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(54) **TRIVALENT CHROMIUM PLATING FORMULATIONS AND PROCESSES**

(57) An electrolyte solution for chrome plating from trivalent chromium is prepared by dissolving in an aqueous medium a trivalent chromium salt (e.g., chromium (III) chloride or chromium (III) sulfate), dissolving an oxalate compound (e.g., sodium oxalate, potassium oxalate, or oxalic acid), dissolving a metal salt (e.g., aluminum sulfate or aluminum chloride), dissolving an alkali metal sulfate (e.g., sodium sulfate or potassium sulfate), and dissolving an alkali metal halide (e.g., sodium fluoride or potassium fluoride). A substrate is chrome plated from trivalent chromium using the electrolyte solution by passing a current between a cathode and an anode through the electrolyte solution to deposit chromium on the substrate.

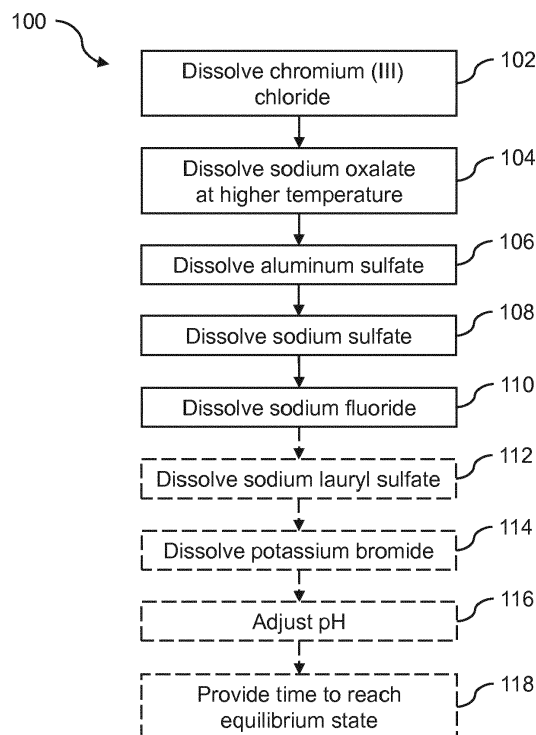


FIG. 1

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Description

BACKGROUND

5 1. Technical Field

[0001] The present disclosure relates to chrome plating and, more particularly, to using trivalent chromium for plating a substrate with chromium.

10 2. Related Art

[0002] Chrome plating is an electroplating process that provides a chrome coating on a substrate. Hard chrome plating provides a chrome coating having a thickness typically about 10 microns or greater, thereby providing hardness and wear resistance to the coated substrate. The other type of chrome plating is decorative chrome plating, which provides a chrome coating having a thickness typically ranging from about 0.1 to about 0.5 microns. Chrome plating is often performed using baths containing chromic acid and catalysts based on fluorides, sulfates or organic acids. Chromic acid has chromium in its hexavalent form, chromium (VI), which is highly toxic and a carcinogen.

[0003] There is a need for improved chrome plating methods and formulations of solutions used in chrome plating.

20 SUMMARY

[0004] In accordance with embodiments of the present disclosure, various methods and formulations are provided for chrome plating a substrate using a trivalent chromium solution that does not include boric acid, while still resulting in a chromium layer (e.g., a chromium coating) formed on the substrate that may be structurally robust and reliable, yet cost-effective. Thus, the methods and formulations described herein may advantageously be used for hard chrome plating to form hard chromium layers (e.g., a robust, functional chromium layer of greater than 10 microns). However, the present disclosure is not limited to hard chrome plating and the methods and formulations described herein may also be advantageously used to effectively and efficiently perform decorative chrome plating, which forms decorative chromium layers (e.g., a chromium layer ranging from 0.25 micron to 1.0 micron).

[0005] In one example embodiment, a method of preparing an electrolyte solution for chrome plating includes dissolving in an aqueous medium a trivalent chromium salt in an amount ranging from about 0.1 mol to about 0.9 mol per liter of the electrolyte solution, dissolving an oxalate compound in an amount ranging from about 0.1 mol to about 3.0 mol per liter of the electrolyte solution, and dissolving a metal salt in an amount ranging from about 0.1 mol to about 4.0 mol per liter of the electrolyte solution, an alkali metal sulfate in an amount ranging from about 0.1 mol to about 2.0 mol per liter of the electrolyte solution, and an alkali metal halide in an amount ranging from about 0.1 mol to about 0.5 mol per liter of the electrolyte solution per liter of the electrolyte solution. The step of dissolving the trivalent chromium salt, the oxalate compound, the metal salt, the alkali metal sulfate, and the alkali metal halide may be performed in the following order: (1) dissolving the trivalent chromium salt, (2) dissolving the oxalate compound, (3) dissolving the metal salt, (4) dissolving the alkali metal sulfate, and (5) dissolving the alkali metal halide. The order of steps (1) and (2) may be reversed or be performed concurrently.

[0006] The trivalent chromium salt may include chromium (III) chloride and/or chromium (III) sulfate. The oxalate compound may include sodium oxalate, potassium oxalate, and/or oxalic acid. The metal salt may include aluminum sulfate and/or aluminum chloride. The alkali metal sulfate may include sodium sulfate and/or potassium sulfate. The alkali metal halide may include sodium fluoride and/or potassium fluoride.

[0007] The step of dissolving the oxalate compound may include stirring the oxalate compound at a temperature ranging from about 70 °C to about 80 °C for a time ranging from about 1 hour to about 3 hours. The method may further include adjusting the pH of the electrolyte solution to a pH ranging from about 2 to about 4.

[0008] The method may further include adding sodium lauryl sulfate and/or potassium lauryl sulfate in an amount ranging from about 0.1 g to about 1 g per liter of the electrolyte solution. The method may further include adding sodium bromide and/or potassium bromide in an amount ranging from about 0.1 g to about 1 g per liter of the electrolyte solution.

[0009] In an additional example embodiment, a method for chrome plating a substrate includes preparing an electrolyte solution by dissolving, a trivalent chromium salt, an oxalate compound, aluminum sulfate, alkali metal sulfate, and alkali metal fluoride; passing a current between a cathode and an anode through the electrolyte solution to deposit chromium on the substrate; and maintaining the electrolyte solution at a pH ranging from about 2 to about 4. The step of preparing the electrolyte solution may include dissolving the trivalent chromium salt in an amount ranging from about 0.1 mol to about 0.9 mol per liter of the electrolyte solution, dissolving the oxalate compound in an amount ranging from about 0.1 mol to about 3.0 mol per liter of the electrolyte solution, and dissolving the metal salt in an amount ranging from about 0.1 mol to about 4.0 mol per liter of the electrolyte solution, an alkali metal sulfate in an amount ranging from about 0.1

mol to about 2.0 mol per liter of the electrolyte solution, and an alkali metal halide in an amount ranging from about 0.1 mol to about 0.5 mol per liter of the electrolyte solution. The method may further include maintaining the electrolyte solution at a temperature ranging from about 30 °C to about 40 °C during the step of passing the current.

[0010] The step of passing the current may be performed using an anode including a carbonaceous electrode material, such as a graphite anode. The step of passing the current may include applying a current density ranging from about 10 A/dm² to about 30 A/dm². The step of the passing the current may include applying a pulsed current having a duty cycle ranging from about 20% to about 80%.

[0011] The step of passing the current may be performed until a chromium layer having a thickness greater than about 5 microns and hardness greater than about 800 HV (Vickers pyramid indenter, suitably measured using ASTM E384-16, suitably using a model MH-6 instrument commercially available from EVERONE ENTERPRISES, Hong Kong) is formed on the substrate. The step of passing the current to deposit chromium on the substrate may include passing the current to deposit chromium on a steel substrate, a copper substrate, a nickel substrate, a copper-coated substrate, or a nickel-coated substrate. The method may further include depositing, responsive to the step of passing the current, chromium on the substrate or co-depositing chromium and carbon on the substrate.

[0012] In another example embodiment, a method of preparing an electrolyte solution for chrome plating includes performing the following steps in order: (1) providing trivalent chromium by dissolving a trivalent chromium salt, (2) forming complexes of oxalate and trivalent chromium by dissolving an oxalate compound, (3) buffering the electrolyte solution by dissolving a metal salt, (4) increasing the conductivity by dissolving an alkali metal sulfate, and (5) increasing the wetting property of the electrolyte solution by dissolving alkali metal halide. The order of steps (1) and (2) may be reversed or be performed concurrently.

[0013] In yet another example embodiment, an electrolyte solution is prepared by one of the methods described above. For example, an electrolyte solution includes, per liter of the electrolyte solution, a trivalent chromium salt in an amount ranging from about 0.1 mol to about 0.9 mol, an oxalate compound in an amount ranging from about 0.1 mol to about 3.0 mol, a metal salt in an amount ranging from about 0.1 mol to about 4.0 mol, an alkali metal sulfate in an amount ranging from about 0.1 mol to about 2.0 mol, and an alkali metal halide in an amount ranging from about 0.1 mol to about 0.5 mol.

[0014] The scope of the invention is defined by the claims, which are incorporated into this section by reference. A better understanding of the methods and formulations for chrome plating of the present disclosure, as well as an appreciation of the above and additional advantages thereof, will be afforded to those of skill in the art by a consideration of the following detailed description of one or more example embodiments thereof. In this description, reference is made to the various views of the appended sheets of drawings, which are briefly described below, and within which, like reference numerals are used to identify like ones of the elements illustrated therein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

FIG. 1 illustrates an example process for preparing a trivalent chromium electrolyte solution in accordance with an embodiment of the present disclosure.

FIG. 2 is an image of example solutions formed during the process of FIG. 1.

FIG. 3 illustrates an example process for chrome plating in accordance with an embodiment of the present disclosure.

FIG. 4 is an image of chrome plated substrates formed by the process of FIG. 3, each plated at a different pH.

FIG. 5 is an image of chrome plated substrates formed by the process of FIG. 3, each plated at a different temperature.

FIG. 6 is an image of chrome plated substrates formed by the process of FIG. 3, each plated at a different current density using direct current plating.

FIG. 7 is an image of chrome plated substrates formed by the process of FIG. 3, each plated at a different average current density using pulsed current plating.

FIG. 8 is a graph showing thickness of chromium layers formed by the process of FIG. 3 using pulsed current plating at different pulse frequencies and duty cycles.

FIG. 9 is an image of a chrome plated substrate formed by the process of FIG. 3 using pulsed current.

FIG. 10 is an image of a chrome plated substrate formed by the process of FIG. 3 using direct current.

FIG. 11 is a scanning electron microscopy (SEM) image of a cross-section of the chrome plated substrate of FIG. 9.

FIG. 12 is an SEM image of a cross-section of the chrome plated substrate of FIG. 10.

FIG. 13 is an image of a chrome plated substrate formed by the process of FIG. 3 using an electrolyte solution prepared by dissolving chromium (III) sulfate and an oxalate compound but not dissolving an alkali metal sulfate.

FIG. 14 is an image of a chrome plated substrate formed by the process of FIG. 3 using the electrolyte solution prepared by the process of FIG. 1 without the step of dissolving the surfactant.

FIG. 15 is an image of a chrome plated substrate formed by the process of FIG. 3 using the electrolyte solution

prepared by the process of FIG. 1 including the step of dissolving the surfactant.

FIGS. 16A-B are SEM images of a part of the chrome plated substrate of FIG. 14.

FIGS. 17A-B are SEM images of a part of the chrome plated substrate of FIG. 15.

FIG. 18 is an SEM image of chrome deposits on a chrome plated substrate formed by the process of FIG. 3.

FIG. 19 is an image of chrome plated substrates formed by the process of FIG. 3 that have been bent to show resilience of chromium layers to bending.

