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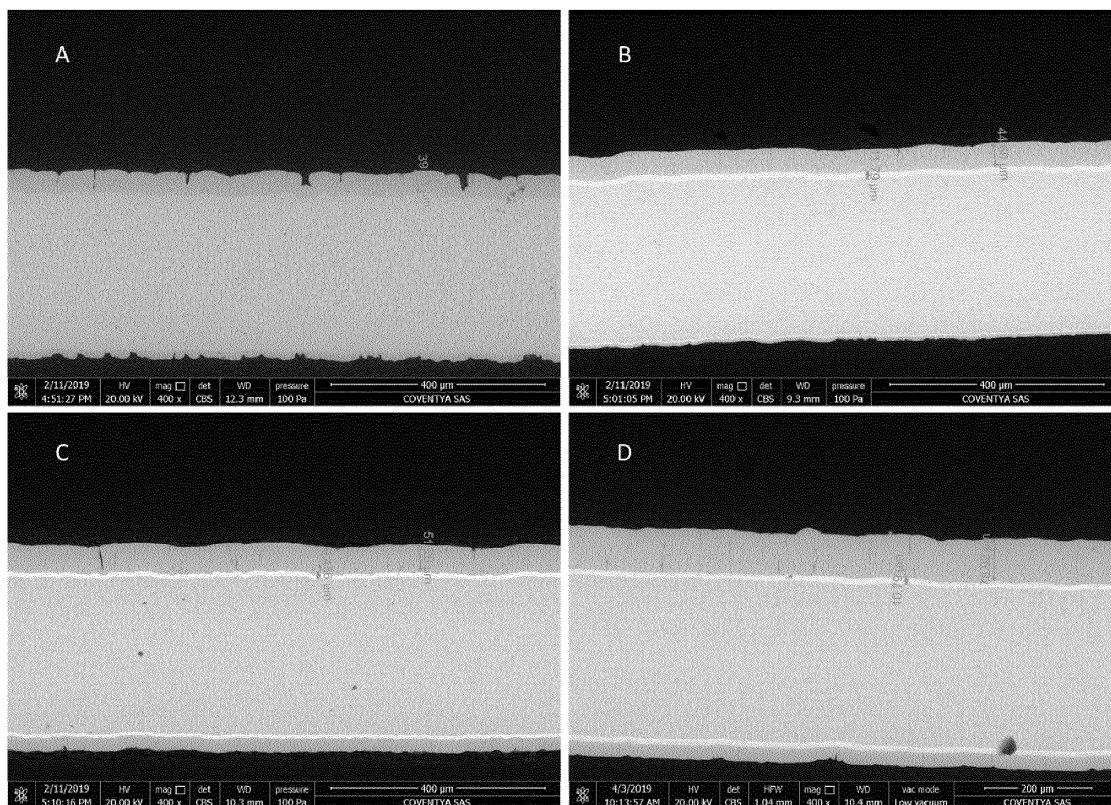
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(54) **ELECTROPLATED PRODUCT WITH CORROSION-RESISTANT COATING**

(57) The present invention refers to an electroplated product comprising a substrate which is coated with a first layer consisting of zinc or a zinc alloy and a second layer composed mainly of chrome with a certain percent-

age of alloying elements like C, O, N but it is produced from an electrolyte containing trivalent chrome as well as a process for obtaining such an electroplated product.

Fig. 1



Description

[0001] The present invention refers to an electroplated product comprising a substrate which is coated with a first layer consisting of zinc or a zinc alloy and a second layer composed mainly of chrome with a certain percentage of alloying elements like C, O, N but it is produced from an electrolyte containing trivalent chrome as well as a process for obtaining such an electroplated product.

[0002] Chrome deposits from trivalent chrome electrolytes are widely used in the industry due to their unique properties they allow substrates to work longer and under tougher conditions that they would normally survive in.

[0003] They have many beneficial characteristics:

- High hardness
- Superior tribological properties
- Chemical resistance
- Corrosion resistance

[0004] Cr(VI) substances are under regulatory pressure due to their toxic nature. They were classified as CMR and the European Union decided to submit its use to specific authorization under REACH regulations.

[0005] It is now very well established that uniform coatings of chromium of a thickness between 0.1 and 1 μm can be produced from trivalent chrome electrolytes. These thicknesses are well suited for the so called decorative applications.

[0006] During the last years, many patents were published regarding applications where higher thickness (1 to 500 μm) are required, e.g. functional applications like hard chrome. However, for the already described functional application only few patents are existing.

