



(11) **EP 3 372 710 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
12.09.2018 Bulletin 2018/37

(51) Int Cl.:
C25D 3/56 (2006.01) C25D 5/18 (2006.01)

(21) Application number: **17160128.9**

(22) Date of filing: **09.03.2017**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME
Designated Validation States:
MA MD

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(54) **ELECTRODEPOSITION OF STAINLESS STEEL LAYER**

(57) The disclosed electrodeposition method for production of a stainless steel coating in form of a Fe-Ni-Cr alloy with less than 20 wt% chromium on a metal or semiconducting substrate in a liquid electrolyte bath is reaching an austenite grade stainless steel alloy coating showing lowered crack densities and an increased brittleness of the resulting stainless steel layers. This is reached with providing a special liquid electrolyte bath comprising salts

of iron, nickel and chromium, a supporting composition, a Ni complexing agent, a pH buffer and a Cr complexing agent, preferably glycine or DMF and running electrodeposition process at temperatures below 25°C, applying sequences of a direct current cathodic pulse with a current density (jc) followed by a relaxation time with zero direct current and repeating sequences of direct current cathodic pulse and relaxation time.

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Description

TECHNICAL FIELD

[0001] The present invention describes an electrodeposition method for production of a stainless steel coating in form of a Fe-Ni-Cr alloy with less than 20 wt% chromium on a metal or semiconducting substrate in a liquid electrolyte bath and a stainless steel layer coating in form of a Fe-Ni-Cr alloy with less than 18 wt% chromium.

STATE OF THE ART

[0002] The electrodeposition of stainless steel involves the electrodeposition of Cr(III) (or Cr(VI)), Fe(II) and Ni(II) ions preferably in chloride containing acidic bath in aqueous medium. The electrodeposition of each of those species and combination of two and three of them has already been published in the literature.

[0003] For the electrodeposition of Cr, the bath usually contains acid radicals that act as catalysts for hexavalent chromium, or a complexing agent for trivalent chromium.

[0004] The mostly used catalysts for hexavalent chromium reduction are sulfate or fluoride whereas, in the case of trivalent chromium plating, numerous chelating agents (e.g. glycine, urea, dimethyl formamide (DMF), formic acid, acetate, sodium citrate, DL-aspartic acid) have been reported in the literature.

[0005] Studies have however mostly pointed out glycine and formic acid. Nevertheless, even with these noteworthy improvements of the bath composition, typical cracking problems remain unsolved yet. The most commonly accepted origin comes from the releasing of internal stress inside the deposit caused by the formation of dihydrogen during the trivalent and hexavalent chromium electrodeposition.

[0006] Alternatively, the hydrogen evolution during the electrodeposition process will lead to a local pH increase at the cathode and might result in the formation of by-products.

[0007] Only few studies have been reported on the electrodeposition of iron-nickel-chromium alloys for different bath compositions. The most widely used bath is based on chloride salts instead of sulfate salts, because of the improved solubility of Cr(III). It also contains a supporting electrolyte (KCl or NaCl), boric acid (H₃BO₃), a pH buffer (NH₄Cl), a complexing agent and/or organic additives (saccharine and SDS).

[0008] In 2008, the laboratory of Mechanics of Materials and Nanostructures of EMPA, Philippe et al., "Electroplating of stainless steel", Chemistry of Materials, May 27 2008;20(10):3377-3384, published their electroplating process for an iron-nickel-chromium alloy. They optimized a system with a copper cathode in a chloride based bath which contains boric acid and ammonium chloride. They examined the effect of several complexing agents such as glycine, acetic acid, formic acid, and

DMF. They found that glycine gave the best deposits by chelating the Cr³⁺ ions through its nitrogen and oxygen atoms. The obtained alloy consisted of 56-58 % of iron, 26 % of nickel, and 14-16 % of chromium, which is close to the standard 316 stainless steel.