FIG. 20 is an image of a chrome plated substrate formed by the process of FIG. 3 on which abrasion testing has been performed to determine wear resistance of a chromium layer.

DETAILED DESCRIPTION

[0016] FIG. 1 illustrates an example process 100 for preparing a trivalent chromium electrolyte solution (also referred to as a trivalent chromium plating formulation). The compound of the first block is dissolved in an aqueous medium such as water, and a respective compound of each subsequent block is dissolved in the solution resulting from the previous block.

[0017] At block 102, a trivalent chromium salt is dissolved. The trivalent chromium salt is a trivalent chromium source. In one or more embodiments, trivalent chromium salt includes a chromium (III) halide, chromium (III) sulfate (e.g., $\text{Cr}_2(\text{SO}_4)_3$, $\text{Cr}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, and/or other chromium (III) sulfates), and/or other chromium (III) salts. The chromium (III) halide may include, for example, chromium (III) chloride (e.g., CrCl_3 , $\text{CrCl}_3 \cdot 5\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and/or other chromium (III) chlorides). The amount of the trivalent chromium salt that is dissolved may range from about 0.1 mol (moles) to about 0.9 mol per liter of the electrolyte solution to be formed. The amount of the trivalent chromium salt that is dissolved may be about 0.1 mol, 0.2 mol, 0.3 mol, 0.4 mol, 0.5 mol, 0.6 mol, 0.7 mol, 0.8 mol, or 0.9 mol per liter of the electrolyte solution, where any value may form an upper end point or a lower end point, as appropriate.

[0018] The trivalent chromium salt may be dissolved by stirring for 15 minutes at ambient temperature, at room temperature, at about 25 °C, or at a temperature ranging from about 20 °C to about 30 °C. The stirring may be performed for about 5 minutes, 10 minutes, 15 minutes, 20 minutes, 25 minutes, or 30 minutes, where any value may form an upper end point or a lower end point, as appropriate, or until all the trivalent chromium salt has been dissolved. The temperature at which block 102 is performed may be about 10 °C, 15 °C, 20 °C, 25 °C, 30 °C, 35 °C, or 40 °C, where any value may form an upper end point or a lower end point, as appropriate.

[0019] At block 104, an oxalate compound is dissolved. The oxalate compound includes oxalate, which may function as a complexing agent. In one or more embodiments, the oxalate compound includes an alkali metal oxalate (e.g., sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$), potassium oxalate ($\text{K}_2\text{C}_2\text{O}_4$), and/or other alkali metal oxalates) and/or an acid of oxalate (e.g., oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) and/or other acids of oxalate). The amount of the oxalate compound that is dissolved may range from about 0.1 mol to about 3.0 mol per liter of the electrolyte solution to be formed. The amount of the oxalate compound that is dissolved may be about 0.1 mol, 0.2 mol, 0.4 mol, 0.6 mol, 0.8 mol, 1.0 mol, 1.2 mol, 1.4 mol, 1.6 mol, 1.8 mol, 2.0 mol, 2.2 mol, 2.4 mol, 2.6 mol, 2.8 mol, or 3.0 mol per liter of the electrolyte solution, where any value may form an upper end point or a lower end point, as appropriate.

[0020] To dissolve the oxalate compound and form a complex of oxalate and trivalent chromium, the oxalate compound may be put in solution (e.g., the solution resulting from block 102 or another block performed prior to block 104), the solution may be heated to a higher temperature ranging from about 70 °C to about 80 °C, and the solution may be stirred for about 1 hour to about 3 hours. The solution may then be cooled (e.g., to ambient temperature, to room temperature, to about 25 °C, or to a temperature ranging from about 20 °C to about 30 °C). Alternatively, the oxalate compound may be dissolved without heating, in which case a complex of oxalate and trivalent chromium is formed in 3 to 4 days. Advantageously, heating the solution to a temperature ranging from about 70 °C to about 80 °C at block 104 allows the electrolyte solution to be prepared more quickly. Accordingly, the stirring may be performed for about 1 hour, 1 hour and 15 minutes, 1 hour and 30 minutes, 1 hour and 45 minutes, 2 hours, 2 hours and 15 minutes, 2 hours and 30 minutes, 2 hours and 45 minutes, 2 hours and 45 minutes, or 3 hours, where any value may form an upper end point or a lower end point, as appropriate. Further, the temperature at which block 104 is performed may be at about 50 °C, 55 °C, 60 °C, 65 °C, 70 °C, 75 °C, 80 °C, 85 °C, or 90 °C, where any value may form an upper end point or a lower end point, as appropriate.

[0021] At block 106, a metal salt is dissolved. The metal salt is a metal ion source that dissolves to provide metal ions such as aluminum ions, which may function as a buffer and may provide ionic strength due to the high valence of the metal ion in solution (e.g., Al^{3+}). In one or more embodiments, the metal salt includes a group 13 metal salt such as an aluminum salt (e.g., aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), an aluminum halide such as aluminum chloride (AlCl_3), and/or other aluminum salts) and/or other metal salts. The amount of the metal salt may range from about 0.1 mol to about 4.0 mol per liter of the electrolyte solution to be formed. The amount of the metal salt that is dissolved may be about 0.1 mol, 0.2 mol, 0.4 mol, 0.6 mol, 0.8 mol, 1.0 mol, 1.2 mol, 1.4 mol, 1.6 mol, 1.8 mol, 2.0 mol, 2.2 mol, 2.4 mol, 2.6 mol, 2.8 mol, 3.0 mol, 3.2 mol, 3.4 mol, 3.6 mol, 3.8 mol, or 4.0 mol per liter of the electrolyte solution, where any value may form

an upper end point or a lower end point, as appropriate.

[0022] The metal salt may be dissolved by stirring for 15 minutes at ambient temperature, at room temperature, at about 25 °C, or at a temperature ranging from about 20 °C to about 30 °C. The stirring may be performed for about 5 minutes, 10 minutes, 15 minutes, 20 minutes, 25 minutes, or 30 minutes, where any value may form an upper end point or a lower end point, as appropriate, or until all the metal salt has been dissolved. The temperature at which block 106 is performed may be about 10 °C, 15 °C, 20 °C, 25 °C, 30 °C, 35 °C, or 40 °C, where any value may form an upper end point or a lower end point, as appropriate.

[0023] At block 108, an alkali metal salt is dissolved. The alkali metal salt may increase the conductivity of the electrolyte solution. In one or more embodiments, the alkali metal salt includes an alkali metal sulfate (e.g., sodium sulfate (Na_2SO_4), potassium sulfate (K_2SO_4), and/or other alkali metal sulfates). The amount of the alkali metal sulfate that is dissolved may range from about 0.1 mol to about 2.0 mol of the electrolyte solution to be formed. The amount of the alkali metal sulfate that is dissolved may be about 0.1 mol, 0.2 mol, 0.3 mol, 0.4 mol, 0.5 mol, 0.6 mol, 0.7 mol, 0.8 mol, 0.9 mol, 1.0 mol, 1.1 mol, 1.2 mol, 1.3 mol, 1.4 mol, 1.5 mol, 1.6 mol, 1.7 mol, 1.8 mol, 1.9 mol, or 2.0 mol per liter of the electrolyte solution, where any value may form an upper end point or a lower end point, as appropriate.

[0024] The alkali metal sulfate may be dissolved by stirring for 15 minutes at ambient temperature, at room temperature, at about 25 °C, or at a temperature ranging from about 20 °C to about 30 °C. The stirring may be performed for about 5 minutes, 10 minutes, 15 minutes, 20 minutes, 25 minutes, or 30 minutes, where any value may form an upper end point or a lower end point, as appropriate, or until all the metal salt has been dissolved. The temperature at which block 106 is performed may be about 10 °C, 15 °C, 20 °C, 25 °C, 30 °C, 35 °C, or 40 °C, where any value may form an upper end point or a lower end point, as appropriate.

[0025] At block 110, an alkali metal halide is dissolved. The alkali metal halide may provide the electrolyte solution with wetting and etching properties, and may help chromium adhesion during chrome plating. In one or more embodiments, the alkali metal halide includes an alkali metal fluoride (e.g., sodium fluoride (NaF), potassium fluoride (KF), and/or other alkali metal fluorides) and/or other alkali metal halides. The amount of the alkali metal halide that is dissolved may range from about 0.1 mol to about 0.5 mol per liter of the electrolyte solution to be formed. The amount of the alkali metal halide that is dissolved may be about 0.10 mol, 0.15 mol, 0.20 mol, 0.25 mol, 0.30 mol, 0.35 mol, 0.40 mol, 0.45 mol, or 0.50 mol per liter of the electrolyte solution, where any value may form an upper end point or a lower end point, as appropriate.

[0026] The alkali metal halide may be dissolved by stirring for 15 minutes at ambient temperature, at room temperature, at about 25 °C, or at a temperature ranging from about 20 °C to about 30 °C. The stirring may be performed for about 5 minutes, 10 minutes, 15 minutes, 20 minutes, 25 minutes, or 30 minutes, where any value may form an upper end point or a lower end point, as appropriate, or until all the alkali metal halide has been dissolved. The temperature at which block 106 is performed may be about 10 °C, 15 °C, 20 °C, 25 °C, 30 °C, 35 °C, or 40 °C, where any value may form an upper end point or a lower end point, as appropriate.

[0027] At block 112, a surfactant may be dissolved. The surfactant may prevent or reduce pitting and reduce gas generation (e.g., chlorine gas, hydrogen gas, etc.) during chrome plating. In some embodiments, the surfactant includes sodium lauryl sulfate ($\text{NaC}_{12}\text{H}_{25}\text{SO}_4$), potassium lauryl sulfate ($\text{KC}_{12}\text{H}_{25}\text{SO}_4$), and/or other surfactants. The amount of the surfactant may range from about 0.0001 mol to 0.01 mol per liter of the electrolyte solution to be formed. The amount of the surfactant that is dissolved may be about 0.0001 mol, 0.0002 mol, 0.0004 mol, 0.0006 mol, 0.0008 mol, 0.0010 mol, 0.0020 mol, 0.0040 mol, 0.0060 mol, 0.0080 mol, or 0.0100 mol per liter of the electrolyte solution, where any value may form an upper end point or a lower end point, as appropriate. For example, the amount of sodium lauryl sulfate or potassium lauryl sulfate may range from about 0.1 g to about 1 g per liter of the electrolyte solution to be formed.

[0028] At block 114, an alkali metal halide (e.g. alkali metal bromide) is dissolved. The alkali metal bromide may reduce the generation of gas (e.g., chlorine gas, hydrogen gas, etc.) during chrome plating. In some embodiments, the alkali metal bromide includes sodium bromide (NaBr), potassium bromide (KBr), or other alkali metal bromides. The amount of the surfactant may range from about 0.001 mol to 0.05 mol per liter of the electrolyte solution to be formed. The amount of the alkali metal bromide that is dissolved may be about 0.001 mol, 0.002 mol, 0.004 mol, 0.006 mol, 0.008 mol, 0.010 mol, 0.020 mol, 0.030 mol, 0.040 mol, or 0.050 mol per liter of the electrolyte solution, where any value may form an upper end point or a lower end point, as appropriate. For example, the amount of sodium bromide or potassium bromide may range from about 0.1 g to about 1 g per liter of the electrolyte solution to be formed.

[0029] At block 116, the pH may be adjusted. In some embodiments, the pH is adjusted using one or more acids or bases, such as potassium hydroxide (KOH), sodium hydroxide (NaOH), and/or sulfuric acid (H_2SO_4). The pH of the electrolyte solution may be adjusted to a range from about 2 to about 4. The pH may be adjusted to about 2, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, or 4.0, where any value may form an upper end point or a lower end point, as appropriate.

