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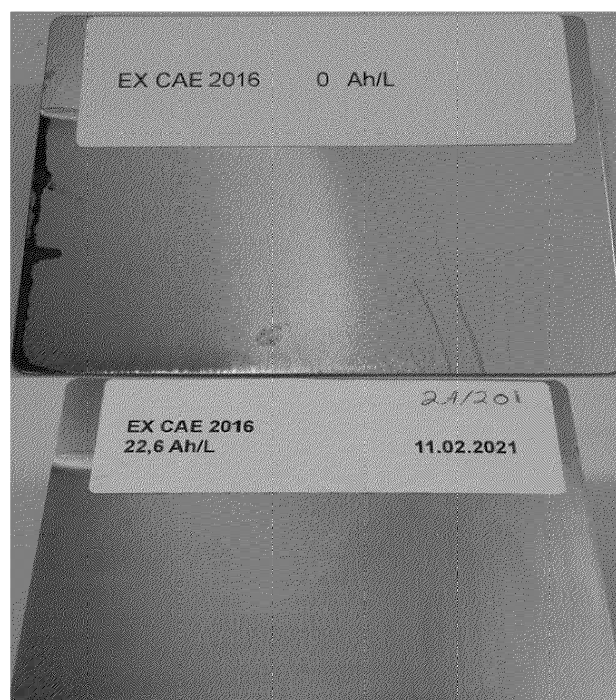
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(54) **ELECTROPLATING DEVICE AND PROCESS FOR DEPOSITING NICKEL ALLOYS WITH A SOLID REPLENISHER**

(57) The present invention refers to an electroplating device for depositing nickel alloys and a process for depositing nickel alloys on a substrate with a solid replenisher.

Fig. 1



Description

[0001] The present invention refers to an electroplating device for depositing nickel alloys and a process for depositing nickel alloys on a substrate with a solid replenisher.

[0002] In the field of plating, electroplating is a popular and efficient method of strengthening metals. It is a necessity in so many industries, and its specific uses provide distinct advantages for each alloy type and application. It is also a complicated process that involves precise chemistry and attention.

[0003] Nickel alloy are a major electroplating product used in the industry for protection and decorative application. It is used in many industries today.

[0004] One of those drawbacks faced with nickel alloy plating is that it generally involves the use of sulfates and chlorides in the plating bath. Those compounds tend to accumulate during the bath operation and cause environmental issues and health issues.

[0005] Also, there is a need to have a replenishment in nickel for the bath that is sufficient for an industrial application. This replenishment solution needs also to be as cost efficient as possible. There is also a need to avoid the practice of bleed and feed. Bleed and feed is the practice of discarding a fraction of old bath and replacing it with new bath. In general, the additives are added to the electroplating bath in liquid form having the consequence that the total volume of the bath increases over time, so a fraction of the electrolyte are discarded.

[0006] JP2012246554 discloses an alkaline zinc-nickel alloy plating liquid contains zinc, nickel, an electric conductive salt, and a complexing agent of nickel, and does not contain an aromatic sulfonic acid, an aromatic sulfonamide, an aromatic sulfonimide, an acetylenic compound, an allyl compound, a nitrile compound, and sulfate. Especially, the nickel source is a water-insoluble nickel compound such as nickel carbonate, nickel hydroxide, and nickel chloride. This solution still favor chloride as a solid replenisher.

[0007] US4428802 discloses a palladium-nickel alloy plating solutions formed from tetramminepalladous chloride is provided. The tetramminepalladous chloride is soluble in aqueous ammonia plating solution and is also water soluble. This permits replenishment of the palladium in a palladium-nickel plating solution during plating operation merely by adding the tetramminepalladous palladium chloride as a solid which is easily dissolved. The palladium-nickel alloy plating solutions contain between about 5 to 30 g/l of palladium and 5 to 30 g/l of nickel. This solution still favor chloride as a solid replenisher.

