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(54) **ELECTRODEPOSITION OF ALUMINUM AND REFRACTORY METALS FROM NON-AROMATIC ORGANIC SOLVENTS**

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(57) **ABSTRACT**

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An electroplating solution includes a non-aqueous non-aromatic organic solvent and a mixture including soluble metallic salts and organic additives dissolved in the non-aqueous non-aromatic organic solvent. Electrodeposition of a metal from the electroplating solution includes preparing an electroplating solution and electrodepositing the metal from the electroplating solution onto a conductive substrate under a cathodic current. An electroplating system has a plating chamber containing an electroplating solution, an entry point to the electroplating system, and a transporting system to convey a part to be electroplated from the entry point to the plating chamber. The electroplating solution includes a non-aqueous non-aromatic organic solvent and a mixture including soluble metallic salts and organic additives, the mixture dissolved in the non-aqueous non-aromatic organic solvent.

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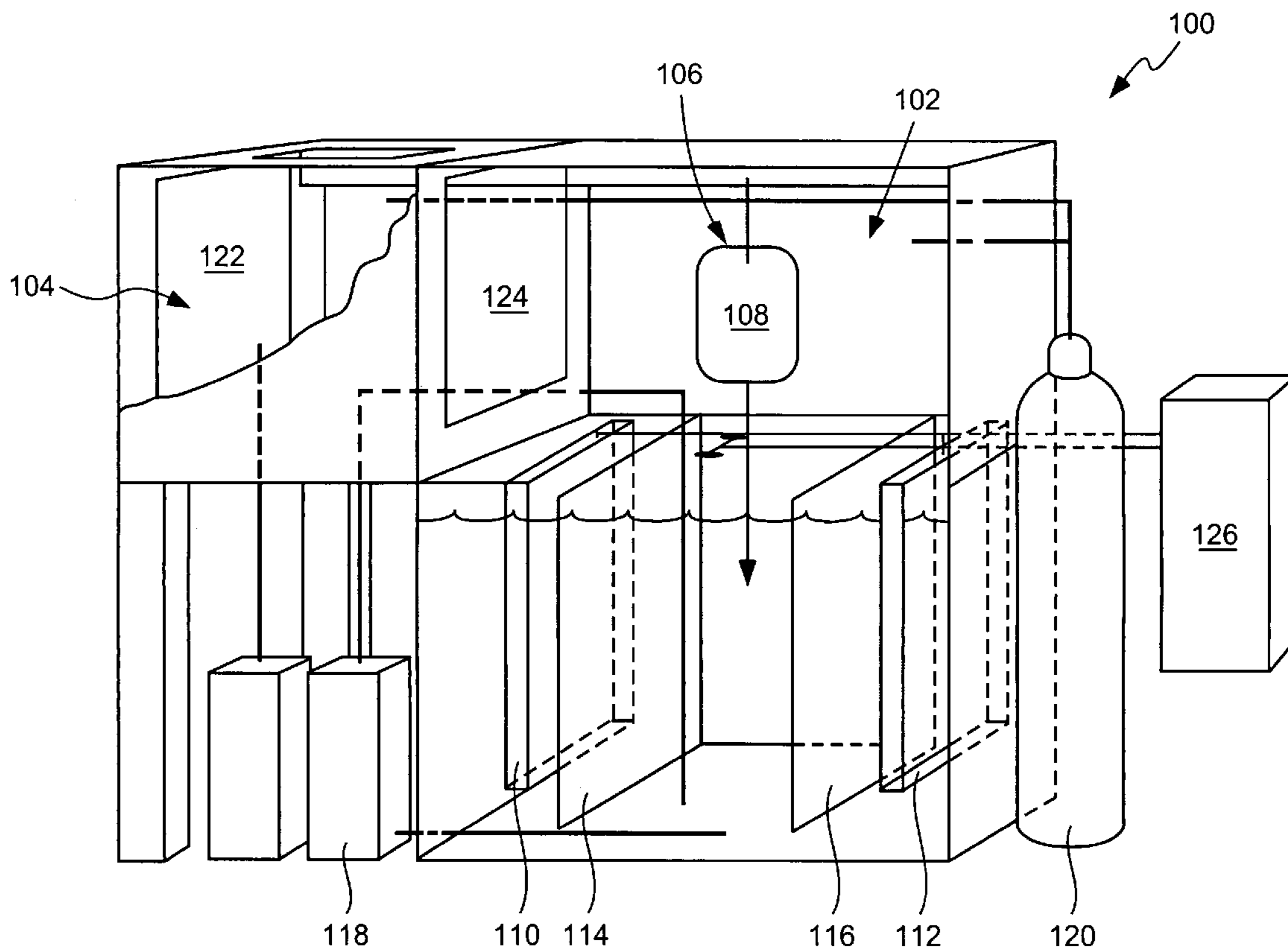
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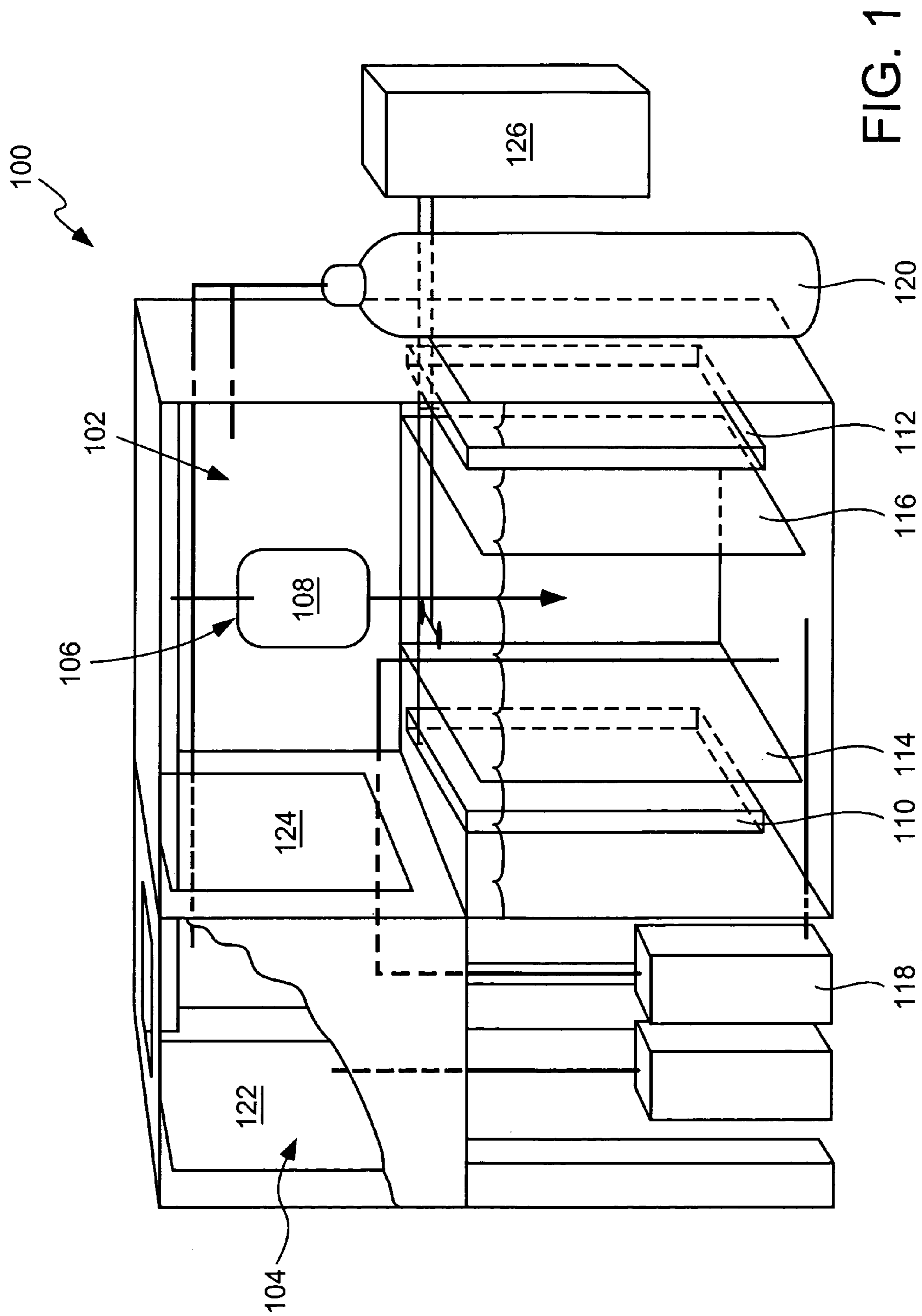
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(60) **Provisional application No. 60/451,631, filed on Mar. 5, 2003.**