[0007] In WO2015110627 a trivalent chromium deposition bath is described which contains an organic acid complexing agent with a specific ratio range between this complexing agent and the trivalent chromium. The drawback of such a deposit obtained from this bath is the limited corrosion resistance of the deposit which is not sufficient for the requirements defined by major original equipment manufacturers.

[0008] WO2018185144 describes the use of a nickel or nickel alloy layer under the chromium or chromium alloy layer. In that case, the target is to use a barrier coating (semi-bright nickel) and not a cathodic protection. The drawback of such a composition is that there will be a nickel release which render such composition unsuitable for certain applications.

[0009] US 3691027 describes the use of an acidic ZnNi process in order to replace a part of the expensive nickel underlayer while maintaining corrosion resistance and brightness of the thin chrome deposit obtained by the use of an hexavalent chromium deposition bath. The drawback of such a process is that the top layer is a chromium deposition obtained from a hexavalent chromium based electrolyte and so with different properties than the one coming from trivalent chromium electrolyte. Also the hexavalent chrome bath contains toxic and harmful substances that can be avoided with a trivalent chrome bath. Also there is the need in this process to have a nickel layer above the ZnNi layer which makes the system more complicated to operate.

[0010] None of those prior art documents has focused on the improvement of the corrosion resistance of chromium plated substrates based on chromium (III).

[0011] When starting from this prior art it was therefore the objective of the present invention to provide a chromium plated products with an improved corrosion resistance with a sacrificial protection first layer that could improve the corrosion resistance of a trivalent chromium or chromium alloy second layer by a sacrificial protection and that. The sacrificial protection ensure that if there is a default in the first layer, the substrate is still protected at the default location contrary to a protection from a nickel first layer where the default will be an entry point for corrosion.

[0012] This problem is solved by the electroplated product with the features of claim 1 and the method for preparing an electroplated product by electroplating a substrate with the features of claim 7. The further dependent claims describe preferred embodiments.

[0013] According to the present invention, an electroplated product is provided wherein the electroplated product comprises a substrate which is coated with a first layer comprising or consisting of zinc or a zinc alloy and a second layer plated directly above the first layer (i.e. on top of the first layer or adjacent to the first layer) comprising or consisting of chromium or chromium alloy plated from a trivalent chromium based electrolyte, wherein the first layer improves the corrosion resistance of the second layer.

[0014] It was surprisingly found that even with a zinc nickel alloy, there were minimal nickel release (less than 0,5 $\mu\text{g}/\text{cm}^2/\text{week}$ as measured during our experiment) that could comply with an alimentary use and the concentration of nickel used in this invention is inferior to the one used with a nickel first layer, so we are decreasing the use of nickel product. The purpose of the present invention is therefore to improve the corrosion resistance of the chrome second layer by using such a first layer.

[0015] The presence of the first layer comprising zinc or a zinc alloy has the effect to avoid the use of harmful compounds during the fabrication process.

[0016] Moreover, the plating is realised at a lower temperature than the one used for nickel first layer plating (around 50°C) having the benefit to decrease the energy consumption and to be less hazardous (decrease in evaporation).

[0017] It is a further advantage of the zinc or zinc alloy first layer of the present invention that compared to a nickel first layer the nickel is passivated faster than zinc and zinc alloy with the consequence that a zinc and zinc alloy first layer has an improved adherence to the second layer in comparison to a nickel first layer.

[0018] In a specific embodiment, the second layer comprises at least 80 wt.-% of chromium and less than 4 wt.-% of carbon and 3 wt.-% of oxygen.

[0019] In a more specific embodiment, the second layer comprises at least 85 wt.-% of chromium and less than 3 wt.-% of carbon and 1 wt.-% of oxygen.

[0020] In a specific embodiment, the first layer comprises a zinc nickel alloy.

[0021] In a more specific embodiment, the first layer comprises percentage nickel in that the zinc nickel alloy comprises from 10 wt.-% to 20 wt.-%, preferably from 11 wt.-% to 18 wt.-%, more preferably from 12 wt.-% to 15 wt.-%.

[0022] In a more specific embodiment, the first layer has a thickness comprised between 1 and 25 µm, preferably between 4 and 16 µm, more preferably between 5 and 12 µm.

[0023] In a specific embodiment, the first layer comprises a zinc iron alloy.

[0024] In a more specific embodiment, the first layer comprises a percentage iron in the zinc iron alloy comprises from 5 wt.-% and to 13 wt.-%, preferably 7 wt.-% and to 10wt.-%, more preferably 7wt.-% and to 8 wt.-%.