[0030] At block 118, time may be provided to reach equilibrium state. In some embodiments, the solution is left to stand for a time ranging from 1 hour to 2 days to reach the equilibrium state. The time provided to reach the equilibrium state may be about 1 hour, 3 hours, 6 hours, 9 hours, 12 hours, 15 hours, 18 hours, 21 hours, 24 hours, 27 hours, 30 hours, 33 hours, 36 hours, 39 hours, 42 hours, 45 hours, or 48 hours, where any value may form an upper end point or

a lower end point, as appropriate.

[0031] In some embodiments, process 100 is performed in the order presented. In other embodiments, process 100 is performed in a different order. Some blocks may be performed in order while other blocks are performed in a different order. For example, blocks 102, 104, and 106 may be performed in order, while blocks 108, 110, 112, 114, 116, and 118 may be performed in a different order after blocks 102, 104, and 106. In another example, blocks 102, 104, 106, 108, and 110 may be performed in order, while blocks 112, 114, 116, and 118 may be performed in a different order. A group of blocks may be performed before another group of blocks. For example, blocks 102, 104, and 106 may be performed in any order, and after blocks 102, 104, and 106 are performed, blocks 106, 108, and 110 may be performed in any order. Other orders are contemplated as one skilled in the art will appreciate. Further, one or more of blocks 112, 114, 116, and 118 may be omitted in some embodiments.

[0032] Example 1. In an example of performing blocks 102 to 110, chromium (III) chloride in the amount of about 159 g (about 0.6 mol) per liter of electrolyte solution to be formed is dissolved in water, which results in a dark green solution. Although chromium (III) chloride was used in this example, one or more other chromium (III) salts (e.g., one or more other chromium (III) halides and/or chromium (III) sulfate) may be used instead of, or in addition to, chromium (III) chloride. A solution 202 shown in FIG. 2 illustrates the dark green solution diluted 10 times for good color contrast. Then, sodium oxalate in the amount of about 80.4 grams (about 0.6 mol) per liter of the electrolyte solution to be formed is dissolved in the dark green solution, which results in a dark grey-purple solution. Although sodium oxalate was used in this example, one or more other oxalate compounds (e.g., one or more other alkali metal oxalates and/or one or more acid of oxalate) may be used instead of, or in addition to, sodium oxalate. A solution 204 shown in FIG. 2 illustrates the dark grey-purple solution diluted 10 times for good color contrast. The color change from dark green to dark grey-purple may indicate the formation of the complex of trivalent chromium and oxalate. Then, aluminum sulfate in the amount of about 126.1 grams (about 0.2 mol), sodium sulfate in the amount of about 184.6 grams (about 1.3 mol), and sodium fluoride in the amount of about 16.8 grams (0.4 mol) per liter of the electrolyte solution to be formed is dissolved in the dark grey-purple solution, which forms a dark grey-green solution, which may be the final electrolyte solution for use in chrome plating. Although aluminum sulfate was used in this example, one or more other metal salts (e.g., one or more other aluminum salts) may be used instead of, or in addition to, aluminum sulfate. Also, although sodium sulfate was used in this example, one or more other alkali metal salts (e.g., one or more other alkali metal sulfates) may be used instead of, or in addition to, sodium sulfate. Further, although sodium fluoride was used in this example, one or more other alkali metal halides (e.g., one or more other alkali metal fluorides) may be used instead of, or in addition to, sodium fluoride. A solution 206 shown in FIG. 2 illustrates the dark grey-green solution diluted 10 times for good color contrast. The electrolyte solution may be left to stand for about 1 day to reach an equilibrium state. The resulting electrolyte solution may have a trivalent chromium concentration of about 0.6 M (moles/L), a chloride concentration of about 1.8 M, an oxalate concentration of about 0.6 M, an aluminum concentration of about 0.4 M, a sodium concentration of about 4.2 M, and a sulfate concentration of about 1.9 M.

[0033] Example 2. In another example of performing blocks 102 to 110, chromium (III) sulfate in the amount of about 235 g (about 0.6 mol) per liter of electrolyte solution to be formed is dissolved in water. Although chromium (III) sulfate was used in this example, one or more other chromium (III) salts (e.g., one or more chromium (III) halides) may be used instead of, or in addition to, chromium (III) chloride. Then, sodium oxalate in the amount of about 80.4 grams (about 0.6 mol) per liter of the electrolyte solution to be formed is dissolved. Although sodium oxalate was used in this example, one or more other oxalate compounds (e.g., one or more other alkali metal oxalates and/or one or more acid of oxalate) may be used instead of, or in addition to, sodium oxalate. Then, aluminum sulfate in the amount of about 126.1 grams (about 0.2 mol), sodium sulfate in the amount of about 184.6 grams (about 1.3 mol), and sodium fluoride in the amount of about 16.8 grams (0.4 mol) per liter of the electrolyte solution to be formed is dissolved. Although aluminum sulfate was used in this example, one or more other metal salts (e.g., one or more other aluminum salts) may be used instead of, or in addition to, aluminum sulfate. Also, although sodium sulfate was used in this example, one or more other alkali metal salts (e.g., one or more other alkali metal sulfates) may be used instead of, or in addition to, sodium sulfate. Further, although sodium fluoride was used in this example, one or more other alkali metal halides (e.g., one or more other alkali metal fluorides) may be used instead of, or in addition to, sodium fluoride. The electrolyte solution may be left to stand for about 1 day to reach an equilibrium state. The resulting electrolyte solution may have a trivalent chromium concentration of about 1.2 M, an oxalate concentration of about 0.6 M, an aluminum concentration of about 0.4 M, a sodium concentration of about 4.2 M, and a sulfate concentration of about 3.7 M.

[0034] FIG. 3 illustrates an example process 300 for chrome plating. At block 302, an electrolyte solution is prepared, such as by process 100 of FIG. 1. At block 304, a cathode and an anode are placed in the electrolyte solution, the cathode including the substrate, and a current is passed between the cathode and the anode through the electrolyte solution to deposit chromium on the substrate. The substrate may be a steel substrate, a copper substrate, a nickel substrate, a copper-coated substrate, or a nickel-coated substrate. However, other substrates are contemplated as one skilled in the art will appreciate.

[0035] The anode may include a carbonaceous electrode material. For example, the carbonaceous anode may be a

graphite anode or other anode that includes carbon. The graphite anode may be used for chloride-based electrolyte solutions (e.g., electrolyte solutions that include one or more compounds with chloride such as chromium (III) chloride), sulfate-based electrolyte solutions (e.g., electrolyte solutions that include one or more compounds with sulfate such as chromium (III) sulfate), or chloride and sulfate-based electrolyte solutions (e.g., electrolyte solutions that include one or more compounds with chloride and one or more other compounds with sulfate). Advantageously, the graphite anode or other carbonaceous anode minimizes gas evolution and formation of undesirable byproducts, as well as facilitating a desirable deposition rate (e.g., ranging from about 1 microns to about 2 microns per minute). Alternatively, a platinum anode or a platinized titanium anode may be used for sulfate-based electrolyte solutions (e.g., electrolyte solutions that include one or more compounds with sulfate such as chromium (III) sulfate) or chloride and sulfate-based electrolyte solutions (e.g., electrolyte solutions that include one or more compounds with chloride and one or more other compounds with sulfate). For example, the platinum anode or platinized titanium anode may be used when the electrolyte solution does not include compounds with chloride such that chlorine gas is not produced, or when the electrolyte solution has less chloride such that less chlorine gas is generated (e.g., there is no need to reduce the generation of chlorine gas using a carbonaceous anode).

[0036] In some embodiments, direct current is used. The direct current may provide a current density ranging from about 5 A/dm² to about 50 A/dm². The value of the current density may be adjusted depending on the separation between the cathode and anode. The current density may be about 5 A/dm², 10 A/dm², 15 A/dm², 20 A/dm², 25 A/dm², 30 A/dm², 35 A/dm², 40 A/dm², 45 A/dm², or 50 A/dm², where any value may form an upper end point or a lower end point, as appropriate, depending on the separation between the cathode and anode. For example, a current density ranging from about 10 A/dm² to about 30 A/dm² may be applied when the cathode and the anode is separated by about 3 cm.

[0037] In other embodiments, pulsed current is used. The pulsed current may provide an average current density ranging from about 5 A/dm² to about 50 A/dm². The value of the average current density may be adjusted depending on the separation between the cathode and anode. The peak current density may be twice of the average current density. The average current density may be about 5 A/dm², 10 A/dm², 15 A/dm², 20 A/dm², 25 A/dm², 30 A/dm², 35 A/dm², 40 A/dm², 45 A/dm², or 50 A/dm², where any value may form an upper end point or a lower end point, as appropriate, depending on the separation between the cathode and anode. For example, an average current density ranging from about 15 A/dm² to about 30 A/dm² may be applied when the cathode and the anode is separated by about 3 cm.

[0038] The pulsed current may have a duty cycle ranging from about 20 % to about 80 %. The duty cycle may be about 20 %, 25 %, 30 %, 35 %, 40 %, 45 %, 50 %, 55 %, 60 %, 65 %, 70 %, 75 %, or 80 %, where any value may form an upper end point or a lower end point, as appropriate. The pulsed current may have a frequency ranging from about 10 Hz to about 100 Hz. The frequency may be about 10 Hz, 20 Hz, 30 Hz, 40 Hz, 50 Hz, 60 Hz, 70 Hz, 80 Hz, 90 Hz, or 100 Hz, where any value may form an upper end point or a lower end point, as appropriate. For example, if the pulsed current has a duty cycle of about 40 % and a frequency of about 25 Hz, the ON time is about 16 milliseconds and the OFF time is about 24 milliseconds.

[0039] At block 306, a pH of the electrolyte solution is maintained at a target pH or a target pH range. The target pH may be a pH ranging from about 2 to about 4. The pH may be maintained at about 2, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, or 4.0, where any value may form an upper end point or a lower end point, as appropriate.

[0040] At block 308, a temperature of the electrolyte solution is maintained at a target temperature or a target temperature range. The target temperature may be a temperature ranging from about 20 °C to about 60 °C. The temperature may be about 20 °C, 25 °C, 30 °C, 35 °C, 40 °C, 45 °C, 50 °C, 55 °C, 60 °C, 65 °C, or 70 °C, where any value may form an upper end point or a lower end point, as appropriate.

[0041] In response to performing block 302, chromium is deposited on the substrate at block 310. In some examples, chromium and carbon are co-deposited on the substrate. Block 302 may be performed until a chromium layer (e.g., a chromium coating) or a chromium-carbon layer (e.g., a chromium carbide coating) having a desired thickness (e.g., a thickness greater than about 5 microns) is formed on the substrate. The chromium layer having a thickness greater than about 5 microns may have hardness greater than about 800 HV.

[0042] FIG. 4 is an image of chrome plated substrates 410, 420, 430, 440, and 450 formed by process 300 of FIG. 3, each plated at a different pH. For each chrome plated substrate 410, 420, 430, 440, and 450, the chrome plating parameters were as follows: the plating time was 1 hour, at a temperature of 35 °C, and at a current density of 22 A/dm².

[0043] Chrome plated substrate 410 was plated at a pH of 1.5, resulting in a chromium layer 412 having a thickness of 4 microns. Chrome plated substrate 420 was plated at a pH of 2.0, resulting in a chromium layer 422 having a thickness of 5 microns. Chrome plated substrate 430 was plated at a pH of 2.5, resulting in a chromium layer 412 having a thickness of 20 microns. Chrome plated substrate 440 was plated at a pH of 3.0, resulting in a chromium layer 442 having a thickness of 30 microns. A chrome plated substrate 450 was plated at a pH of 3.5, resulting in a chromium layer 452 having a thickness of 14 microns.