[0009] Afterwards, they discussed the problem of electrodepositing stable and crack-free micro-structures into molds. They tested two sulfur-containing organic additives: saccharine and sodium dodecyl sulfate. The effects of these additives on the deposit were various: they did not reduce its internal stress but they modified its composition by increasing the chromium and oxygen contents while decreasing both the iron and nickel concentrations. Solving the problem of cracks by adding organic additives has not yet been achieved.

[0010] However, the electrodeposited alloy was comparable to stainless steel 316 in terms of hardness and corrosion resistance. Finally, the researchers demonstrated the feasibility of utilizing their electroplating method for depositing stainless steel alloys onto flat surfaces. The employment of glycine as a complexing agent allows obtaining stainless steel deposits up to a few microns for functional purposes. However, further studies were necessary to refine the process in order to obtain crack-free and crystallized deposits.

[0011] In conclusion, there are few electrochemical developments for electrodepositing Fe-Ni-Cr alloy layers in the literature. However, they never meet two main conditions in order to call the deposit stainless steel:

either they are having a too low Cr content, less than 10wt%, in order to be classify in the stainless steel class,
either, there is no development of conditions in order to produce a nearly crack-free coating with less internal stress.

[0012] The disadvantage of the disclosed electrodeposition method is the high resulting crack density of the alloy layer and the high brittleness of the layer. Use of electrodeposited layers in processing of micro/nanocomponents for UV LIGA processes was not feasible.

DESCRIPTION OF THE INVENTION

[0013] With the method according to the invention, an alternative method for reaching an austenite grade stainless steel alloy coating by electrodeposition could be found, resulting in more crackfree coating layer with lower crack densities and an increased brittleness of the resulting stainless steel layers.

[0014] The method can lead to thick and conformal coatings of stainless steel alloys with austenite structure.

[0015] We are presenting an electrodepositing Fe-Ni-Cr stainless steel alloy with a Cr content of higher than 16wt%, showing a nearly stressfree respectively crack-free coating layer.

[0016] A more ductile stainless steel alloy layer with

reduced crack density, applicable in different technical fields can be prepared in an efficient and fast way by the presented method without necessary following preparation steps.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] A preferred exemplary embodiment of the subject matter of the invention is described below in conjunction with the attached drawings.

Figure 1 shows different composition of Fe-Cr-Ni alloys as a function of the applied direct cathodic current density before using the invented process comprising pulsed sequences.

Figures 2 are showing optical microscope images of Fe-Cr-Ni coatings obtained at (a) 10 A.dm⁻² and (b) 5 A.dm⁻² after applying direct cathodic currents.

Figure 3 shows a schematic representation of the invented pulsed current sequences with different options.

Figure 4 shows examples of surface response plots obtained for an average current density of 5 A.dm⁻², which allow predicting the Fe, Ni, and Cr contents in weight percent and the crack density as a function of the duty cycle and frequency. The dots represent the experimental data points.

Figures 5 are showing SEM micrographs of the surface of the stainless steel coating obtained with the set of optimized parameters.

DESCRIPTION

[0018] The disclosed invention allows the electrodeposition of crack-free stainless steel coatings onto a surface of an electrically conductive substrate, acting as cathode, by using a special liquid electrolyte bath applying sequences of pulsed current densities between the cathode and an anode in the electrolyte bath. The reached coating layer thickness was 50 microns and more. As cathode for example a copper plate was used, but also possible is a silicon bulk coated with a gold layer. As anode material preferably noble metals are used, for example platinum.

liquid electrolyte bath:

[0019] The liquid electrolyte bath is comprising at least:

- salts of iron, nickel and chromium, between 0.001 and 2 M.

- a supporting electrolyte, between 0 and 6 M, preferably NaCl or KCl,
- a Ni complexing agent, between 0-1 M, preferably H₃BO₃
- a pH buffer, between 0-5 M, preferably NH₄Cl and
- a Cr complexing agent, between 0-5 M, preferably glycine or DMF,

[0020] Because the final density of the electrolyte bath depends on its components, we are stating these values in molarity (M).