[0025] In a specific embodiment, the first layer comprises a zinc tin alloy.

[0026] In a more specific embodiment, the first layer comprises percentage tin in that the zinc nickel alloy comprises from 65 wt.-% to 80 wt.-%, preferably from 70 wt.-% to 75 wt.-%.

[0027] In a specific embodiment, the first layer comprises a zinc copper alloy.

[0028] In a more specific embodiment, the first layer comprises percentage copper in that the zinc nickel alloy comprises from 55 wt.-% to 75 wt.-%, preferably from 60 wt.-% to 70 wt.-%.

[0029] In a specific embodiment, the first layer comprises a zinc tin copper alloy.

[0030] In a more specific embodiment, the first layer comprises percentage tin in that the zinc nickel alloy comprises from 25 wt.-% to 40 wt.-%, preferably from 30 wt.-% to 35 wt.-%.

[0031] In a more specific embodiment, the first layer comprises percentage copper in that the zinc nickel alloy comprises from 45 wt.-% to 55 wt.-%.

[0032] In a specific embodiment, the second layer is a finish layer and no other layer is added on the second layer.

[0033] In a specific embodiment, the plating is qualitatively characterized by Glow-discharge optical emission spectroscopy (GDOES) showing first a chrome, carbon and oxygen spectra with a higher chrome profile representing the composition of the second layer. Then the chrome spectrum will reach its maximum and decrease. Once the decrease of the chrome spectrum has started, a zinc spectrum will increase representing the composition of the first layer. The carbon and oxygen spectra will progressively decrease.

[0034] In a more specific embodiment, a nickel spectrum will increase at the same moment than the zinc spectrum representing the composition of the zinc nickel first layer.

[0035] In a more specific embodiment, an iron spectrum will increase at the same moment than the zinc spectrum representing the composition of the zinc iron first layer. The iron spectrum will reach a plateau as the zinc spectrum start to decrease.

[0036] According to the present invention a method for preparing an electroplated product by electroplating a substrate is also provided comprising the following steps:

a) Electroplating a substrate with a first layer comprising or consisting of zinc or an zinc alloy with an electrolyte comprising at least one source of zinc ions,

b) Electroplating of a second layer plated directly above the first layer comprising or consisting of chromium or chromium alloys with an electrolyte comprising at least one trivalent chromium salt.

[0037] In a specific embodiment, both electroplating baths are free of divalent sulphur compounds, boric acids and hexavalent chromium ions.

[0038] In a specific embodiment, the concentration of the source of zinc ions is from 4 g/L to 80 g/L, preferably from 5 g/L to 50 g/L, more preferably from 6 g/L to 20 g/L.

[0039] In a specific embodiment, the electroplating step a) also comprises at least one source of nickel ions.

[0040] In a more specific embodiment, the concentration of the source of nickel ions is from 0,1 g/L to 10 g/L.

[0041] In a specific embodiment, the electroplating step a) also comprises at least one source of ferrous or ferric ions.

[0042] In a more specific embodiment, the concentration of the source of ferrous or of ferric ions is comprised between 0,1 g/L and 10 g/L, preferably between 0,5 g/L and 5 g/L, more preferably between 0,7 g/L and 3 g/L.

[0043] In a specific embodiment, the electroplating step a) also comprises at least one source of tin ions.

[0044] In a specific embodiment, the electroplating step a) also comprises at least one source of copper ions.

[0045] In a specific embodiment, the temperature of the bath during step a) is comprised between 10 to 40 °C, preferably between 15 to 35 °C.

[0046] In a specific embodiment, the electroplating step a) is realized in an alkaline bath defined by a pH above 13.

[0047] In a specific embodiment, the electroplating step a) is obtained in a current density range from 0,01 to 10 A/dm², preferably from 0,02 to 5 A/dm², more preferably from 0,02 to 3 A/dm².

[0048] In a specific embodiment, the electroplating step a) is realized in an acidic bath defined by a pH below 6, preferably below 5.3, more preferably below 5.

[0049] In a specific embodiment, the electroplating step a) is realized in a barrel.

[0050] In a specific embodiment, the electroplating step a) is realized by rack.

[0051] In a specific embodiment, the electroplating step b) is realized in a bath at pH comprised between 3 to 9, preferably between 4 to 7, more preferably between 5 to 6.

[0052] In a specific embodiment, the concentration of trivalent chromium salt is comprised between 100 to 400 g/L, preferably between 110 to 300 g/L.

[0053] In a specific embodiment, the electroplating step b) also comprises at least one complexing agent.