[0044] As illustrated by FIG. 4, any pH ranging from about 1.5 to about 3.5 provides deposition of a chromium layer. A pH ranging from about 2 to about 4 advantageously provides a thicker chromium layer than a pH that is higher or lower. Further, a pH ranging from about 2.5 to about 3.0 advantageously provides the thickest chromium layer.

[0045] FIG. 5 is an image of chrome plated substrates 510, 520, 530, 540, and 550 formed by process 300 of FIG. 3, each plated at a different temperature. For each chrome plated substrate 510, 520, 530, 540, and 550, the chrome plating was performed at a pH of 2.8.

[0046] Chrome plated substrate 510 was plated at a temperature of 30 °C, resulting in a chromium layer 512 having a thickness of 32 microns. Chrome plated substrate 520 was plated at a temperature of 40 °C, resulting in a chromium layer 522 having a thickness of 45 microns. Chrome plated substrate 530 was plated at a temperature of 50 °C, resulting in a chromium layer 532 having a thickness of 20 microns. Chrome plated substrate 540 was plated at a temperature of 60 °C, resulting in a chromium layer 542 having a thickness of 16 microns. Chrome plated substrate 550 was plated at a temperature of 70 °C, resulting in a chromium layer 552 having a thickness of 32 microns.

[0047] As illustrated by FIG. 5, any temperature ranging from about 30 °C to about 70 °C provides deposition of a chromium layer. A temperature ranging from about 30 °C to about 40 °C advantageously provides the thickest chromium layer than a temperature that is higher or lower.

[0048] FIG. 6 is an image of chrome plated substrates 610, 620, 630, 640, and 650 formed by process 300 of FIG. 3, each plated at a different current density using direct current plating. For each chrome plated substrate 610, 620, 630, 640, and 650, the chrome plating parameters were as follows: the plating time was 1 hour, and the distance between the cathode and the anode was 3 cm.

[0049] Chrome plated substrate 610 was plated using a current density of 40 A/dm², resulting in a chromium layer at a first location 612 having a thickness of 60 microns, a chromium layer at a second location 614 having a thickness of 60 microns, a chromium layer at a third location 616 having a thickness of 60 microns, and an uncoated area 618 surrounding chromium layer at locations 612, 614, and 616. Chrome plated substrate 620 was plated using a current density of 30 A/dm², resulting in a chromium layer at a first location 622 having a thickness of 30 microns, a chromium layer at a second location 624 having a thickness of 30 microns, a chromium layer at a third location 636 having a thickness of 30 microns, and an uncoated area 628 surrounding chromium layer at locations 622, 624, and 626 that is smaller than uncoated area 618. Chrome plated substrate 630 was plated using a current density of 20 A/dm², resulting in a chromium layer at a first location 632 having a thickness of 25 microns, a chromium layer at a second location 634 having a thickness of 18 microns, and a chromium layer at a third location 636 having a thickness of 20 microns. Chrome plated substrate 640 was plated using a current density of 10 A/dm², resulting in a chromium layer at a first location 642 having a thickness of 2 microns, a chromium layer at a second location 644 having a thickness of 2 microns, and a chromium layer at a third location 646 having a thickness of 2 microns. Chrome plated substrate 650 was plated using a current density of 5 A/dm², resulting in a chromium layer at a first location 652 having a thickness of 0 microns, a chromium layer at a second location 654 having a thickness of 0 microns, and a chromium layer at a third location 656 having a thickness of 0 microns.

[0050] As illustrated by FIG. 6, any current density ranging from about 5 A/dm² to about 40 A/dm² provides deposition of a chromium layer when the distance between the cathode and the anode is about 3 cm. A current density ranging from about 10 A/dm² to about 30 A/dm² advantageously provides a chromium layer that is thick and at the same time uniform, as a current density of 5 A/dm² does not provide chromium layer deposition and a current density of 40 A/dm² provides a less uniform chromium layer deposition as shown by uncoated area 618. Further, a current density of about 20 A/dm² may advantageously provide the thickest chromium layer while still coating the whole substrate surface, and also minimize generation of chlorine gas.

[0051] FIG. 7 is an image of chrome plated substrates 710, 720, 730, and 740 formed by process 300 of FIG. 3, each plated at a different average current density using pulsed current plating. For each chrome plated substrate 710, 720, 730, and 740, the chrome plating parameters were as follows: the plating time was 1 hour, and the distance between the cathode and the anode was 3 cm, and the duty cycle was 40 %.

[0052] Chrome plated substrate 710 was plated using an average current density of 40 A/dm², resulting in a chromium layer at a first location 712 having a thickness of 62 microns, a chromium layer at a second location 714 having a thickness of 62 microns, a chromium layer at a third location 716 having a thickness of 85 microns, and an uncoated area 718 around chromium layer at locations 712, 714, and 716. Chrome plated substrate 720 was plated using an average current density of 30 A/dm², resulting in a chromium layer at a first location 722 having a thickness of 38 microns, a chromium layer at a second location 724 having a thickness of 50 microns, and a chromium layer at a third location 736 having a thickness of 60 microns. Chrome plated substrate 730 was plated using an average current density of 20 A/dm², resulting in a chromium layer at a first location 732 having a thickness of 10 microns, a chromium layer at a second location 734 having a thickness of 15 microns, and a chromium layer at a third location 736 having a thickness of 20 microns. Chrome plated substrate 740 was plated using an average current density of 10 A/dm², resulting in a chromium layer at a first location 742 having a thickness of 0 microns, a chromium layer at a second location 744 having a thickness of 0 microns, and a chromium layer at a third location 746 having a thickness of 0 microns.

[0053] As illustrated by FIG. 7, any average current density ranging from about 20 A/dm² to about 40 A/dm² provides deposition of a chromium layer when the distance between the cathode and the anode is about 3 cm. A current density ranging from about 20 A/dm² to about 30 A/dm² advantageously provides a chromium layer that is thick and at the same

time uniform, as an average current density of 10 A/dm² does not provide chromium layer deposition and an average current density of 40 A/dm² provides a less uniform chromium layer deposition as shown by uncoated area 718. Further, an average current density of about 20 A/dm² may advantageously provide the thickest chromium layer while still coating the whole substrate surface, and also minimize generation of chlorine gas.

[0054] FIG. 8 is a graph showing thickness of chromium layers formed by process 300 of FIG. 3 using pulsed current plating at different pulse frequencies and duty cycles. Pulse plating was carried out at the frequencies of 10 Hz, 25 Hz, 50 Hz, and 100 Hz, and at duty cycles of 10 %, 20 %, 40 %, and 80 % for each frequency.

[0055] As illustrated by FIG. 8, any frequency ranging from about 10 Hz to 100 Hz, and any duty cycle ranging from about 10 % and 80 % provides deposition of a chromium layer. A duty cycle of about 40% at a frequency of about 25 Hz, which corresponds to an ON time of 16 milliseconds and an OFF time of about 24 milliseconds, advantageously provides the thickest chromium layer having a thickness of about 16 microns.

[0056] FIG. 9 is an image of a chrome plated substrate 900 formed by process 300 of FIG. 3 using pulsed current, while FIG. 10 is an image of a chrome plated substrate 1000 formed by process 300 of FIG. 3 using direct current. As shown in FIG. 9, chrome plated substrate 900 has a chromium layer 902 that is uniformly and compactly deposited. FIG. 11 is a scanning electron microscopy (SEM) image of a cross-section of chrome plated substrate 900, showing that chromium layer 902 is well adhered to a substrate 910 and compact. As shown in FIG. 10, chrome plated substrate 1000 has non-adherent areas 1004 and has a chromium layer 1002 that is less compactly deposited. FIG. 12 is a SEM image of a cross-section of chrome plated substrate 1000, showing that chromium layer 1002 has parts 1006 that are less-adherent to a substrate 1010 and less compact.

[0057] As illustrated by FIGS. 9-12, for thick hard chromium coating (e.g., coating thickness of greater than about 30 microns), chrome plating using pulsed current advantageously provides more adherent and more compact chromium deposits compared to chrome plating using direct current.

[0058] FIG. 13 is an image of a chrome plated substrate such as a chrome plated Hull cell panel 1300 formed by the process of FIG. 3 using an electrolyte solution prepared by dissolving chromium (III) sulfate and an oxalate compound but not dissolving alkali metal sulfate. The chrome plating was performed in a Hull cell at 5 Amperes for 10 minutes. Chrome plated Hull cell panel 1300 shows only about 50% coverage, with an area 1302 covered by a chromium layer and an area 1304 not covered by chromium.

[0059] FIG. 14 is an image of a chrome plated substrate such as a chrome plated Hull cell panel 1400 formed by the process of FIG. 3 using the electrolyte solution prepared by the process of FIG. 1 without the step of dissolving the surfactant. The electrolyte solution was prepared by dissolving chromium (III) chloride, an oxalate compound, and also an alkali metal sulfate such as sodium sulfate. Chrome plated Hull cell panel 1400 shows more than 80% coverage, with an area 1402 covered by a chromium layer and an area 1404 not covered by chromium. The electrolyte solution prepared from chromium (III) chloride and sodium sulfate provided improved coverage compared to the electrolyte solution prepared from chromium (III) sulfate and no sodium sulfate used for chrome plated Hull cell panel 1300 in FIG. 13.

[0060] FIG. 15 is an image of a chrome plated substrate such as a chrome plated Hull cell panel 1500 formed by the process of FIG. 3 using the electrolyte solution prepared by the process of FIG. 1 including the step of dissolving the surfactant. The electrolyte solution was prepared by dissolving chromium (III) chloride, an oxalate compound, an alkali metal sulfate such as sodium sulfate, and the surfactant such as sodium lauryl sulfate. Chrome plated Hull cell panel 1500 shows more than 80% coverage, with an area 1502 covered by a chromium layer and an area 1504 not covered by chromium.

[0061] As illustrated by FIGS. 13-15, an electrolyte solution in which an alkali metal sulfate such as sodium sulfate is dissolved advantageously provides improved chrome plating, with a significantly higher percent coverage of the substrate. The alkali metal sulfate may, for example, provide increased conductivity to the electrolyte solution, resulting in an improved chromium layer deposition.

[0062] FIGS. 16A-B are SEM images of a part of chrome plated Hull cell panel 1600 of FIG. 14. A 1 cm² portion was cut out from the middle of chrome plated Hull cell panel 1400 and SEM images were taken-FIG. 16A is an SEM image at 1000X magnification, and FIG. 16B is an SEM image at 2500X magnification. Chrome plated Hull cell panel 1400 formed using the electrolyte solution without the surfactant showed many pits, appearing as black spots on the SEM images of FIGS. 16A and 16B.

[0063] FIGS. 17A-B are SEM images of a part of chrome plated Hull cell panel 1500 of FIG. 15. A 1 cm² portion was cut out from the middle of chrome plated Hull cell panel 1500 and SEM images were taken-FIG. 17A is an SEM image at 1000X magnification, and FIG. 17B is an SEM image at 2500X magnification. Chrome plated Hull cell panel 1500 formed using the electrolyte solution with the surfactant did not show pits, as there are no black spots on the SEM images of FIGS. 17A-B compared to FIGS. 16A-B.

[0064] As illustrated by FIGS. 16A-B and 17A-B, including the surfactant in the electrolyte solution advantageously has the effect of reducing pitting. The surfactant may function as a wetting agent that reduces the surface tension, and may reduce the generation of gas (e.g., chlorine gas, hydrogen gas, etc.) during chrome plating. The generation of gas may form pores in the chromium that is deposited, which may appear as pits when the gas generation is in excess. The

surfactant, by reducing gas evolution, prevents or reduces such pitting during chrome plating.