[0021] Preferably Fe(II), Ni(II) and Cr(III) chloride salts are used. Beside a source of trivalent chromium also a source of hexavalent chromium can be used. Due to the high toxicity of Cr(VI) compounds, use of Cr(III) salts is preferred.

[0022] The pH of the liquid electrolyte bath should be kept below 2 and the electrolyte bath temperature T should be kept between 20°C and 23°C, while electrodeposition process is carried out. The liquid electrolyte bath is preferably agitated while electrodeposition process is carried out. The agitation can be performed by stirring or rotation of the cathode in the liquid electrolyte bath.

optional ingredients

[0023] As experiments showed organic additives between 0-0.1 M, preferably saccharine (C₇H₅NO₃S) and SDS (sodium dodecyl sulfate) can be added prior the electrodeposition process to the liquid electrolyte bath, for increasing long-time usability of the liquid electrolyte bath.

preferable preparation of electrolyte

[0024] Different preparation methods for preparing the liquid electrolyte bath were tried to reach optimum results. It shows that a chromium-glycine part of the electrolyte bath should be prepared separated in a reservoir:

- adding chromium salt and glycine to deionized water,
- mixing the solution in the reservoir,
- heating the solution at 80°C for at least 30 minutes, before
- resting for at least 12 hours at room temperature,
- mixing the other constituents in a separate reservoir forming a second part,
- mixing both parts at room temperature, forming the liquid electrolyte bath and
- adjustment of pH value.
- Before electrodeposition process, the bath is degassed by flowing a gas through it, preferably Argon or Nitrogen, and for at least 20 min. After this step, an inert atmosphere is maintained at the surface of the electrolyte during the whole electrodeposition process in order to avoid solvation of atmospheric

components (e.g. oxygen, carbon dioxide).

[0025] The results as presented here were achieved using copper plates as cathodes and the anode was made of platinum.

[0026] The liquid electrolyte bath comprised

0.4 M $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$,
0.2 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$,
0.03 M $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$,
0.5 M NH_4Cl ,
0.5 M NaCl ,
0.15 M H_3BO_3 , and
0.4 M $\text{C}_2\text{H}_5\text{NO}_2$ (glycine).

[0027] The pH of the solution was of about 1.4 and its temperature was maintained at 23°C.

electrodeposition process

[0028] We started with direct current deposition processes, using the above disclosed liquid electrolyte bath, cathode and anode and constant cathodic current densities. We found effects of the current density on the coating composition, depending on the cathodic current densities, as shown in Figure 1. Optical microscope images of resulted Fe-Cr-Ni coatings obtained at (a) 10 A/dm² and (b) 5 A/dm² after applying direct cathodic currents are shown in Figures 2a) and b).

[0029] We found, that electrodeposition process should be performed after introducing the liquid electrolyte bath in at least one electrochemical cell, using an inserted anode and a cathode, where a surface of the cathode is to be coated, keeping the electrolyte temperature (T) below 25°C.

[0030] The disclosed values of the current densities are averaged current densities applied.

sequence of cathodic pulse + zero current pulse

[0031] The direct current density results showed that a direct cathodic current density of 5 A/dm² is the most appropriate for obtaining a composition close to that of standard stainless steel 304 with reduced crack density and width.

[0032] We adapted the deposition process by using different plating condition, based on sequences of at least one cathodic pulse and following at least one zero current pulse. The sequence of pulsed currents is described by the current densities, the frequency, and the duty cycle in Figure 3.

[0033] As a function of time t, we applied sequences of:

a direct current cathodic pulse with a current density j_c between 2 A/dm² and 10 A/dm² for a cathodic-pulse time t_c of at least 0.2 milliseconds, followed by a relaxation time t_{off} with zero direct current for at least 4 milliseconds, reaching a period t_c+t_{off} greater

than 4 milliseconds and

repeating sequences of direct current cathodic pulse and relaxation time for at least n times for a process time of at least 1 minutes.