[0054] In a more specific embodiment, the complexing agent is at concentration comprised between 100 to 300 g/L, more preferably between 150 to 250 g/L.

[0055] In a more specific embodiment, the complexing agent is preferably selected from the group consisting of carboxylic acids and carboxylate salts, preferably formic acid, acetic acid, propionic acid, glycolic acid, lactic acid, oxalic acid, malic acid, citric acid, tartaric acid, succinic acid, gluconic acid, glycine, aspartic acid, glutamic acid, and mixtures thereof, or their salts and mixtures thereof.

[0056] In a specific embodiment, the temperature of the bath during step b) is comprised between 30 to 70 °C, preferably between 35 to 65 °C, more preferably between 40 to 60 °C.

[0057] In a specific embodiment, the product of the step a) is pre-activated before the step b). This pre-activation comprises the application of a hydrochloric acid solution on the product of the step a).

[0058] In a specific embodiment, the product of the step b) is then submitted to a thermal treatment (TTH) comprising of 4 hours at 190°C in an oven.

[0059] With reference 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.

[0060] For those examples when we say that a metal is acid or alkaline, we refer to the pH of the plating bath. If we say a alkaline zinc nickel first layer, we mean that this first layer was obtained from an alkaline plating bath.

Fig.1 shows scanning electron microscope (SEM) 400X cross section images of

- A) Control sample with no first layer under the second layer
- B) Sample with nickel first layer
- C) Sample with alkaline zinc nickel first layer
- D) Sample with alkaline zinc first layer

Fig.2 shows pictures of the samples after 624 hours of Neutral Salt Spray (NSS) ISO 9227

- A) Alkaline Zinc-nickel first layer 5 µm and 12-15% Nickel without TTH
- B) Alkaline Zinc-nickel first layer 5 µm and 12-15% Nickel with TTH
- C) Alkaline zinc-iron first layer 10 µm - 8% Iron without TTH
- D) Alkaline zinc-iron first layer 10 µm - 8% Iron with TTH

Fig.3 shows pictures of the samples after 600 hours of Natural Salt Spray (NSS)

- A) Nickel first layer without TTH
- B) Nickel first layer with TTH
- C) Alkaline zinc first layer 10 µm without TTH
- D) Alkaline zinc first layer 10 µm with TTH
- E) Alkaline Zinc-nickel first layer 5 µm and 12-15% Nickel without TTH
- F) Alkaline Zinc-nickel first layer 5 µm and 12-15% Nickel with TTH
- G) Alkaline Zinc-nickel first layer 10 µm and 12-15% Nickel without TTH
- H) Alkaline Zinc-nickel first layer 10 µm and 12-15% Nickel with TTH
- I) Acid zinc-nickel first layer 10 µm - 12-15% Nickel without TTH

J) Acid zinc-nickel first layer 10 μm - 12-15% Nickel with TTH

Fig.4 shows pictures of the GDOES spectrum of the samples without and with TTH

- A) Chrome (thickness =5 μm) without TTH
- B) Chrome (thickness =20 μm) without TTH
- C) Chrome (thickness =5 μm) with TTH
- D) Chrome (thickness =5 μm) Nickel first layer (thickness=10 μm) without TTH
- E) Chrome (thickness =5 μm) Nickel first layer (thickness=10 μm) with TTH
- F) Chrome (thickness =5 μm) Alkaline Zinc-nickel first layer (thickness=10 μm) without TTH
- G) Chrome (thickness =5 μm) Alkaline Zinc-nickel first layer (thickness=10 μm) with TTH
- H) Chrome (thickness =5 μm) Alkaline zinc-iron first layer (thickness=10 μm) without TTH
- I) Chrome (thickness =5 μm) Alkaline zinc-iron first layer (thickness=10 μm) with TTH

Examples

Electroplating:

[0061] The electroplating bath used for the deposition of zinc and zinc alloy first layer are described below. The plating were realized on a steel substrate.

Alkaline zinc nickel

[0062] Alkaline zinc-nickel bath containing 120 g/L of sodium hydroxide, 10 g/L of zinc, 1.5 g/L of nickel, 20 g/L de tetraethylenpentamine (TEPA) and 2 g/L of Quadrol (THEED). Parts are plated during 40 minutes at 2A/dm² and at room temperature.