[0065] FIG. 18 is an SEM image of chrome deposits 1802 on a chrome plated substrate formed by the process of FIG. 3. As shown in FIG. 18, chrome deposits 1802 have an amorphous morphology. A Vickers indent test was performed on chrome deposits 1802 at location 1804, which revealed that chrome deposits 1802 had a hardness of about 1100 HV at a 100 g load.

[0066] FIG. 19 is an image of a chrome plated substrates 1900 formed by the process of FIG. 3 that have been bent to show resilience of chromium layers 1902 to bending. Even when chrome plated substrates 1900 are bent, chromium layers 1902 do not come off, revealing that chromium layer 1902 are strongly adherent to the underlying substrate.

[0067] FIG. 20 is an image of a chrome plated substrate 2000 formed by the process of FIG. 3 on which abrasion testing has been performed to determine wear resistance of a chromium layer 2002.

[0068] A CS 10 wheel under 1000 g load was used, resulted in a wear index of about 0.013 to about 0.021 at a tested area 2004 of chromium layer 2002. A further test was performed using a CS 17 wheel under 1000 g load, which resulted in a wear index of about 0.015 to 0.025.

[0069] Wear resistance (Taber abrasion) may be measured as described in ASTM G195-13a with abrasion wheels from Taber industries. The procedure was carried out with a substrate sample having an initial weight before abrading of 59.1623 g, with 42.7 micron (1.68 mils) layer thickness. The sample was mounted on an abraser turntable platform with the side to be abraded facing up. The sample was secured with a clamp plate and nut. Abrading wheels were placed on the sample. A load of 1000 g (per wheel CS17) was used. To ensure that the abrading function of the wheels is maintained at a constant level, the abrading wheels are re-surfaced prior to each test.

[0070] The sample was subject to abrasion for a specified number of cycles (tests with 1000, 2000, 3000, 4000 and 5000 cycles). Any loose abrading material remaining on the sample was removed by light brushing. The final weight of the sample after abrasion was recorded.

[0071] Compute weight loss, L, of the test specimen as follows:

$$L = A - B$$

A = weight of test specimen before abrasion, mg

B = weight of test specimen after abrasion, mg

[0072] Compute the wear index, I, of a test specimen as follows;

$$I = (A - B)1000/C$$

A = weight of test specimen before abrasion, mg

B = weight of test specimen after abrasion, mg

C = number of cycles of abrasion recorded

Initial weight (g)	Final weight (g)	Weight loss value (mg)	No of cycles	Wear index (I)
59.1623	59.1350	27.3	1000	0.0273
59.1623	59.1224	39.9	2000	0.0199
59.1623	59.1084	53.9	3000	0.0179
59.1623	59.1031	59.2	4000	0.0148
59.1623	59.0958	66.5	5000	0.0133

[0073] The abrasion testing revealed that the wear property is similar to hard chromium layers formed by chrome plating using hexavalent chromium.

[0074] Although there have been some successes at implementing the use of trivalent chromium baths for thin, decorative chrome plating, conventional chrome plating processes that use trivalent chromium baths were unsuitable for thicker, hard chrome plating. Moreover, even trivalent chromium baths used for decorative chrome plating often contained boric acid as a buffering agent. Further, conventional chrome plating processes that use trivalent chromium risked the trivalent chromium being oxidized to hexavalent chromium at the anode.

[0075] Advantageously, chrome plating according to process 300 provides hard chromium layers that may be at least as structurally robust, reliable, adherent, and wear resistant as chrome plating using hexavalent chromium, while avoiding the use of chemicals such as hexavalent chromium and boric acid. Further, oxidation of trivalent chromium to hexavalent chromium, generation of toxic gas byproducts, and the production of further undesirable byproducts are avoided or significantly reduced.

[0076] Further, the description comprises embodiments according to the following clauses:

Clause 1. A method for chrome plating a substrate using an electrolyte solution, the method comprising:

dissolving in an aqueous medium a trivalent chromium salt in an amount ranging from 0.1 mol to 0.9 mol per liter of the electrolyte solution;
dissolving an oxalate compound in an amount ranging from 0.1 mol to 3.0 mol per liter of the electrolyte solution;
dissolving a metal salt in an amount ranging from 0.1 mol to 4.0 mol per liter of the electrolyte solution, an alkali metal sulfate in an amount ranging from 0.1 mol to 2.0 mol per liter of the electrolyte solution, and an alkali metal halide in an amount ranging from 0.1 mol to 0.5 mol per liter of the electrolyte solution; and
passing a current between a cathode and an anode through the electrolyte solution to deposit chromium on the substrate.

Clause 2. The method of Clause 1, wherein the step of dissolving the trivalent chromium salt comprises dissolving chromium (III) chloride and/or chromium (III) sulfate.

Clause 3. The method of Clauses 1 or 2, wherein the step of dissolving the oxalate compound comprises dissolving sodium oxalate in an amount ranging from 0.1 mol to 1.0 mol per liter of the electrolyte solution, potassium oxalate in an amount ranging from 0.1 mol to 1.0 mol per liter of the electrolyte solution, and/or oxalic acid in an amount ranging from 0.1 mol to 3.0 mol per liter of the electrolyte solution.

Clause 4. The method of any of Clauses 1 - 3, wherein:

dissolving the metal salt comprises dissolving aluminum sulfate in an amount ranging from 0.1 mol to 0.4 mol per liter of the electrolyte solution and/or aluminum chloride in an amount ranging from 0.1 mol to 4.0 mol per liter of the electrolyte solution;
dissolving the alkali metal sulfate comprises dissolving sodium sulfate and/or potassium sulfate; and
dissolving the alkali metal halide comprises dissolving sodium fluoride and/or potassium fluoride.

Clause 5. The method of any of Clauses 1 - 4, wherein the dissolving the trivalent chromium salt, the oxalate compound, the metal salt, the alkali metal sulfate, and the alkali metal halide is performed in the following order:

- (1) dissolving the trivalent chromium salt and the oxalate compound;
- (2) dissolving the metal salt;
- (3) dissolving the alkali metal sulfate; and
- (4) dissolving the alkali metal halide.

Clause 6. The method of any of Clauses 1 - 5, wherein the step of dissolving the oxalate compound comprises stirring the oxalate compound at a temperature ranging from 70 °C to 80 °C for a time ranging from 1 hour to 3 hours.

Clause 7. The method of any of Clauses 1 - 6, further comprising adjusting the pH of the electrolyte solution to a pH ranging from 2 to 4.

Clause 8. The method of any of Clauses 1 - 7, further comprising adding sodium lauryl sulfate and/or potassium lauryl sulfate in an amount ranging from 0.1 g to 1 g per liter of the electrolyte solution.

Clause 9. The method of any of Clauses 1 - 8, further comprising adding sodium bromide and/or potassium bromide in an amount ranging from 0.1 g to 1 g per liter of the electrolyte solution.

Clause 10. The method of any of Clauses 1 - 9, further comprising maintaining the electrolyte solution at a pH ranging from 2 to 4.

Clause 11. The method of any of Clauses 1 - 10, further comprising maintaining the electrolyte solution at a tem-

perature ranging from 30 °C to 40 °C during the step of passing the current.

Clause 12. The method of any of Clauses 1 - 11, wherein the step of passing the current is performed using a carbonaceous anode, a platinum anode, or a platinized titanium anode, and wherein the trivalent chromium salt comprises chromium (III) sulfate.

Clause 13. The method of any of Clauses 1 - 12, wherein the step of passing the current is performed using a carbonaceous anode, and wherein the trivalent chromium salt comprises chromium (III) chloride.

Clause 14. The method of any of Clauses 1 - 13, wherein the step of passing the current comprises applying a pulsed current or a direct current having a current density ranging from about 5 A/dm² to about 50 A/dm².

Clause 15. The method of any of Clauses 1-14, wherein the step of the passing the current comprises applying a pulsed current having a duty cycle ranging from about 20% to about 80%.

Clause 16. The method of any of Clauses 1 - 15, wherein the step of passing the current is performed until a chromium layer having a thickness greater than 5 microns and hardness greater than 800 HV is formed on the substrate.

Clause 17. The method of any of Clauses 1 - 16, wherein the step of passing the current to deposit chromium on the substrate comprises passing the current to deposit chromium on a steel substrate, a copper substrate, a nickel substrate, a copper-coated substrate, or a nickel-coated substrate.

Clause 18. The method of any of Clauses 1-17, further comprising responsive to the step of passing the current, depositing chromium on the substrate or co-depositing chromium and carbon on the substrate.

Clause 19. A method for preparing an electrolyte solution for chrome plating, the method comprising:

providing trivalent chromium by dissolving a trivalent chromium salt;
forming complexes of oxalate and trivalent chromium by dissolving an oxalate compound;
buffering the electrolyte solution by dissolving a metal salt;
increasing the conductivity by dissolving an alkali metal sulfate; and
increasing the wetting property of the electrolyte solution by dissolving alkali metal halide.

Clause 20. An electrolyte solution prepared by the method of any of Clauses 1 - 19.

[0077] Embodiments described above illustrate but do not limit the invention. It should also be understood that numerous modifications and variations are possible in accordance with the principles of the present disclosure. Accordingly, the scope of the invention is defined only by the following claims.

Claims

1. A method for chrome plating a substrate using an electrolyte solution, the method comprising:

dissolving in an aqueous medium a trivalent chromium salt in an amount ranging from 0.1 mol to 0.9 mol per liter of the electrolyte solution;
dissolving an oxalate compound in an amount ranging from 0.1 mol to 3.0 mol per liter of the electrolyte solution;
dissolving a metal salt in an amount ranging from 0.1 mol to 4.0 mol per liter of the electrolyte solution, an alkali metal sulfate in an amount ranging from 0.1 mol to 2.0 mol per liter of the electrolyte solution, and an alkali metal halide in an amount ranging from 0.1 mol to 0.5 mol per liter of the electrolyte solution; and
passing a current between a cathode and an anode through the electrolyte solution to deposit chromium on the substrate.

2. The method of claim 1, wherein the step of dissolving the trivalent chromium salt comprises dissolving chromium (III) chloride and/or chromium (III) sulfate.

3. The method of claims 1 or 2, wherein the step of dissolving the oxalate compound comprises dissolving sodium oxalate in an amount ranging from 0.1 mol to 1.0 mol per liter of the electrolyte solution, potassium oxalate in an

amount ranging from 0.1 mol to 1.0 mol per liter of the electrolyte solution, and/or oxalic acid in an amount ranging from 0.1 mol to 3.0 mol per liter of the electrolyte solution.

4. The method of any of claims 1 - 3, wherein:

dissolving the metal salt comprises dissolving aluminum sulfate in an amount ranging from 0.1 mol to 0.4 mol per liter of the electrolyte solution and/or aluminum chloride in an amount ranging from 0.1 mol to 4.0 mol per liter of the electrolyte solution;
dissolving the alkali metal sulfate comprises dissolving sodium sulfate and/or potassium sulfate; and
dissolving the alkali metal halide comprises dissolving sodium fluoride and/or potassium fluoride.

5. The method of any of claims 1 - 4, wherein the dissolving the trivalent chromium salt, the oxalate compound, the metal salt, the alkali metal sulfate, and the alkali metal halide is performed in the following order:

(1) dissolving the trivalent chromium salt and the oxalate compound;
(2) dissolving the metal salt;
(3) dissolving the alkali metal sulfate; and
(4) dissolving the alkali metal halide.

6. The method of any of claims 1 - 5, wherein the step of dissolving the oxalate compound comprises stirring the oxalate compound at a temperature ranging from 70 °C to 80 °C for a time ranging from 1 hour to 3 hours.

7. The method of any of claims 1 - 6, further comprising adjusting the pH of the electrolyte solution to a pH ranging from 2 to 4.