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**ELECTRODEPOSITION OF ALUMINUM AND  
REFRACTORY METALS FROM NON-AROMATIC  
ORGANIC SOLVENTS**

CROSS-REFERENCE TO RELATED  
APPLICATIONS

[0001] The present application claims the benefit of U.S. Provisional Patent Application No. 60/451,631, filed in the United States on Mar. 5, 2003, the entire contents of which are incorporated herein by reference.

BACKGROUND

[0002] 1. Field of the Invention

[0003] The present method relates generally to electrodeposited coatings. More specifically, the method relates to metallic coatings of aluminum, magnesium and refractory metals, such as titanium, tantalum, zirconium, and their alloys, obtained by electrodeposition from non-aromatic organic solvents.

[0004] 2. Background of the Invention

[0005] In the description of the background of the present invention that follows reference is made to certain structures and methods, however, such references should not necessarily be construed as an admission that these structures and methods qualify as prior art under the applicable statutory provisions. Applicants reserve the right to demonstrate that any of the referenced subject matter does not constitute prior art with regard to the present invention.

[0006] Surface protection against corrosion and wear can be applied to ferrous and non-ferrous metal parts. A suitable method to obtain such protection is coatings. For example, in the aerospace industry cadmium coating is used to protect parts, such as landing gear or fasteners against corrosion. The cadmium coating functions as a sacrificial coating that provides protection even when scratched. However, cadmium is a toxic metal electrodeposited from a plating solution based on cyanide, which affects the handling and disposal precautions. Substitute metallic coatings for cadmium are needed.

[0007] One aspect of the protection supplied by the coating is a result of the salt water electrochemical potential of the cadmium coating being negative relative to the underlying material. Thus, suitable substitute coating materials for cadmium include those materials with similar, e.g., negative, salt water electrochemical potentials relative to the underlying material. For example, zinc, manganese, beryllium and magnesium are included in candidate materials to replace cadmium in coatings. However, these candidate materials have drawbacks. Zinc, while easy to electroplate, suffers from environmental embrittlement and is thus unsuitable for high strength steels. Manganese can be electroplated by aqueous methods, but exposure can cause pulmonary and neurological effects. Beryllium similarly has environmental drawbacks and magnesium is highly active in this application when not alloyed within a coating.

[0008] Aluminum and refractory metals, such as titanium, are substitute candidates for protective coatings and for replacing of cadmium coatings. Aluminum coatings can provide a sacrificial protective barrier against corrosion for ferrous metal parts. Refractory metal coatings can provide a

protective barrier against damage to the underlying material, e.g., ferrous and non-ferrous metal parts, by mechanisms such as corrosion, erosion, wear, abrasion and embrittlement.

[0009] Aluminum and refractory metals, such as titanium, are typically obtained electrochemically from fused salts bath chemistry, such as those based on lithium chloride, or from toxic organic solvents, such as those based on benzene and toluene, or by electrophoresis. These known methods have negative drawbacks on coating quality and cost. For example, molten salt bath methods may avoid embrittlement during plating, but trapped salts can be a source of subsequent corrosion and embrittlement.

[0010] Metallic coatings of aluminum and refractory metals can also be obtained by other methods. For example, physical techniques, such as arc spraying, physical vapor deposition techniques, such as ion vacuum deposition of aluminum (otherwise known as ivadizing), and chemical techniques, such as sol-gel or electrodeposition from toxic organic solvents or by fused salts, can be employed to form coatings of aluminum and refractory metals.

[0011] U.S. Pat. No. 4,145,261 discloses a plating solution that is a mixture of toluene, organics including benzene, and aluminum halides. U.S. Pat. No. 4,759,831 discloses a load-lock isolated electrolyte chamber for the electrodeposition of aluminum. The nature of the plating solution, e.g., the environmental aspects and the tendency to be contaminated when exposed to air, render this disclosed solution and process costly, inefficient, and potentially hazardous to the environment and to health.

[0012] Japanese patent 55-158289 discloses various low molecular weight organic solvents in which were dissolved synthesized aluminum salts. However, no details on coating properties were provided.