[0034] The sequences were performed using average cathodic current densities between 2 A/dm² to 6 A/dm², with frequencies ($1/(t_c+t_{off})$) of 80 to 200 Hz and duty cycles ($t_c/(t_c+t_{off})$) between 8% to 25%, leading to the best electrodeposition results.

[0035] The cathodic-pulse time t_c varied between 0.2 ms to 4 ms, while the relaxation time t_{off} varied between 3 to 12 ms, leading to periods t_c+t_{off} between 3.2 ms to 16 ms.

[0036] The total time for all n sequences was at least 4000 s for reaching a layer thickness of 20 microns.

[0037] The optimization of pulsed current parameters was performed using a "design of experiment" approach with the software Design-Expert. The average cathodic current density, the frequency, and the duty cycle were set as the "inputs" whereas the chromium, iron, nickel contents and the crack density were chosen as the "outputs".

[0038] The set of surface response plots obtained at an average current density of 5 A/dm² are shown in Figure 4 as examples. Defining the set of outputs which needs to be obtained for the coating, Design-Expert can then provide a set of optimized parameters. As an example, if the coating must contain 20 % of chromium, 10-12 % of nickel and 50-60 % of iron with no crack on its surface, the software predicted the following set of optimized conditions:

an average cathodic current density of 4.84 A/dm²,
a frequency of 104.6 Hz and a duty cycle of 14.9 %.

The characteristics of the obtained crack-free Fe-Cr-Ni coatings obtained are shown in Figures 5 with different resolution.

[0039] In this study, the liquid electrolyte bath conditions were chosen to be constant since they allow obtaining the composition which was targeted for the project. As experiments showed, the process can be applied for other bath conditions in the stated parameter ranges, concentration of constituents, temperature, and agitation. This process can be applied for the electrodeposition of crack-free stainless steel coatings or UV-LIGA microcomponents.

optional anodic pulses

[0040] For optimization of the electrodeposition results, we programmed the control of the potentiostat to perform at least one direct current anodic pulse for an anodic pulse time t_a of at least 0.1 milliseconds, after a direct current cathodic pulse of a sequence. For the direct current anodic pulse the current direction of the cathodic current pulse was reversed.

[0041] The at least one direct current anodic pulse could be applied directly after a direct current cathodic pulse, before the relaxation time or after cathodic current pulse and while the zero current pulse was started.

[0042] The used anodic current density lay between 1 A/dm² and 10 A/dm². As shown in Figure 3, the direct current anodic pulse can be applied in a multiplicity of sequences. The current densities and anodic pulse times of anodic pulses could be varied between the sequences, this can be done by the control of the potentiostat used.

optional pre-pulse

[0043] For optimization of the electrodeposition results, especially for electrodeposition of crack-free stainless steel layers in molds, we introduced a direct current cathodic pre-pulse. Before the sequenced electrodeposition process is performed, at least one direct current cathodic pre-pulse with a current density j_p between 1 A/dm² and 10 A/dm² for a pre-pulse time t_p of at least 0.1 second was applied. After that pre-pulse, the n sequences with alternating cathodic pulse and zero current pulse are started. As shown in Figure 3, a pre-pulse relaxation with zero current can be performed for a pre-pulse off time t_{poff} , before the n sequences are performed.

[0044] The pulse parameters for the deposition of crack-free coatings for a wide range of composition could be optimized for example as stated above. An alternative way to electrodeposit stainless steel with low stress is to replace the aqueous solvent by an organic one. However, there will be in this solution no possibilities to grow thick layer or to galvanofarm the stainless steel. For other deposition techniques competitive to electrodeposition such as physical vapor deposition, there is no possibility to deposit thick and conformal coatings.