8. The method of any of claims 1 - 7, further comprising adding sodium lauryl sulfate and/or potassium lauryl sulfate in an amount ranging from 0.1 g to 1 g per liter of the electrolyte solution.

9. The method of any of claims 1 - 8, further comprising adding sodium bromide and/or potassium bromide in an amount ranging from 0.1 g to 1 g per liter of the electrolyte solution.

10. The method of any of claims 1 - 9, further comprising maintaining the electrolyte solution at a pH ranging from 2 to 4.

11. The method of any of claims 1 - 10, further comprising maintaining the electrolyte solution at a temperature ranging from 30 °C to 40 °C during the step of passing the current.

12. The method of any of claims 1 - 11, wherein the step of passing the current is performed using a carbonaceous anode, a platinum anode, or a platinized titanium anode, and wherein the trivalent chromium salt comprises chromium (III) sulfate.

13. The method of any of claims 1 - 12, wherein:

the step of passing the current is performed using a carbonaceous anode, and wherein the trivalent chromium salt comprises chromium (III) chloride; and/or
the step of passing the current comprises applying a pulsed current or a direct current having a current density ranging from about 5 A/dm² to about 50 A/dm²; and/or
the step of the passing the current comprises applying a pulsed current having a duty cycle ranging from about 20% to about 80%; and/or
the step of passing the current is performed until a chromium layer having a thickness greater than 5 microns and hardness greater than 800 HV is formed on the substrate; and/or
the step of passing the current to deposit chromium on the substrate comprises passing the current to deposit chromium on a steel substrate, a copper substrate, a nickel substrate, a copper-coated substrate, or a nickel-coated substrate.

14. The method of any of claims 1 - 13, further comprising responsive to the step of passing the current, depositing chromium on the substrate or co-depositing chromium and carbon on the substrate.