Acid zinc nickel

[0063] Acid zinc-nickel bath containing 60-70 g/L of zinc chloride, 100-130 g/L of nickel chloride $\times 6\text{H}_2\text{O}$, 190-220 g/L of potassium chloride, 25 g/L of sodium acetate $\times 3\text{H}_2\text{O}$, 30 g/L of aminoacetic acid, 2-4 g/L of sodium saccharine, 0,025-0,20 g/L of benzal acetone, 0,006-0,01 g/L of orthochlorobenzaldehyde, 0,8-1,2 g/L of octanolethoxylate, 2,5-3,2 g/L of potassium salt of the sulfopropy-lated polyalkoxylated naphthol. pH is adjusted at 5-6 and bath is heated up to 33-36°C. Parts are plated at 2 A/dm² during 25 minutes.

Alkaline zinc

[0064] Alkaline zinc bath containing 130 g/L of sodium hydroxide, 10 g/L of zinc and crosslinked polymers mentioned in EP 2111484 from TASKEM. Parts are plated during 40 minutes at 2A/dm² and at room temperature.

Alkaline zinc iron

[0065] Alkaline zinc-iron containing 80 g/L of sodium hydroxide, 8,125 g/L of zinc, 74,6 g/L of complexing agent (as used in patent application WO2014154884), 0,2 g/L of Mirapol WT and the percentage of iron deposited is 7% or 13%. Parts are plated during 10 minutes at 5A/dm² and at room temperature.

Nickel (reference)

[0066] 350 mL/L of nickel sulfamate, 35 g/L of boric acid and 5 mL/L of surfactant. pH is adjusted at 4.0 and bath is heated up to 50°C. Parts are plated at 5 A/dm² during 10 minutes.

[0067] The electroplating bath used for the deposition of trivalent chromium second layer were similar to the one described in Table 1 of the examples of the patent application WO 2015/110627 from Coventya S.P.A.

[0068] The properties of the layers obtained were investigated by using SEM cross section as presented in Fig.1.

Corrosion resistance:

[0069] The corrosion resistance was evaluated by the resistance to the NSS Test. Those experiments were conducted with a Braive 2000L corrosion chamber following the norm ISO 9227.

[0070] The thermal treatment (TTH) of the samples comprises of 4 hours at 190°C in an oven.

[0071] The different samples were submitted to different duration to the NSS to evaluate their corrosion resistance. To assess the corrosion resistance, we observed the samples and noted the white aspect and the presence of red rust (RR). The results from those tests are presented on the Table 1 below and also on the Fig. 2 and Fig. 3.

Table 1 : Results obtained from our samples in NSS

Hours spent in the NSS		Thermal treatment	48 h	168 h	384 h	504 h	720 h
Hard trivalent chrome 60 μm		without TTH	RR	RR	RR	RR	RR
		with TTH...	RR	RR	RR	RR	RR
Nickel first layer 10μm	+ Hard Trivalent chrome 60 μm	without TTH	-	-	-	-	-
		with TTH	-	Pits of RR	Pits of RR	Pits of RR	Pits of RR
alkaline zinc first layer 10μm		without TTH	-	-	-	-	-
		with TTH	-	White aspect	White aspect	White aspect	White aspect
Alkaline Zinc nickel first layer 5 μm - 12-15% Nickel		without TTH	-	-	-	-	-
		with TTH	-	-	-	-	-
Alkaline Zinc nickel first layer 10 μm - 12- 15% Nickel		without TTH	-	-	-	-	-
		with TTH	-	-	-	-	-
Acid zinc nickel first layer 10 μm - 12- 15% Nickel		without TTH	-	-	-	-	-
		with TTH	-	-	-	-	-

Alkaline zinc iron first layer 10 μm - 8% Iron		without TTH	-	-	-	Pits of RR	Pits of RR
		with TTH	-	-	Pits of RR	Pits of RR	Pits of RR

[0072] We can see that our samples have a better corrosion resistance than the hard trivalent chrome with no first layer. We can also see that we have better performance for the zinc nickel and zinc first layer than nickel first layer after TTH. For the zinc iron first layer, the performance are similar than nickel first layer with TTH.

5 GDOES Measurement:

[0073] The GDOES values were measured on a GD-Profilier 2 from Horiba. The software used is QUANTUM V2.08. The Pressure was set at 650 Pa, Power at 35 W, without Pulse, the Module Voltage 6V and the Phase Voltage 5V. TTH was conducted for 8 hours at 300°C in an oven.

[0074] The results from those measurements are presented on the Fig. 4. We can see on C that the TTH harden the chrome plating. The chrome spectrum is slower to decrease and still linger as the iron spectrum reach its maximum.