[0008] None of those prior art documents has focused on a solid replenisher for nickel with a limited amount of sulfate and chloride.

[0009] It was therefore an object of the present invention to provide an electroplating bath for depositing nickel alloys with a solid replenisher that is compatible with this focus.

[0010] This problem is solved by the electroplating bath with the features of claim 1 and the process for depositing nickel alloys with the features of claim 12. The further dependent claims mention preferred embodiments.

[0011] According to the present invention, a device for depositing nickel alloys with an electroplating unit comprising an electroplating bath and, separated from the electroplating unit, a replenishing unit comprising or consisting of a chamber, a line, a compartment or combinations thereof is provided wherein the electroplating bath comprises:

- a) at least one nickel ion,
- b) at least one additional metal ion,
- c) at least one alkali metal ion,
- d) at least one aromatic compound,

wherein the replenishing unit comprises a nickel replenisher which is a nickel source in a solid state via being dissolved in the replenishing unit, wherein the bath comprises less than 2000 ppm of chloride and less than 2000 ppm of sulfate, wherein the concentration of nickel in the nickel replenisher is higher than the nickel concentration in the electroplating bath, wherein the nickel replenisher comprises less than 50 g/kg of chloride and less than 50 g/kg of sulfate.

[0012] In a preferred embodiment, the at least one alkali metal ion derives from an alkali metal ion source selected from the group consisting of potassium hydroxide, sodium hydroxide, and mixtures thereof and the pH of the electroplating bath is above or equal to 14.

[0013] In a preferred embodiment, the nickel ion derives from a nickel ion source selected from the group consisting of nickel(II) hydroxide, nickel(II) carbonate, nickel(II) hydroxide carbonate, nickel(II) chloride, nickel(II) sulfate, nickel(II) acetate, nickel(II) sulfamate, nickel(II) formate, hydrates thereof, and mixtures thereof, wherein less than 50% of the Ni ions are provided by nickel(II) sulfate and/or nickel(II) chloride.

[0014] In a preferred embodiment, the concentration of nickel in the nickel replenisher is at least twice the nickel concentration in the electroplating bath.

[0015] In a preferred embodiment, the replenishing unit is connected to electroplating unit.

[0016] In a more preferred embodiment, the replenishing unit is connected to electroplating unit by one or more tubes and/or pipes.

[0017] In a preferred embodiment, the at least one alkali metal ion is present in an amount of 0.1 to 10 mol/L, preferably 1 to 8 mol/L, more preferably 2 to 4 mol/L.

[0018] In a preferred embodiment, the nickel ion is present in an amount of 0.01 to 1 mol/L, preferably 0.015 to 0.5 mol/L, more preferably 0.02 to 0.03 mol/L.

[0019] In a preferred embodiment, the additional metal ion is a zinc ion.

[0020] In a more preferred embodiment, the zinc ion derives from a zinc ion source selected from the group

consisting of zinc(II) oxide, zinc(II) hydroxide, zinc (II) chloride, zinc (II) sulfate, zinc (II) carbonate, wherein less than 50% of the Zn ions are provided by zinc (II) sulfate and/or zinc (II) chloride

[0021] In a preferred embodiment, the electroplating bath comprises of at least one amine.

[0022] In a preferred embodiment, the least one amine is present in an amount of 0.001 to 1 mol/L, preferably of 0.005 to 0.8 mol/L, more preferably of 0.01 to 0.5 mol/L.

[0023] In a preferred embodiment, the at least one amine is selected from a group of aliphatic amines from the polymerisation of alkylamines and also monoethanolamine, diethanolamine, triethanolamine, ethylenediamine, diethylenetriamin, tetraethylenepentamine, pentaethylenehexamine, and heptaethyleneoctamine.

[0024] In a preferred embodiment, the at least one aromatic compound is present in an amount of 0.001 to 3 mmol/L, preferably 0.5 to 2.5 mmol/L, more preferably 1 to 2 mmol/L.

[0025] In a preferred embodiment, the bath is free of any epoxy compounds.