[0045] We solved the stress problem with implementing the right deposition conditions and therefore we render possible to use the process for developing products using a Cr(III) liquid electrolyte bath. A non-corroding stainless steel coating, comprising a content of Chromium above 12 weight per cent was deposited on a substrate. The deposition was carried out directly without a following preparation step.

[0046] Stainless steel layers with homogeneous composition and 50 microns and more layer thickness were reached, showing lowered crack densities, low internal stress and lower brittleness as known prior art layers. We have for the first time met the chemistry and plating condition in order to produce stainless steel coating for microcomponents in the right chemical composition needed.

[0047] The here disclosed experiments were performed in galvanostatic mode, applying the disclosed current densities. The electrodeposition process could also be performed in potentiostatic mode, as long as the resulting current densities are lying in the explained pa-

rameter ranges. The electrochemical deposition process by pulse is a relatively difficult process to control. It requires sophisticated potentiostats for pulse the current. In addition, the chemistry of the bath developed in the process is difficult to maintain for a long time and bath aging remains a challenge for industrialisation.

LIST OF REFERENCE NUMERALS

[0048]

pulsed cathodic current density

j average current density $j_c t_c F$

F frequency (1/period)

period = time for interval = $t_c + t_{off}$

D duty cycle = t_c /period in percent

sequence

comprising at least one direct current cathodic pulse and at least one relaxation time

direct current cathodic pulses

j_c

t_c

relaxation time/zero current pulse

toff time while current is off

direct current anodic pulses

j_a current density of direct current anodic pulse

t_a time of current anodic pulse

direct current cathodic pre-pulse

j_p current density of direct current cathodic pre-pulse

t_p time of current cathodic pre-pulse

Claims

1. Electrodeposition method for production of a stainless steel coating in form of a Fe-Ni-Cr alloy with less than 20 wt% chromium on a metal or semiconducting substrate in a liquid electrolyte bath, comprising the following steps:

a) providing a liquid electrolyte bath comprising:

- salts of iron, nickel and chromium, between 0.001-2 M,

- a supporting electrolyte greater 0 up to 6 M, preferably NaCl or KCl,
 - a Ni complexing agent, greater 0 up to 1 M, preferably H_3BO_3
 - a pH buffer, greater 0 up to 5 M, preferably NH_4Cl and
 - a Cr complexing agent, greater 0 up to 5 M, preferably glycine or DMF,
- b) running electrodeposition process after introducing the liquid electrolyte bath in at least one electrochemical cell, using an inserted anode and a cathode, where a surface of the cathode is to be coated, keeping the electrolyte temperature (T) below 25°C,
- applying a sequence of a direct current cathodic pulse with a current density (j_c) between 2 A/dm² and 10 A/dm² for a cathodic-pulse time (t_c) of at least 0.2 milliseconds, followed by
 - a relaxation time (t_{off}) with zero direct current for at least 4 milliseconds, reaching a period t_c+t_{off} greater than 4 milliseconds and
 - repeating sequences of direct current cathodic pulse and relaxation time for at least n times for a process time of at least 1 minute.
2. Electrodeposition method according to claim 1, wherein before the electrodeposition process flowing nitrogen gas or argon gas through the electrolyte for at least 20 minutes in order to remove dissolved oxygen and carbonates before maintaining an inert atmosphere at the electrolyte surface.
 3. Electrodeposition method according to claim 1, wherein a period (t_c+t_{off}) of at least 4 microseconds of each sequence is performed.
 4. Electrodeposition method according to claim 1, wherein frequencies ($f=1/t_c+t_{off}$) between 80 to 200 Hz and duty cycles ($D=t_c/t_c+t_{off}$ in percent) between 8% to 25% are used.
 5. Electrodeposition method according to claim 1, wherein at least one direct current anodic pulse, after reversing the current direction from cathodic current to anodic current, is applied directly after a direct current cathodic pulse before the relaxation time or after cathodic current pulse and start of the relaxation time, for an anodic pulse time (t_a) of at least 0.1 milliseconds, with an anodic current density between 1A/dm² and 10 A/dm².
 6. Electrodeposition method according to one of the preceding claims, wherein before applying the first sequence of direct current cathodic pulses and following relaxation time, at least one direct current cathodic pre-pulse with a current density (j_p) between 1 A/dm² and 10 A/dm² for a pre-pulse time (t_p) of at least 0.1 milliseconds is applied.
 7. Electrodeposition method according to claim 6, wherein a relaxation with zero current is performed for a pre-pulse off time (t_{poff}), before the n sequences are performed.
 8. Electrodeposition method according to one of the preceding claims, wherein the pH value of the electrolyte is below 2 and the electrolyte temperature (T) is between 20°C and 23°C.
 9. Electrodeposition method according to one of the preceding claims, wherein the liquid electrolyte bath is agitated while electrodeposition process is carried out.
 10. Electrodeposition method according to one of the preceding claims, wherein an organic additive, below 0.1 M, preferably saccharine and/or SDS is mixed in the liquid electrolyte bath prior the electrodeposition process is carried out.
 11. Electrodeposition method according to one of the preceding claims, wherein the liquid electrolyte bath is prepared before starting deposition, by
 - adding chromium salt and glycine to deionized water, forming a first part and
 - mixing the first part in a reservoir,
 - heating the s first part at 80°C for at least 30 minutes, before
 - resting for at least 12 hours at room temperature,
 - mixing the other constituents in a separate reservoir forming a second part,
 - mixing both parts at room temperature, forming the liquid electrolyte bath and
 - adjustment of pH value.