15 Claims

1. Electroplated product comprising a substrate which is coated with first layer comprising or consisting of zinc or a zinc alloy and a second layer plated directly above the first layer comprising or consisting of chromium or chromium alloy plated from a trivalent chromium based electrolyte, wherein the first layer improves the corrosion resistance of the second layer.
2. Electroplated product of claim 1, **characterised in that** the first layer comprises or consists of a zinc nickel alloy or a zinc iron alloy.
3. Electroplated product of claim 2, characterised the percentage nickel in the zinc nickel alloy comprises from 10 wt.-% to 20 wt.-%, preferably from 11 wt.-% to 18 wt.-%, more preferably from 12 wt.-% to 15 wt.-%.
4. Electroplated product of claim 2, **characterised in that** the percentage iron in the zinc iron alloy comprises from 5 wt.-% to 13 wt.-%, preferably 7 wt.-% to 10wt.-%, more preferably 7wt.-% to 8 wt.-%.
5. Electroplated product according to any one of claims 1 to 4, **characterised in that** the underlayer has a thickness from 1 to 25 μm , preferably from 5 to 16 μm , more preferably from 8 to 12 μm .
6. Electroplated product according to any one of claims 1 to 5, **characterised in that** the top layer comprises at least 80 wt.-% of chromium and less than 4 wt.-% of carbon and 3 wt.-% of oxygen.
7. Method for preparing an electroplated product by electroplating a substrate comprising the following steps:
 - a) Electroplating a substrate with a first layer comprising or consisting of zinc or an zinc alloy with an electrolyte comprising at least one source of zinc ions,
 - b) Electroplating of a second layer plated directly above the first layer comprising or consisting of chromium or chromium alloys with an electrolyte comprising at least one trivalent chromium salt,
8. Method of claim 7, **characterised in that** the first layer improves the corrosion resistance of the second layer and both electroplating baths are free of divalent sulphur compounds, boric acids and hexavalent chromium ions.
9. Method according to any one of claims 7 or 8, **characterised in that** the concentration of the source of zinc ions is from 4 g/L to 80 g/L, preferably from 5 g/L to 50 g/L, more preferably from 6 g/L to 20 g/L.
10. Method according to any one of claims 7 to 9, **characterised in that** the electroplating step a) also comprises at least one source of nickel ions or at least one source of ferrous or ferric ions.
11. Method according to any one of claims 7 to 9, **characterised in that** the electroplating step a) is realized in an alkaline bath defined by a pH above 13.
12. Method according to any one of claims 7 to 11, **characterised in that** the electroplating step a) is obtained in a current density range from 0,01 to 10 A/dm², preferably from 0,02 to 5 A/dm², more preferably from 0,02 to 1 A/dm².
13. Method according to any one of claims 7 to 12, **characterised in that** the temperature of the bath of step a) is from

10 to 40 °C, preferably from 15 to 35 °C.

14. Method according to any one of claims 7 to 13, **characterised in that** the electroplating step a) is realized in an electroplating bath which is substantially free of boric acids.

15. Method according to any one of claims 7 to 14, **characterised in that** the temperature of the bath of step b) is from 30 to 70 °C, preferably from 35 to 65 °C, more preferably from 40 to 60 °C.

