3, 5-13		
Y	US 4,602,318 A (LASSEN) 22 July 1986 (22.07.1986) entire document	2, 3, 10-13		
Y	US 4,663,005 A (EDSON) 05 May 1987 (05.05.1987) entire document	5		
Y	US 3,219,560 A (LEENDERS et al) 23 November 1965 (23.11.1965) entire document	7, 8		
A	US 4,427,123 A (KOMEDA et al) 24 January 1984 (24.01.1984) entire document	1-13		
A	US 3,667,110 A (GWYN JR) 06 June 1972 (06.06.1972) entire document	1-13		
☐ Further documents are listed in the continuation of Box C.				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; border: none;"> * Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "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 </td> <td style="width: 50%; vertical-align: top; border: none;"> "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 </td> </tr> </table>			* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "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
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "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 18 March 2015	Date of mailing of the international search report 06 MAY 2015			
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774			