[0026] In a preferred embodiment, the at least one aromatic compound is selected from a group of organic and inorganic brighteners.

[0027] In a preferred embodiment, the nickel source is provided as a sludge, paste and/or powder.

[0028] In a preferred embodiment, the replenishing unit comprises a cartridge system, a filter, a dissolution system, and combinations thereof.

[0029] In a preferred embodiment, the bath comprises less than 1000 ppm of chloride and/or less than 1000 ppm of sulfate.

[0030] In a more preferred embodiment, the bath is free of sulfate ions.

[0031] In a preferred embodiment, the nickel replenisher comprises less than 40 g/kg of chloride and/or less than 40 g/kg of sulfate.

[0032] According to the present invention, a process for depositing nickel alloys on a substrate from a nickel alloy bath is also provided including the following steps:

- Providing an electroplating device according to the invention,
- Immersing a substrate in the electroplating bath and
- Applying an electrical current to deposit the nickel alloy on the substrate.

wherein a nickel source in a solid state is dissolved in the separate replenishing unit.

[0033] In a preferred embodiment, the electroplating bath performs under 2000 ppm of chloride and sulfate for at least 1000 Ah/L.

[0034] In a preferred embodiment, the nickel alloy deposit has a thickness from 2 to 15 μm .

[0035] In a preferred embodiment, the deposition rate of the nickel alloy is above 0.25 $\mu\text{m}/\text{min}$.

[0036] In a preferred embodiment, the nickel source is provided as a sludge, paste and/or powder. With refer-

ence to the following figures and examples, the subject matter according to the present invention is intended to be explained in more detail without wishing to restrict said subject matter to the specific embodiments shown here.

[0037] Fig. 1 shows two plated parts with the invention, above with a bath that has just started working and plate below with a bath that has worked at 22,6 Ah/L.

10 Examples

Bath composition:

[0038] The bath used for the example is a zinc nickel plating bath that has the following composition:

- Zinc 9 g/L,
- Nickel 1.4 g/L,
- KOH 160 g/L,
- 20 g/L TEPA,
- 6.5 g/L TEA,
- 0.21 g/L Trigonelline

Plating preparation:

[0039] A 50L plating bath was prepared according to the concentrations stated above. Dissolution line/device were prepared with 5L of the plating bath described above.

[0040] 35 g of Nickel hydroxide carbonate (32 % Nickel) were loaded in a cartridge. The Nickel powder or paste is slightly wetted with water. The loaded cartridge is fitted into a nickel dissolution line/device, where the electrolyte is flowing through the cartridge. After complete dissolution of the Nickel powder, the cartridge is refilled with Nickel hydroxide powder or paste.

Plating:

[0041] A barrel is half filled with M8 steel (10.9) screws.
[0042] The barrel goes through the following pre-treatment steps:

- Hot degreaser with Presol SFD from Coventya
- Rinsing with water
- Etching with HCl of the screws incl. Piclane 50 from Coventya
- Rinsing with water
- Anodic cleaning with AK80 from Coventya
- Rinsing with water
- Acidic Activation
- Rinsing with water

[0043] For the plating, two steel anodes are used at a constant current of 12 A for 30 minutes.

[0044] The barrel is after cleaned with water.

Re-dosing the nickel:

[0045] The Nickel and Zinc concentration is checked in the plating Bath. The Nickel concentration is checked in the Nickel dissolution line/device.

[0046] Zinc ion is re-dosed by Zinc pellets or zincate solution. Nickel ion is re-dosed by exchanging the Bath electrolyte with the higher loaded/concentrated nickel electrolyte from the Nickel dissolution line/device as much as needed.

Results:

[0047] Dissolution rate of the nickel hydroxide carbonate is up to 1.4 g/Lh (highest dissolution rate only in fresh Nickel-free electrolyte).

[0048] The plate obtained even after 22 Ah/L is like the one obtained with a plating bath at 0 Ah/L as seen in Fig. 1.