15. An electrolyte solution prepared by the method of any of claims 1 - 14.

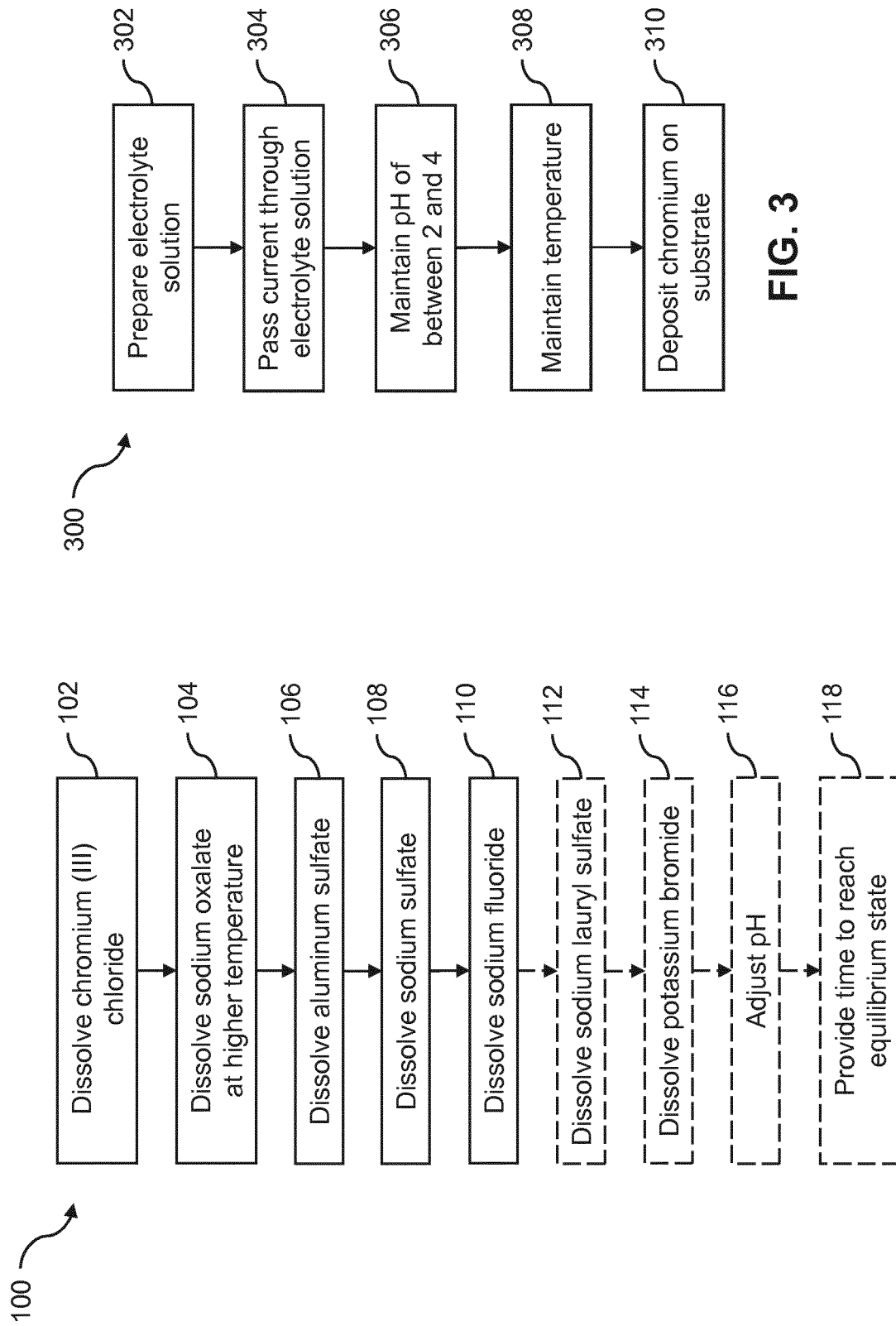


FIG. 1

FIG. 3

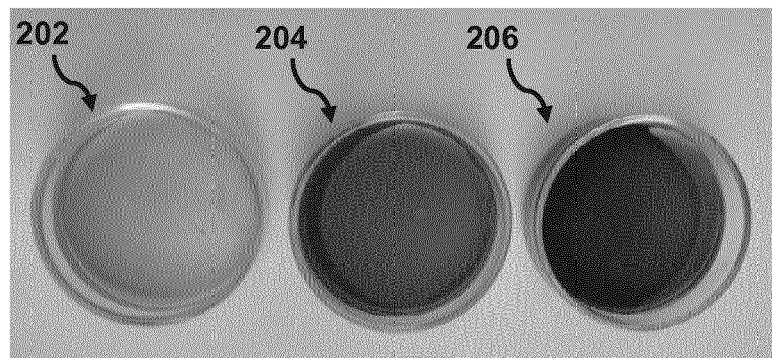


FIG. 2

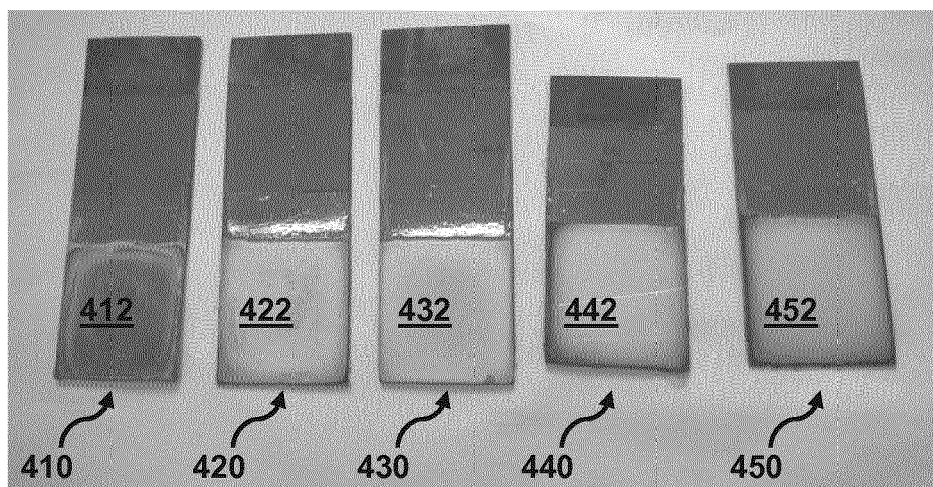


FIG. 4

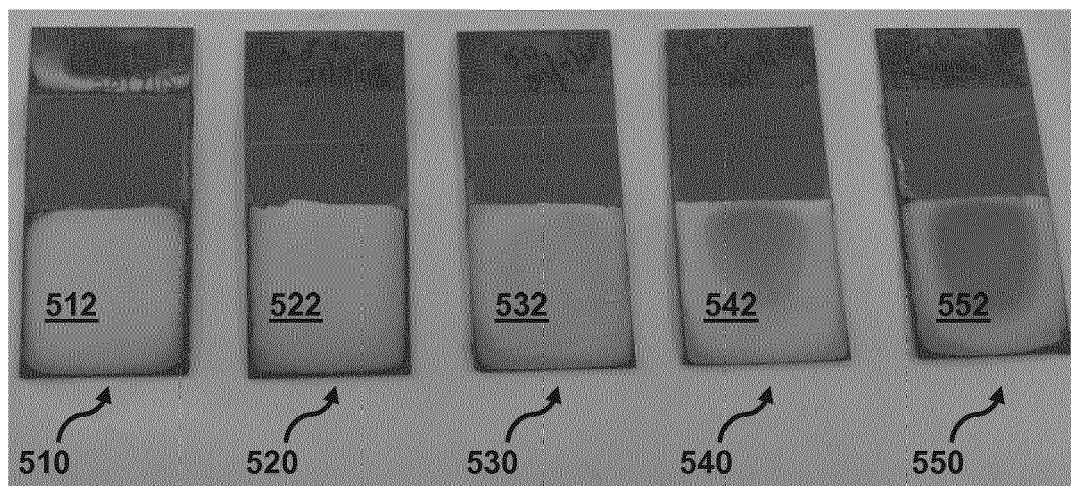


FIG. 5

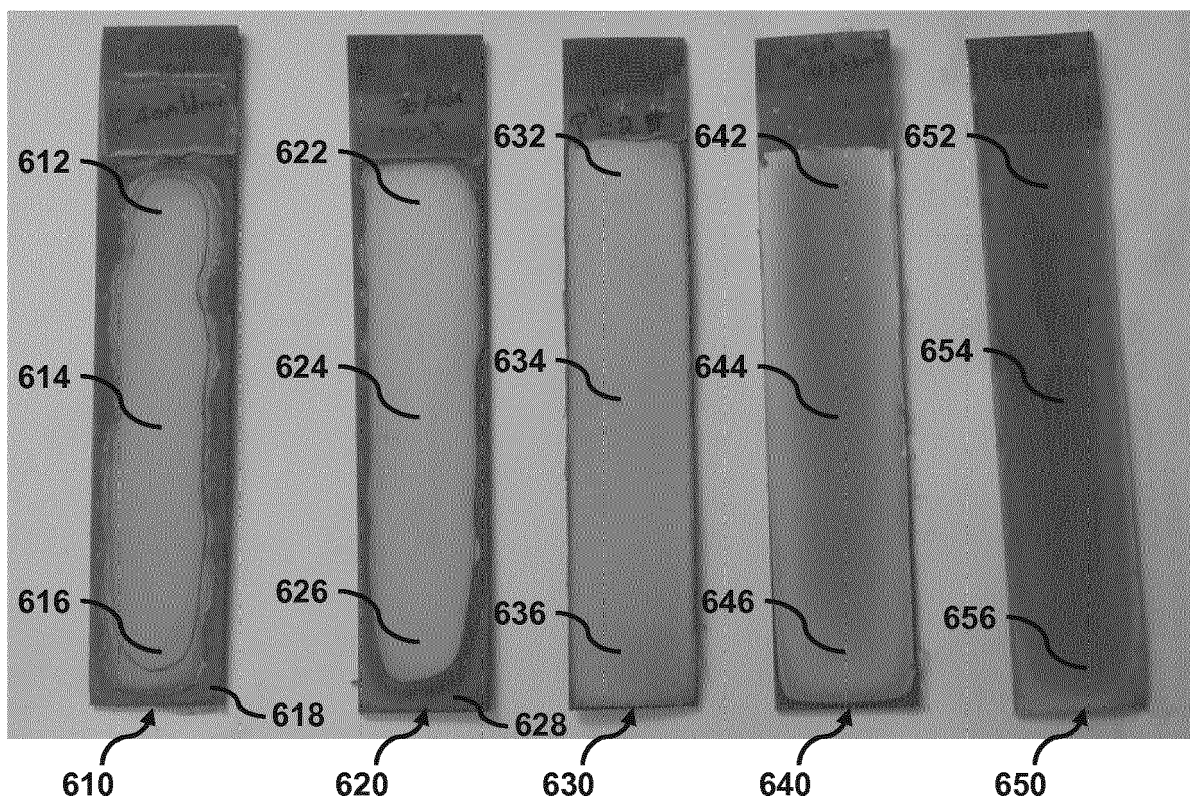


FIG. 6

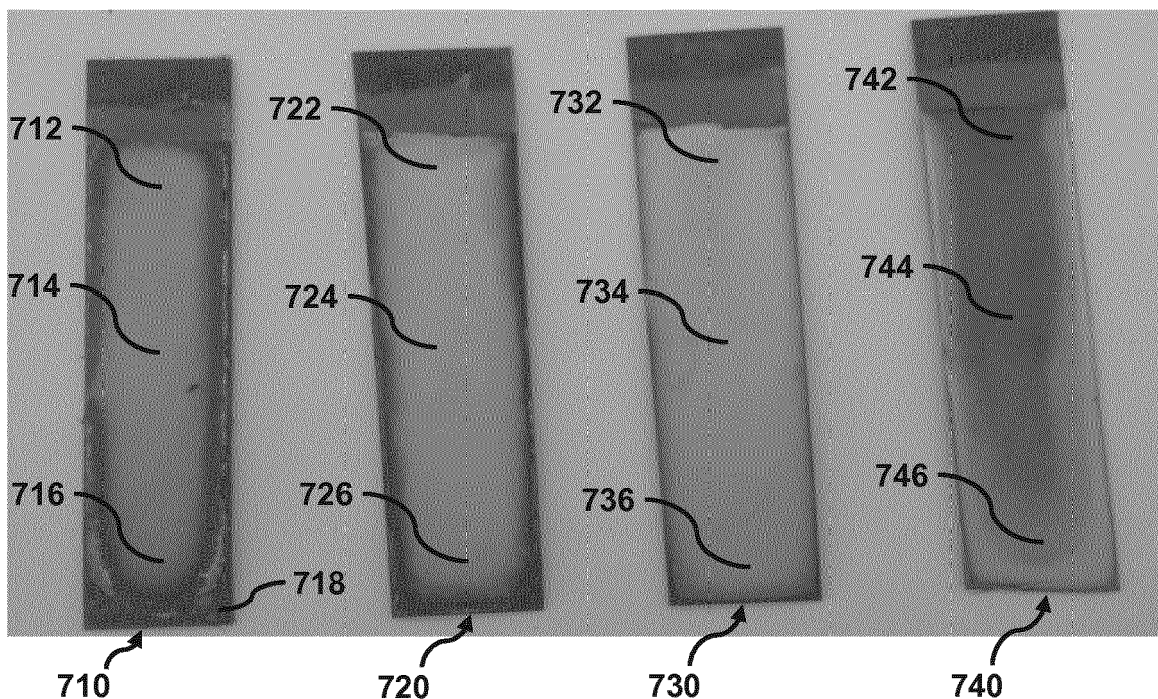


FIG. 7

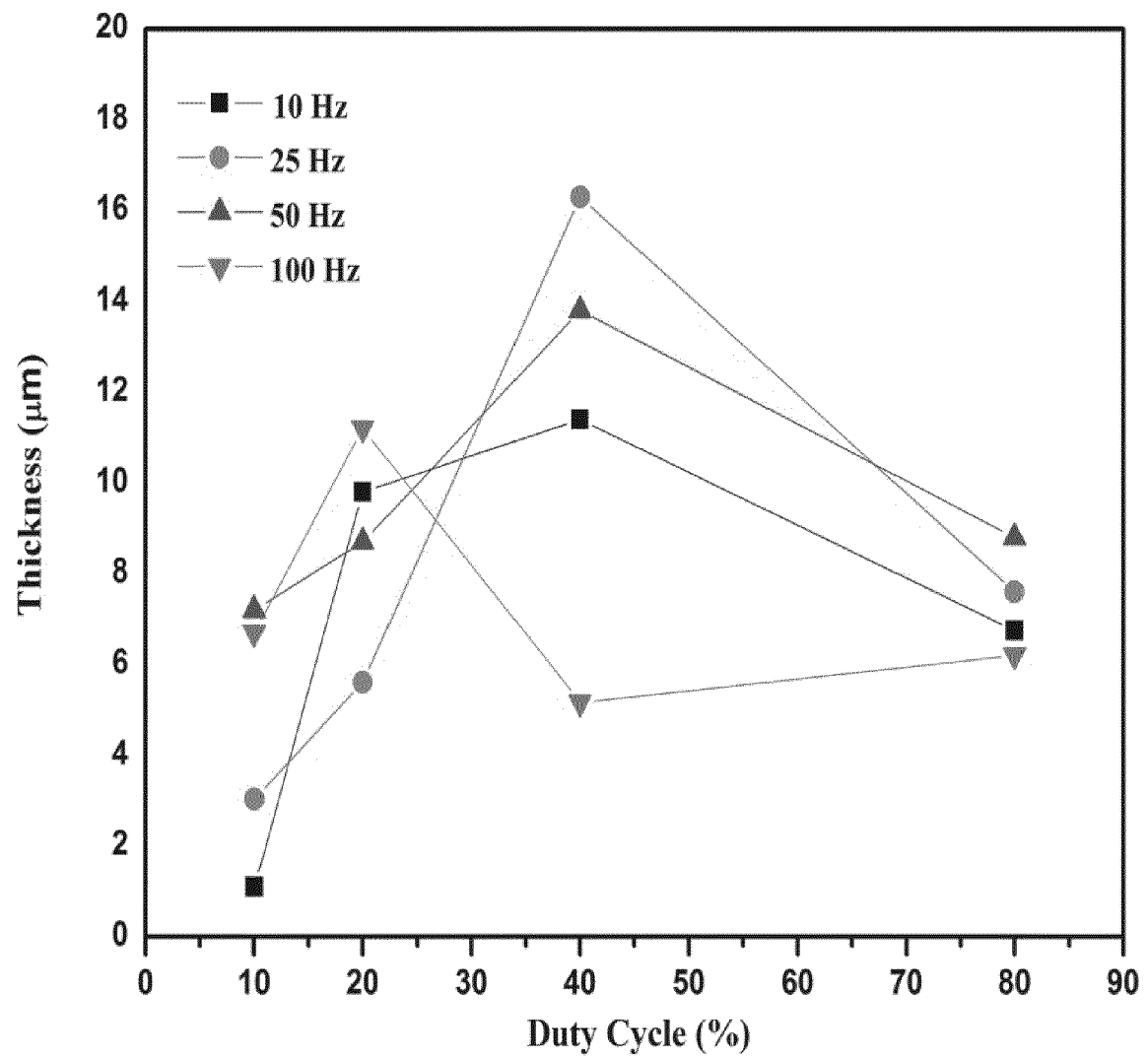


FIG. 8

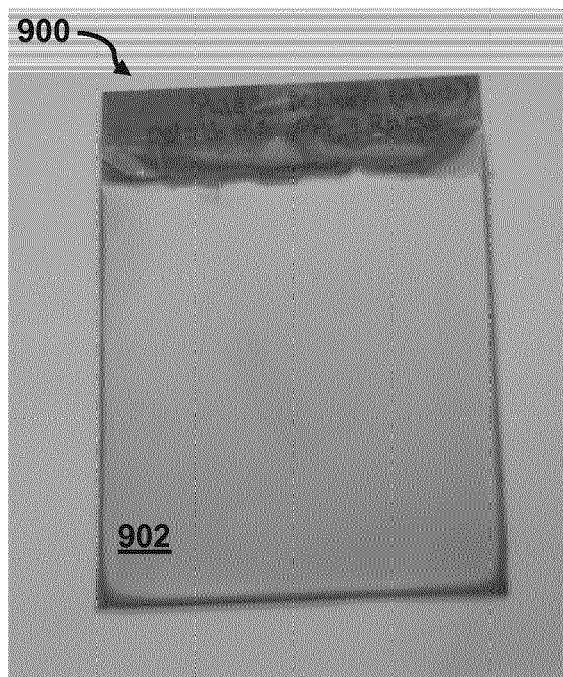


FIG. 9

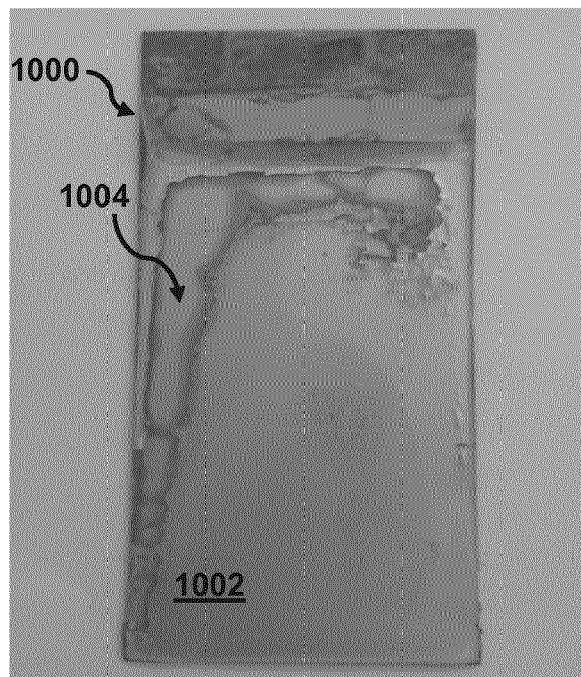


FIG. 10

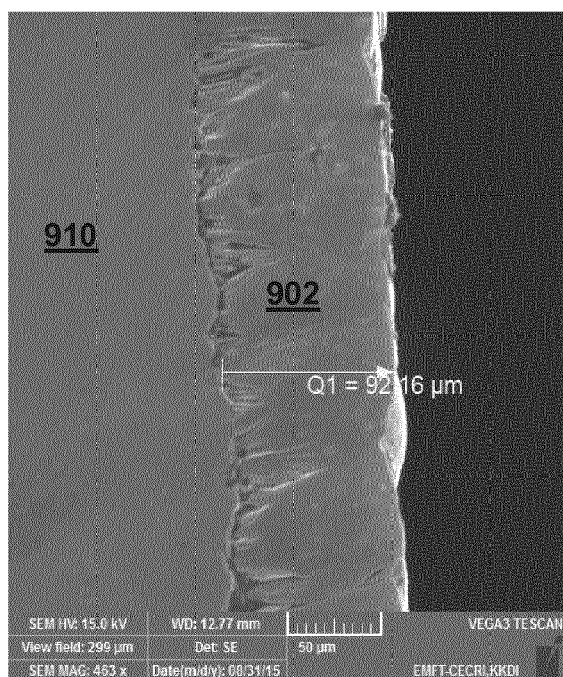