Fig. 1

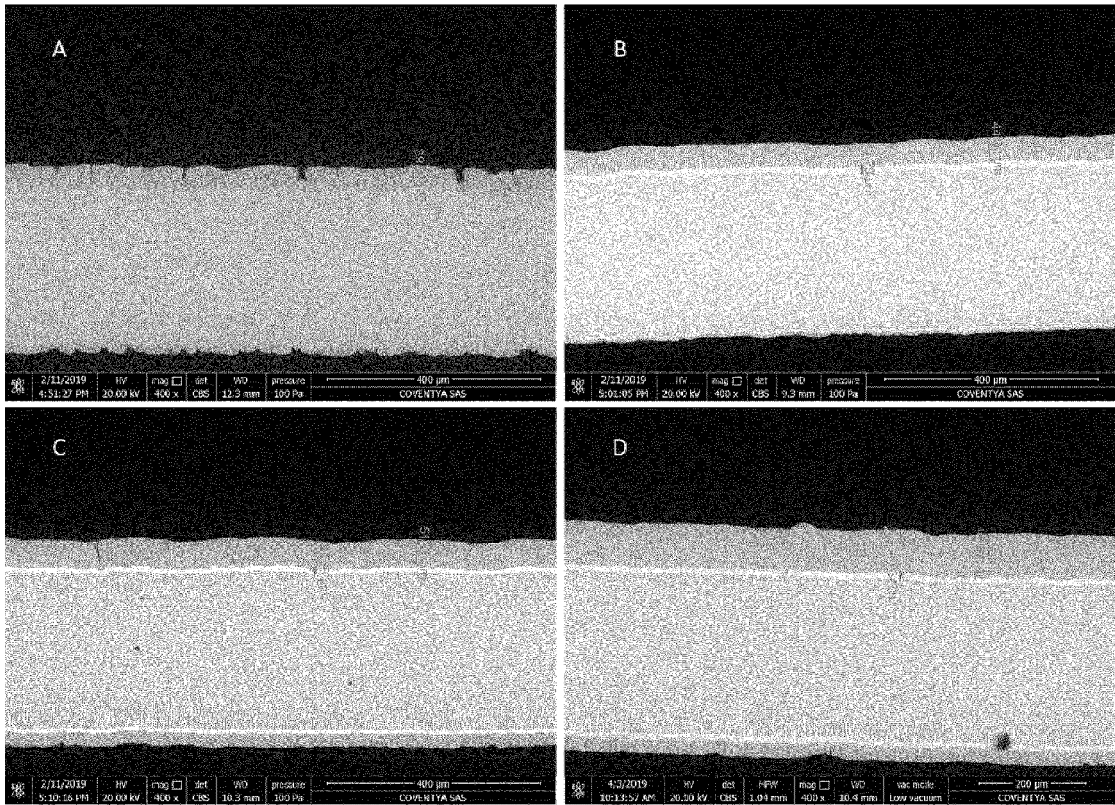


Fig. 2

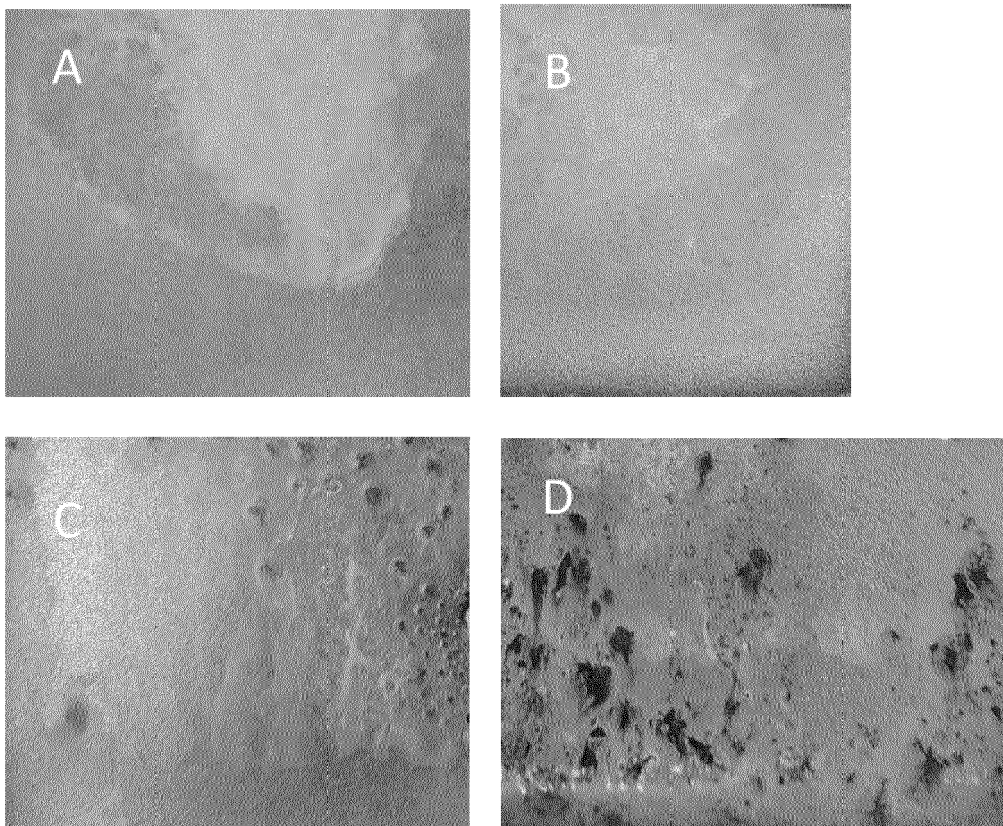


Fig. 3

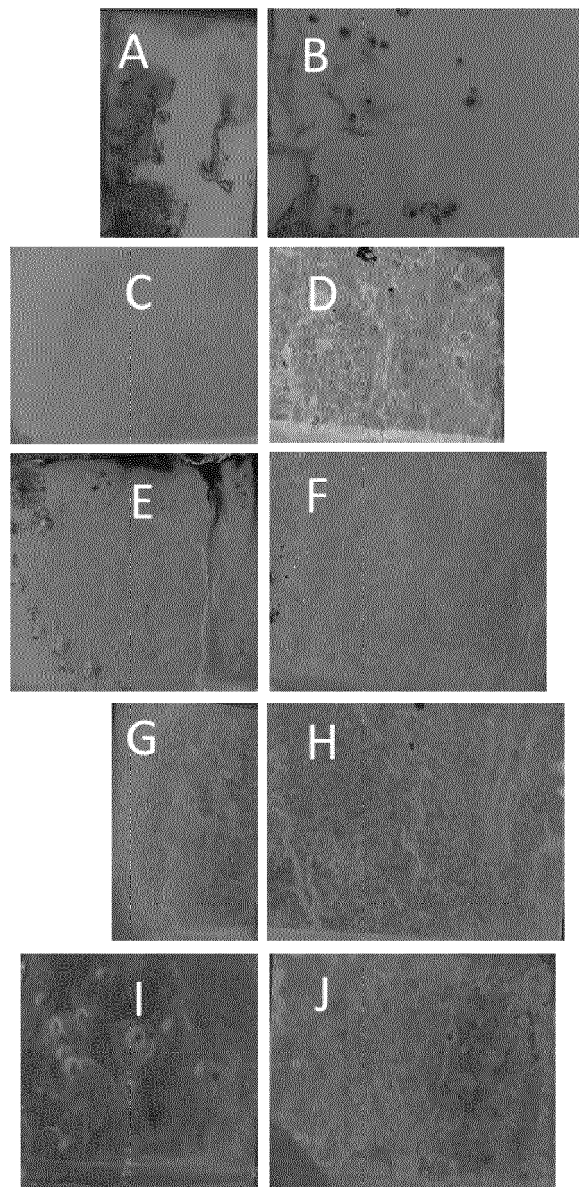