[0049] The deposition rate on screws is approximately 0.35 $\mu\text{m}/\text{min}$. It must be compared with a classical ZnNi deposition rate in sodium-based electrolyte that is approx. 0.2 $\mu\text{m}/\text{min}$. Nevertheless, it is already well known that potassium based ZnNi systems are faster than sodium based ZnNi electrolyte systems.

[0050] In comparison to known ZnNi system based with Nickel sulfate or Nickel chloride as the Nickel source, this invention may be performed up to 25 Ah/L with less than 200 ppm of sulphate and less than 30 ppm of chloride. In a known ZnNi system based with Nickel sulfate or Nickel chloride as the Nickel source, the electrolyte accumulate up to 4000 ppm of sulfate or up to 3500 ppm chloride at an electrolyte stage of 25 Ah/L, respectively. In a Nickel sulphate based ZnNi electrolyte the percentage volume increase due to addition of Nickel as a liquid would be already 2.5 % and 2.9 % in a nickel chloride based ZnNi electrolyte after 25 Ah/L, whereas with this invention no volume increase is possible due to addition of Nickel as a solid.

Claims

1. Electroplating device for depositing nickel alloys with an electroplating unit comprising an electroplating bath and, separated from the electroplating unit, a replenishing unit comprising or consisting of a chamber, a line, a compartment or combinations thereof, wherein the electroplating bath comprising:

- a) at least one nickel ion,
- b) at least one additional metal ion,
- c) at least one alkali metal ion,
- d) at least one aromatic compound,

wherein the replenishing unit comprises a nickel replenisher which is a nickel source in a solid state via being dissolved in the replenishing unit,

wherein the bath comprises less than 2000 ppm of chloride and less than 2000 ppm of sulfate, wherein the concentration of nickel ions in the nickel replenisher is higher than the nickel concentration in the electroplating bath, wherein the nickel replenisher comprises less than 50 g/kg of chloride and less than 50 g/kg of sulfate.

2. Electroplating device of claim 1, wherein the at least one alkali metal ion comprises potassium hydroxide, sodium hydroxide, and mixtures thereof and the pH of the electroplating bath is above or equal to 14.
3. Electroplating device of claims 1 or 2, wherein the nickel ion derives from a nickel ion source selected from the group consisting of nickel(II) hydroxide, nickel(II) carbonate, nickel(II) hydroxide carbonate, nickel(II) chloride, nickel(II) sulfate, nickel(II) acetate, nickel(II) sulfamate, nickel(II) formate, hydrates thereof, and mixtures thereof, wherein less than 50% of the Ni ions are provided by nickel(II) sulfate and/or nickel(II) chloride.
4. Electroplating device of any of the preceding claims, wherein the at least one alkali metal salt is present in an amount of 0.1 to 10 mol/L, preferably 1 to 8 mol/L, more preferably 2 to 4 mol/L.
5. Electroplating device of any of the preceding claims, wherein the nickel ion is present in an amount of 0.01 to 1 mol/L, preferably 0.015 to 0.5 mol/L, more preferably 0.02 to 0.03 mol/L.
6. Electroplating device of any of the preceding claims, wherein the additional metal ion is a zinc ion, which preferably derives from a zinc ion source selected from the group consisting of zinc(II) oxide, zinc(II) hydroxide, zinc(II) chloride, zinc(II) sulfate, zinc(II) carbonate, wherein less than 50% of the Zn ions are provided by zinc(II) sulfate and/or zinc(II) chloride.
7. Electroplating device of any of the preceding claims, wherein the electroplating bath further comprises of at least one amine, preferably selected from the group consisting of aliphatic amines from the polymerisation of alkylamines and also monoethanolamine, diethanolamine, triethanolamine, ethylenediamine, diethylenetriamin, tetraethylenepentamine, pentaethylenehexamine, and heptathylenooctamine, preferably in an amount of 0.001 to 1 mol/L, more preferably of 0.005 to 0.8 mol/L, and even more preferably of 0.01 to 0.5 mol/L.
8. Electroplating device of any of the preceding claims, wherein the at least one aromatic compound is selected from the group consisting of organic and inorganic brighteners, wherein the at least one aro-

matic compound is preferably present in an amount of 0.001 to 3 mmol/L, more preferably 0.5 to 2.5 mmol/L, and even more preferably 1 to 2 mmol/L.