[0013] Thus, there remains a need for coating technologies that can replace the current cadmium coatings, particularly in high strength steels and aerospace applications. Further, there is a need for aluminum electrodeposition technologies that are environmentally safe and clean, while also being cost and time efficient.

SUMMARY

[0014] An exemplary method of electrodeposition of a metal comprises preparing an electroplating solution and electrodepositing the metal from the electroplating solution onto a conductive substrate under a cathodic current. The electroplating solution includes a mixture of soluble metallic salts and organic additives dissolved in a non-aqueous non-aromatic organic solvent.

[0015] An exemplary electroplating solution comprises a non-aqueous non-aromatic organic solvent and a mixture including soluble metallic salts and organic additives, the mixture dissolved in the non-aqueous non-aromatic organic solvent.

[0016] An exemplary embodiment of an electroplating system comprises a plating chamber containing an electroplating solution, an entry point to the electroplating system, and a transporting system to convey a part to be electroplated from the entry point to the plating chamber. The electroplating solution includes a non-aqueous non-aromatic

organic solvent and a mixture including soluble metallic salts and organic additives, the mixture dissolved in the non-aqueous non-aromatic organic solvent.

#### BRIEF DESCRIPTION OF DRAWING FIGURES

[0017] The following detailed description of preferred embodiments can be read in connection with the accompanying drawings in which like numerals designate like elements and in which:

[0018] **FIG. 1** is a schematic representation of an electroplating system.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0019] Electrodeposition from non-aromatic organic solvents (NAOS) can deposit metals and alloys that cannot be obtained otherwise by conventional (aqueous) electroplating. Since there is little or no water present in solution (as in the water of aqueous solutions), hydrogen embrittlement of high tensile strength materials is reduced or minimized. In addition, NAOS processes have similar or the same characteristics as conventional electroplating in terms of parts handling, some equipment and methods, allowing for efficient substitution of NAOS in typical electrodeposition facilities.

[0020] An exemplary method of electrodeposition of a metal comprises preparing an electroplating solution and electrodepositing the metal from the electroplating solution onto a conductive substrate under a cathodic current. The electroplating solution includes a mixture of soluble metallic salts and organic additives dissolved in a non-aqueous non-aromatic organic solvent.

[0021] The non-aqueous non-aromatic organic solvent can be any suitable solvent. For example, a suitable solvent includes low molecular weight non-aromatic organic solvents. In this context, low molecular weight means 200 g/mole or less. Such solvents include the family of alcohols, such as ethanol, propanol, isopropanol, butanol, 2-butanol and their corresponding alcohols having more than one OH functional group, ethanolamine and amines. Carboxylic acids, such as oxalic acid, citric acid and ammonium citrate, can be used as support electrolytes or as solvents as well. In addition, plating electrolytes can have a combination of two or more of these suitable solvents. Further, although other families of organic solvents, such as ketones, aldehydes, alkenes, alkynes, ethers, amides and toxic aromatic compounds, can be used, the toxicity level of these solvents make them less desirable.

[0022] Into these solvents, soluble metallic salts are dissolved. Such metallic salts include metal alkoxides, such as ethoxides, propoxides, isopropoxides, butoxides and their corresponding halides, phosphates, carbonates and other inorganic and organic compounds capable of providing metallic ions to be reduced at the cathode during electrodeposition. The metallic salts may be present individually or other salts plus mixtures thereof may be used.

[0023] Targeted metals for electrodeposition in the exemplary method are those metals that cannot readily be electroplated from aqueous solutions. Examples of targeted metals include aluminum, titanium, tantalum, zirconium, molybdenum, tungsten, niobium, osmium, hafnium, mag-

nesium and alloys of any combination of these metals, or other metals from salts soluble into the above mentioned solvents.

[0024] In the electroplating solution, the concentration of the metallic salt may vary from 5% to 100% of the saturation concentration for the respective metallic salt in the solvent at the operational temperature for electrodeposition. Conductive additives, such as oxalic acid, phosphoric acid and other low molecular weight organic acids can also be added into such electroplating electrolytes. In this context, low molecular weight means 200 g/mole or less. Any organic or inorganic compound that increases the solvent conductivity and is soluble into such solvent may be added, either alone or in combination. For instance, in ethanol the following secondary products are soluble: sodium hydroxide, boric acid, ammonium chloride, calcium carbonate, sodium iodine, ammonium fluoride, aluminum nitrate, stearate or chlorohydrate, aluminum chloride, aluminum phosphate and aluminum potassium phosphate.