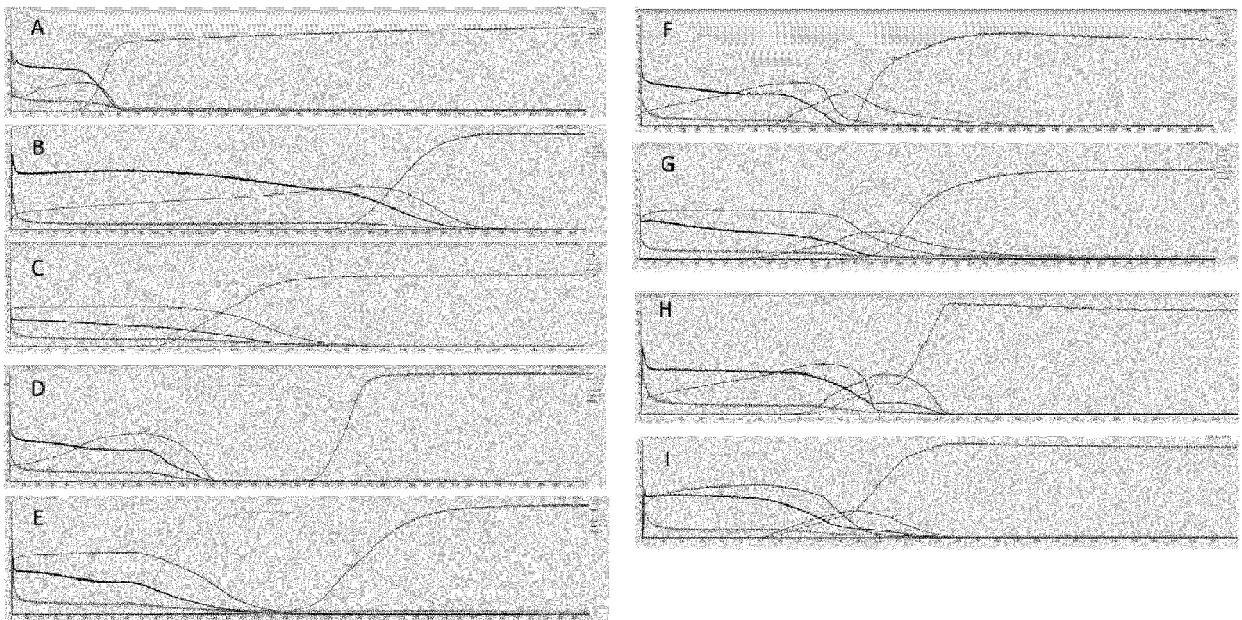


Fig. 4





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Application Number
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