FIG. 11

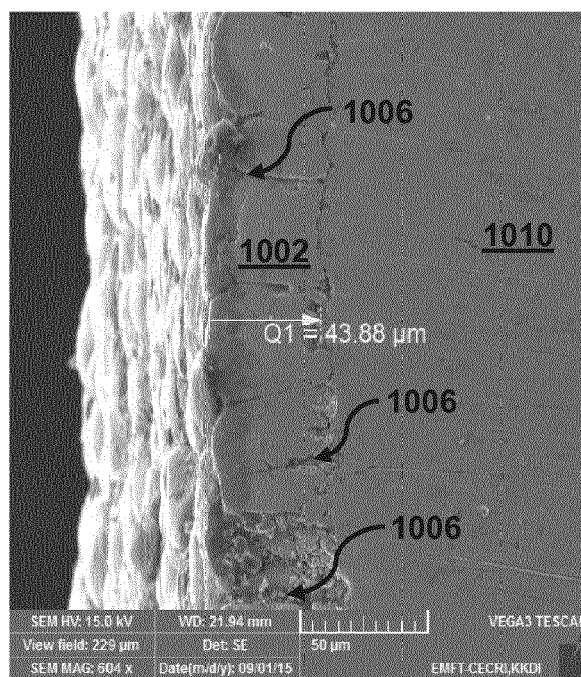


FIG. 12

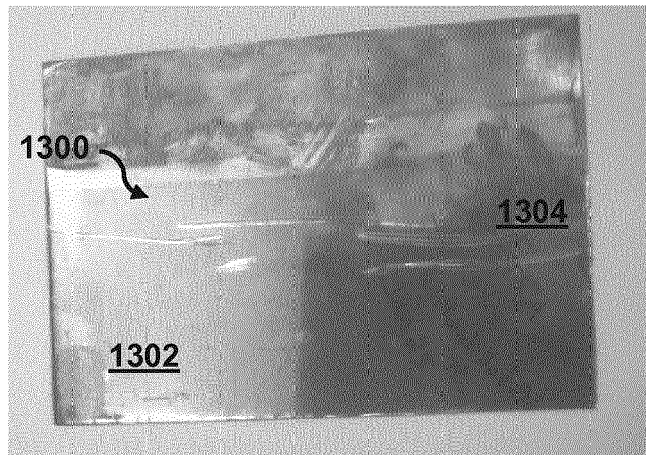


FIG. 13

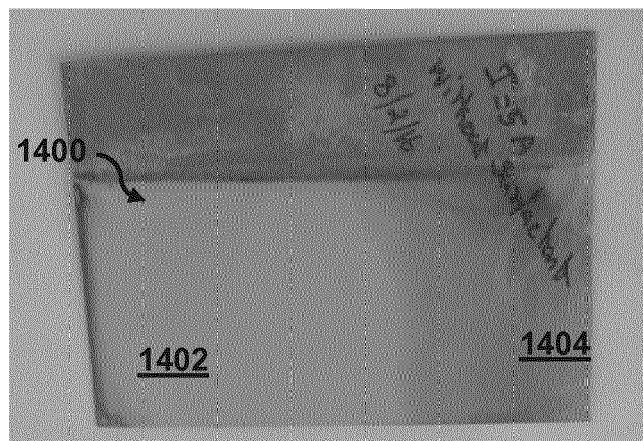


FIG. 14

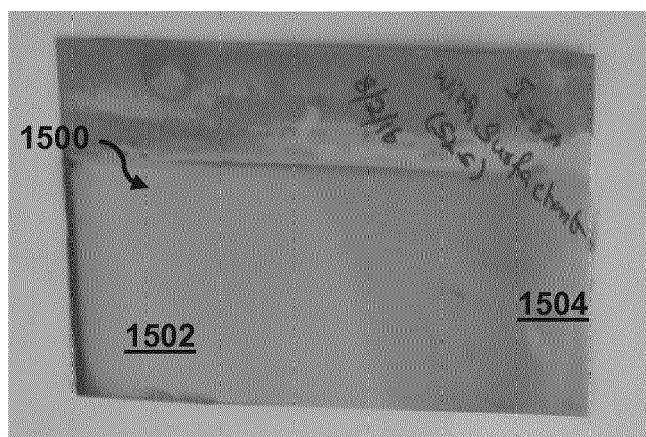


FIG. 15

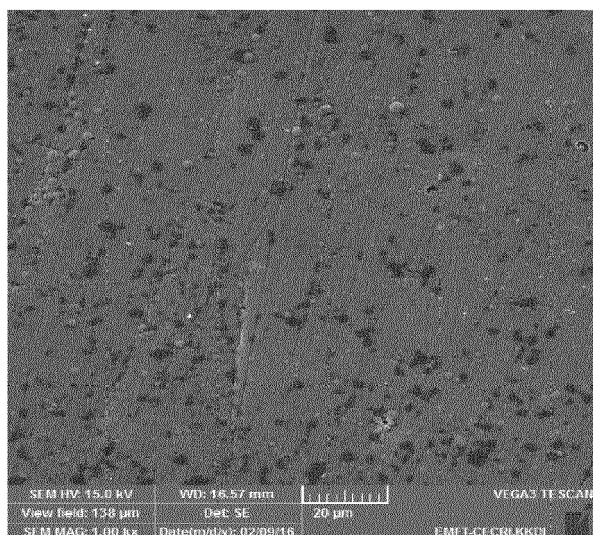


FIG. 16A

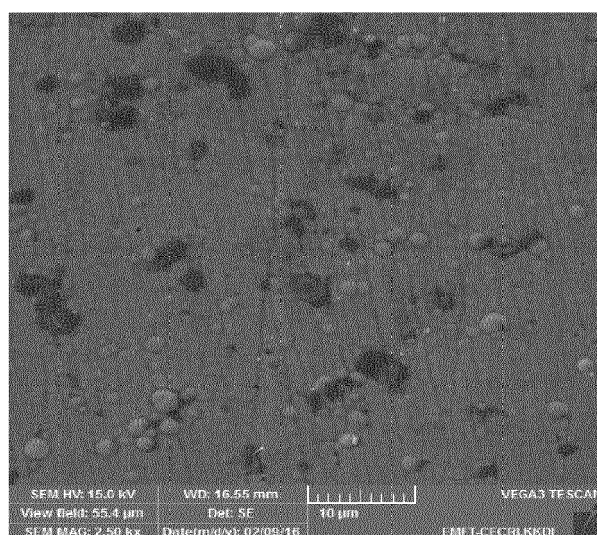


FIG. 16B

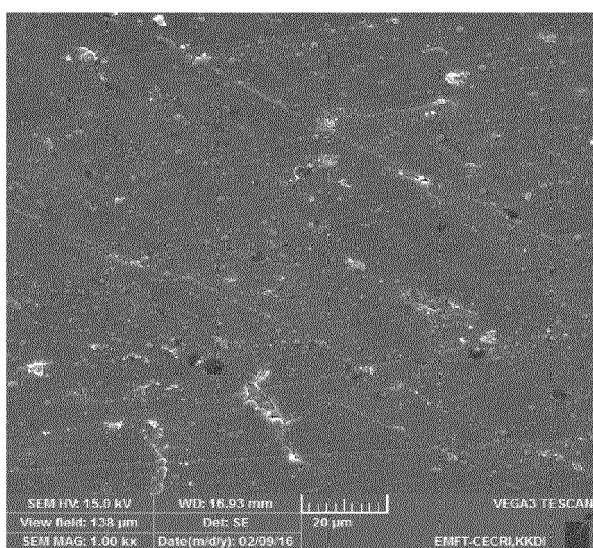


FIG. 17A

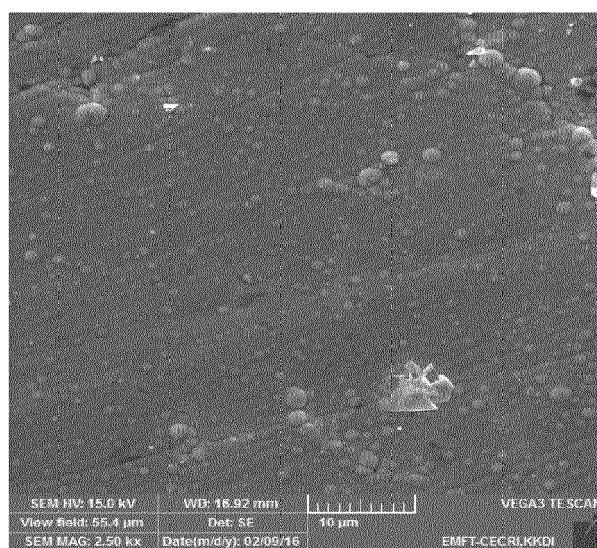


FIG. 17B

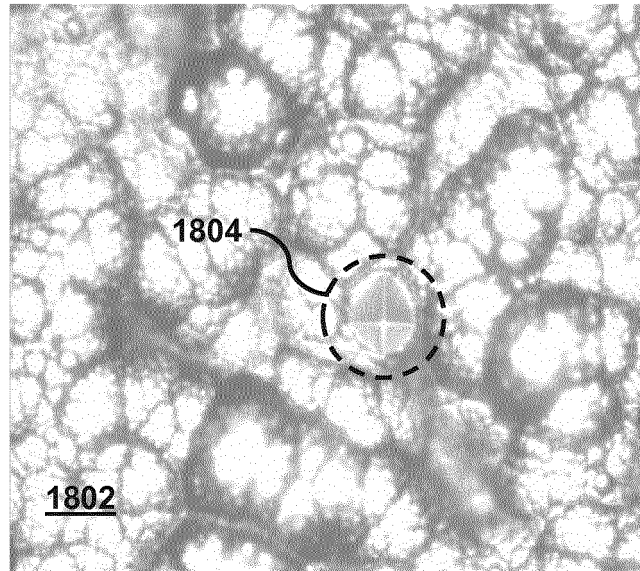


FIG. 18

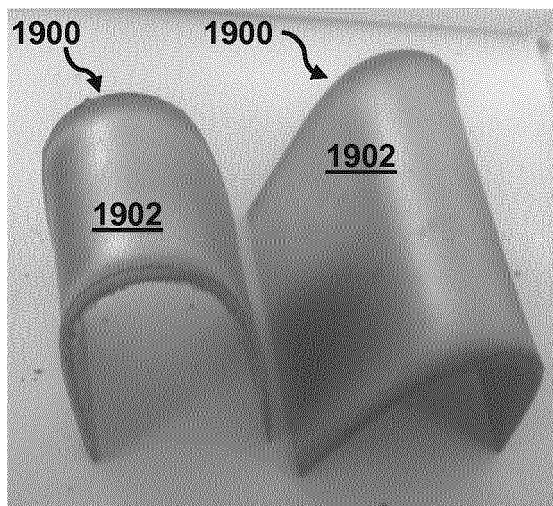


FIG. 19

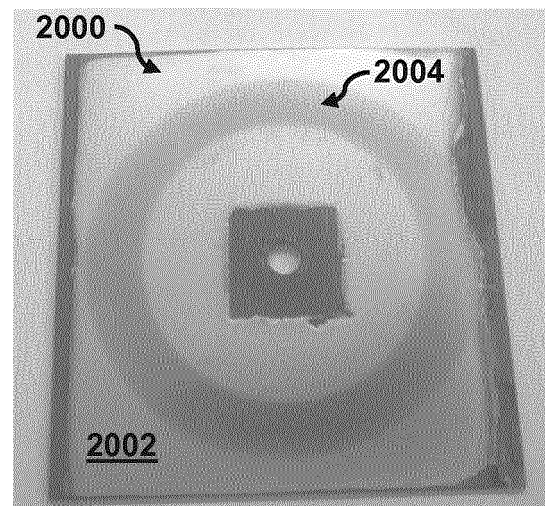


FIG. 20