[0025] Minimizing electrolyte contamination promotes adhesion and coating performance. Contamination of the plating electrolyte may lead to deposit non-uniformity, porosity, galling, pitting, blistering and may even result in no deposition at all. There are various ways to prevent or minimize contamination of the electrolyte with air, water, or solution or electrodeposition by-products. Electrolyte filtration and a controlled atmosphere (e.g., where the plating solution is housed) may both be utilized to assist in maintaining the proper operation of the electrodeposition bath. For example, electroplating electrolytes can be continuously filtered on molecular sieves to minimize contamination by water. A suitable molecular sieve for this application is a 3 angstrom molecular sieve. In another example, an inert atmosphere can be maintained over the electroplating solution during at least the electrodepositing of the metal on the substrate. The inert atmosphere can minimize contamination by oxygen and water, by, for example, maintaining the atmosphere in contact with the electroplating solution substantially oxygen-free and moisture-free. For example, the oxygen content can be 1-10 ppm, preferably less than 5 ppm, and the water content can be 1-10 ppm, preferably less than 5 ppm, but the actual conditions can vary depending on the metal being electrodeposited. Preferably where an inert atmosphere is used, the inert atmosphere is continually maintained over the electroplating solution. An example of an inert atmosphere includes bubbling nitrogen through the electrolytes and/or gas regulation of a nitrogen atmosphere over the electroplating bath.

[0026] In a further example, positive pressure inside the plating chamber can be used to reduce contamination. Preferably, the positive pressure is maintained at 1 atmosphere, but the atmosphere can be lower or higher than 1 atmosphere, depending on the sensitivity of the process and the design of the plating chamber.

[0027] In a still further example, a glove-box type or closed double-compartment chamber filled with an inert gas, such as nitrogen, and filtered from water and oxygen through an adequate catalyst can be used for NAOS. Electroplating solutions within the glove-box type or the closed double-compartment chamber can be arranged as a single electrolyte bath or can be split into separate catholyte and anolyte compartments. Splitting into separate catholyte and anolyte

compartments is preferred where possible decomposition of the respective solutions due to electrolysis may be encountered. When the catholyte and the anolyte compartments are split, the possible decomposition can be contained by, for example, a suitable ion-permeable membrane between the chambers. For plating chemistries that require splitting of the electrolyte, a suitable ion-permeable membrane is a polymeric membrane, although a wide variety of commercial fully permeable or semi-permeable membranes can be used. Membrane separation can also be used between electrodes so as to use different anode and cathode electrolytes.

[0028] In the exemplary method of electrodeposition, suitable anode materials include metals that are identical or similar electrochemically to those being electroplated, provided they do not form an insulating barrier upon their surface, or metals that are compatible with the electrolyte, whether soluble or insoluble. To avoid an electrolyte contamination, suitable insoluble anodes or soluble anodes formed of a material including a metal that is to be plated can be used. Otherwise, other anode material such as platinized titanium, DSA-type anodes or other insoluble but conductive material can be used.

[0029] Suitable cathodic current density at the conductive substrate may vary between 0.05 to 1000 amperes per  $\text{dm}^2$ , depending upon electrolyte composition and the metal to be electroplated. In each NAOS process, electrode surface ratio is determined such that equilibrium between the quantity of metal that is dissolved from anodes and metal being electroplated is reached, in order to maintain chemical balance of the electrolyte.

[0030] The conductive substrate may optionally have the surface prepared prior to electrodeposition. For example, the surface can be grit blasted, masked and then alkali or acid cleaned prior to electroplating. After alkali or acid cleaning, the conductive substrate is alcohol dipped or sprayed to remove any aqueous cleaners. In some instances, a reverse etch can be used to promote adhesion.

[0031] Any type of agitation of the electroplating solution or parts of the solution can be incorporated into the process. For example, moving or vibrating bus-bars, nitrogen or other inert gas bubbling, or ultrasonic devices can be used.

[0032] The electroplating solution temperature for each NAOS process can be regulated such that solvent surface tension is not more than approximately 50% (+10%) of its vaporization pressure, or such that the electroplating solution is chilled to improve plating conditions and efficiency. For example, the electroplating solution can be regulated by the use of a heat exchanger or a chiller.