9. Electroplating device of any of the preceding claims, wherein the nickel ion source is provided as a sludge, paste and/or powder. 5
10. Electroplating device of any of the preceding claims, wherein the replenishing unit comprises a cartridge system, a filter, a dissolution system, and combinations thereof. 10
11. Electroplating device of any of the preceding claims, wherein the at least one aromatic compound is selected from a group of organic and inorganic brighteners. 15
12. Process for depositing a nickel alloy on a substrate including the following steps: 20
 - Providing an electroplating device of any of the preceding claims,
 - Immersing a substrate in the electroplating bath and 25
 - Applying an electrical current to deposit the nickel alloy on the substrate

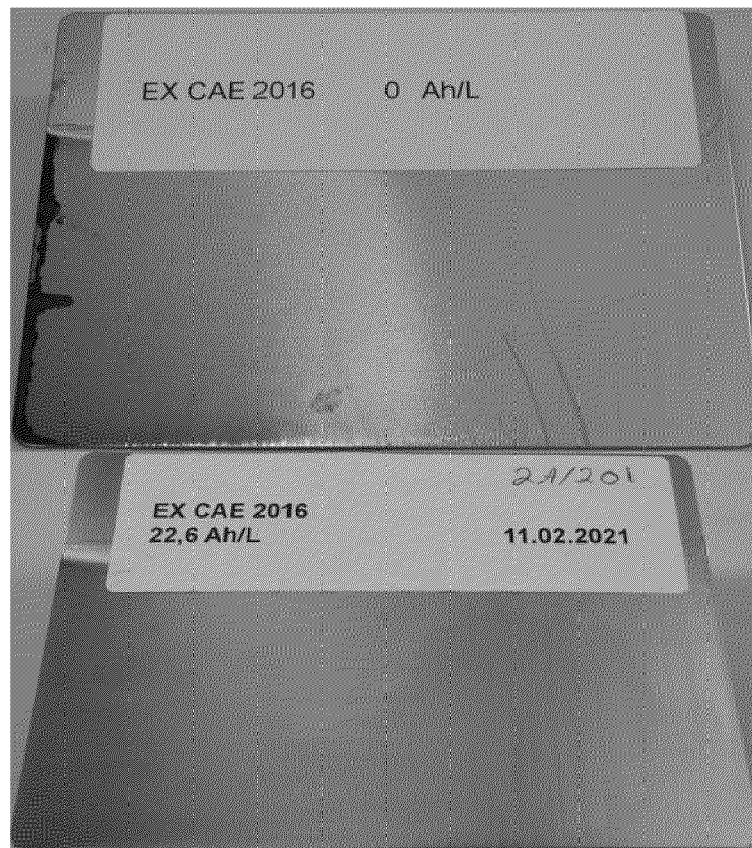
wherein a nickel source in a solid state is dissolved in the separate replenishing unit. 30
13. Process of claim 12, wherein the electroplating bath is performed with less than 2000 ppm of chloride and less than 2000 ppm sulfate for at least 1000 Ah/L. 35
14. Process of claim 12 or claim 13, wherein the deposition rate of the nickel alloy is above 0.25 $\mu\text{m}/\text{min}$. 40
15. Process of any of the preceding claims, wherein the nickel source is provided as a sludge, paste and/or powder. 45

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Fig. 1





EUROPEAN SEARCH REPORT

Application Number
EP 21 16 6236

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Place of search The Hague		Date of completion of the search 13 September 2021	Examiner Telias, Gabriela
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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