[0033] Electrolyte evaporation can be reduced by adding floating devices, such as polymeric balls or by adding a chemical compound on top of the liquid surface that prevents evaporation but allows the introduction of parts into the bath.

[0034] FIG. 1 is a schematic representation of an electroplating system. An exemplary embodiment of an electroplating system 100, includes a plating chamber 102 containing an electroplating solution, an entry point 104 to the electroplating system 100 and a transporting system 106 to convey parts 108 to be electroplated from the entry point 104 to the plating chamber 102.

[0035] The plating chamber 102 includes either a single electroplating compartment or a split compartment for anolyte and catholyte as discussed herein. As shown in FIG.

1, the chamber 102 contains a split compartment having two anodes 110, 112 arranged essentially opposing each other with a catholyte in between. Each anode 110, 112 is separated from the catholyte by a membrane 114, 116.

[0036] The electroplating solution is continuously agitated by circulation through an external chamber 118 housing molecular sieves, which scavenge water molecules. An associated pump (not shown) helps to circulate and recycle the electrolyte between the plating chamber 102 and the external chamber 118 to assist in control of electrolyte purity and composition.

[0037] Further, an inert atmosphere is maintained within at least the plating chamber 102, preferably within the electroplating system 100, by gas regulation. In FIG. 1, the gas regulation is shown as regulated nitrogen gas tanks 120. However, any suitable inert atmosphere and any suitable regulation system can be used. Typically, a positive pressure, e.g., about 1 atm, is maintained in the plating chamber 102.

[0038] The entry point 104 to the electroplating system 100 can be any suitable entry point that accommodates the part 108 and can interface with the plating chamber 102 while maintaining adequate containment and bath vapor control. For example, FIG. 1 shows the entry point 104 as an air-lock type transfer point with a first exterior door 122 and a second interior door 124. Generally, operation of the exterior door 120 and the interior door 122 is coordinated with a vacuum pump and inert gas backfilling valve to minimize the introduction of air from outside the electroplating system 100 into the plating chamber 102.

[0039] The transporting system 106 places the part 108 into position within the plating chamber 102 for electrodeposition. For example and as shown in FIG. 1, the transporting system 106 places the part 108 into the catholyte and in electrical contact with a source 126. The source 126 may be either gravimetric or potentiostatic, depending on the electrochemical conditions. The source 126 is also in electrical contact with each anode 110, 112.

[0040] The transporting system 106 can include any suitable transporting system for the part 108. Examples of suitable transport systems include hydraulic lifts, chain lifts, conveyors, elevator systems, rack-up systems rotating systems and so forth. For example, large parts may be racked up and electroplated from the racked position, smaller parts may be plated in a barrel plating manner. In barrel plating, the parts are placed in a rotating cage which rotates within the electroplating solution such that the parts are totally submerged within the plating solution. In barrel plating, residual unplated points from the racking step are reduced to a minimum and the entire part is electroplated.

[0041] Solutions that allow the electroplating of aluminum based on NAOS are illustrated in the following examples (Example 1-Example 3):

#### EXAMPLE 1

[0042]

Component	Chemical name	Concentration	Other Information
Solvent	Ethanol	—	
Aluminum Source #1	Aluminum isopropoxide	0-5 g/L	

-continued

Component	Chemical name	Concentration	Other Information
Conductive Additive #1	Oxalic acid	0–100 g/L	
Aluminum Source #2	Aluminum chloride	0–900 g/L	
Conductive Additive #2	Boric acid	0–50 g/L	
Temperature Anode material			room temperature aluminum

## EXAMPLE 2

[0043]

Component	Chemical name	Concentration	Other Information
Solvent	Ethanol-isopropanol	0–50 V/V	
Aluminum Source #1	Aluminum isopropoxide	0–5 g/L	
Conductive Additive #1	Oxalic acid	0–100 g/L	
Aluminum Source #2	Aluminum chloride	0–900 g/L	
Temperature Anode material			room temperature aluminum

## EXAMPLE 3

[0044]

Component	Chemical name	Concentration	Other Information
Solvent	Butanol	—	
Aluminum Source #1	Aluminum butoxide	0–10 g/L	
Conductive Additive #1	Oxalic acid	0–100 g/L	
Aluminum Source #2	Aluminum chloride	0–500 g/L	
Temperature Anode material			room temperature aluminum

[0045] Solutions that allow the electroplating of titanium based on NAOS are illustrated in the following examples (Example 4):

## EXAMPLE 4

[0046]

Component	Chemical name	Concentration	Other Information
Solvent	Ethanol	—	
Titanium Source #1	Titanium ethoxide	0–10 g/L	
Conductive Additive #1	Boric acid	0–50 g/L	

-continued

Component	Chemical name	Concentration	Other Information
Titanium Salt #2	Titanium chloride	0–50 g/L	
Temperature Anode material			Room temperature titanium

[0047] Solutions that allow the electroplating of tantalum based on NAOS are illustrated in the following example (Example 5):

## EXAMPLE 5

[0048]

Component	Chemical name	Concentration	Other Information
Solvent	Ethanol	—	
Tantalum Source #1	Tantalum isopropoxide	0–100 g/L	
Conductive Additive #1	Oxalic acid	90 ± 15 g/L	
Tantalum Source #2	Tantalum pentachloride	0–5000 g/L	
Temperature Anode material			room temperature tantalum

[0049] Solutions that allow the electroplating of zirconium based on NAOS are illustrated in the following example (Example 6):

## EXAMPLE 6

[0050]

Component	Chemical name	Concentration	Other Information
Solvent	Ethanol	—	
Zirconium Source #1	Zirconium ethoxide	0–50 g/L	
Conductive Additive #1	Oxalic acid	0–100 g/L	
Zirconium Source #2	Zirconium tetrachloride	0–500 g/L	
Temperature Anode material			room temperature zirconium

[0051] Although various anodes, cathodes, and solution chemistries can be used in the metal deposition process, a preferred electrodeposition process for aluminum uses aluminum anodes and benign organic and inorganic aluminum salts and other conductivity promoter chemicals. However, both other metals and refractory metals can be obtained by electrodeposition from organic solvents of the same functional group.

[0052] The properties of the electrodeposition method and the performance of electroplated aluminum from the process were analyzed. It was found that throwing power, which is a consideration for uniform coatings on complex structures

and inner diameters, was approximately equivalent to the throwing power of cadmium deposition. Because the aluminum electroplating process is non-aqueous, the process does not release free hydrogen at the cathode that can cause hydrogen embrittlement in high strength steels. Further, and unlike conventional cadmium, electroplated aluminum can be anodized to increase the hardness from a typical 10-25 Vicker's hardness (Hv) to an as-plated coating hardness of about 500 Hv (using the ASTM standard test protocol for Vicker's Hardness in this range of hardness) contributing to reduced scratches and damage both in-production and in-service.

[0053] Among applications of the invention is the electrodeposition of aluminum over high strength steel parts encountered in aerospace. The NAOS processes can be applied on any conductive substrates as long as the substrate is not susceptible to be chemically attacked by the chemistry of the plating solutions.

[0054] Although the present invention has been described in connection with exemplary embodiments thereof, it will be appreciated by those skilled in the art that additions, deletions, modifications, and substitutions not specifically described may be made without departing from the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. A method of electrodeposition of a metal, the method comprising:

preparing an electroplating solution, the electroplating solution including a mixture of soluble metallic salts and organic additives dissolved in a non-aqueous non-aromatic organic solvent; and

electrodepositing the metal from the electroplating solution onto a conductive substrate under a cathodic current.

2. The method of claim 1, wherein the soluble metallic salts are a metal alkoxide.

3. The method of claim 2 wherein the metal alkoxide is selected from the group consisting of metal ethoxides, propoxides, isopropoxides, butoxides, corresponding halides, phosphates, and carbonates, and mixtures thereof.

4. The method of claim 1, wherein the metal is selected from the group consisting of aluminum, titanium, tantalum, zirconium, molybdenum, tungsten, niobium, osmium, hafnium, magnesium and alloys and combinations thereof.

5. The method of claim 1, wherein the non-aqueous non-aromatic organic solvent is a low molecular weight non-aromatic solvent.

6. The method of claim 1, wherein the non-aqueous non-aromatic organic solvent is an alcohol or an amine.

7. The method of claim 6, wherein the alcohol has more than one OH functional group.

8. The method of claim 1, wherein the non-aqueous non-aromatic organic solvent is selected from the group consisting of ethanol, propanol, isopropanol, butanol, 2-butanol and ethanolamine.

9. The method of claim 1, wherein a concentration of the soluble metallic salt in the electroplating solution is from 5% to 100% of a saturation concentration for the metallic salt in the non-aqueous non-aromatic organic solvent at an operational temperature for electrodeposition.

10. The method of claim 1, comprising adding a conductive additive to the electroplating solution to increase solvent conductivity.

11. The method of claim 10, wherein the conductive additive is a low molecular weight organic solid.

12. The method of claim 10, wherein the conductive additive is oxalic acid, citric acid, ammonium citrate or a chloride, a pentachloride, a tetrachloride of the metal, or an organic or inorganic compound soluble in the electroplating solution.

13. The method of claim 1, comprising continuously filtering the electroplating solution over molecular sieves and maintaining an inert atmosphere over the electroplating solution during at least electrodeposition.

14. The method of claim 13, wherein the inert atmosphere maintains a substantially oxygen-free and moisture-free atmosphere in contact with the electroplating solution.

15. The method of claim 1, comprising splitting the electroplating solution into a separate catholyte compartment and a separate anolyte compartment, the catholyte compartment and the anolyte compartment separated by a membrane.

16. The method of claim 1, comprising agitating the electroplating solution or agitating a part being electroplated.

17. The method of claim 1, comprising preparing a surface of the conductive substrate for electrodeposition by grit blasting the surface, masking the surface, cleaning with an alkali or acid cleaning solution and removing the cleaning solution by an alcohol dip or spray.

18. An electroplating solution, comprising:

a non-aqueous non-aromatic organic solvent; and

a mixture including soluble metallic salts and organic additives, the mixture dissolved in the non-aqueous non-aromatic organic solvent.

19. The electroplating solution of claim 18, wherein the soluble metallic salts includes aluminum salts that allow the electrodeposition of aluminum.

20. The electroplating solution of claim 18, wherein the soluble metallic salts includes titanium salts that allow the electrodeposition of titanium.

21. The electroplating solution of claim 18, wherein the soluble metallic salts includes tantalum salts that allow the electrodeposition of tantalum.

22. The electroplating solution of claim 18, wherein the soluble metallic salts includes zirconium salts that allow the electrodeposition of zirconium.

23. The electroplating solution of claim 18, wherein the soluble metallic salts includes at least one refractory metal salt that allows the electrodeposition of a refractory metal.

24. The electroplating solution of claim 23, wherein the refractory metal is molybdenum, tungsten, niobium, osmium, hafnium, alloys or combinations thereof.

25. The electroplating solution of claim 18, wherein the soluble metallic salts are a metal alkoxide.

26. The electroplating solution of claim 18, wherein the non-aqueous non-aromatic organic solvent is a low molecular weight non-aromatic solvent.

27. An electroplating system, comprising:

a plating chamber containing an electroplating solution;

an entry point to the electroplating system; and

a transporting system to convey a part to be electroplated from the entry point to the plating chamber,

wherein the electroplating solution includes a non-aqueous non-aromatic organic solvent and a mixture including soluble metallic salts and organic additives, the mixture dissolved in the non-aqueous non-aromatic organic solvent.

**28.** The electroplating system of claim 27, wherein the plating chamber includes a single electroplating compartment or a split electroplating compartment for an anolyte and a catholyte.

**29.** The electroplating system of claim 27, wherein the plating chamber includes a split electroplating compartment having two anodes arranged essentially opposing each other with the catholyte in between, each anode separated from the catholyte by a membrane.

**30.** The electroplating system of claim 27, comprising an external chamber housing molecular sieves and wherein the electroplating solution is continuously agitated by circulation through the external chamber.

**31.** The electroplating system of claim 27, comprising a source of inert gas and an inert atmosphere maintained within at least the plating chamber by gas regulation of the source of inert gas.

**32.** The electroplating system of claim 31, wherein the inert atmosphere is maintained at a positive pressure.

**33.** The electroplating solution of claim 27, wherein the soluble metallic salts are a metal alkoxide.

**34.** The electroplating solution of claim 27, wherein the non-aqueous non-aromatic organic solvent is a low molecular weight non-aromatic solvent.

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