FIG. 1

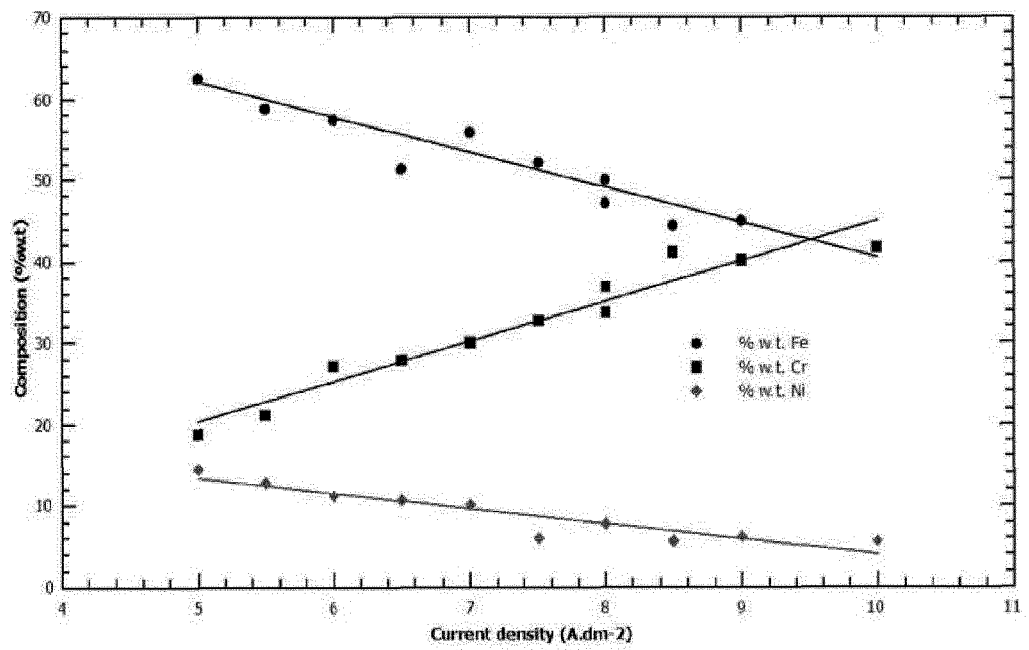


FIG. 2

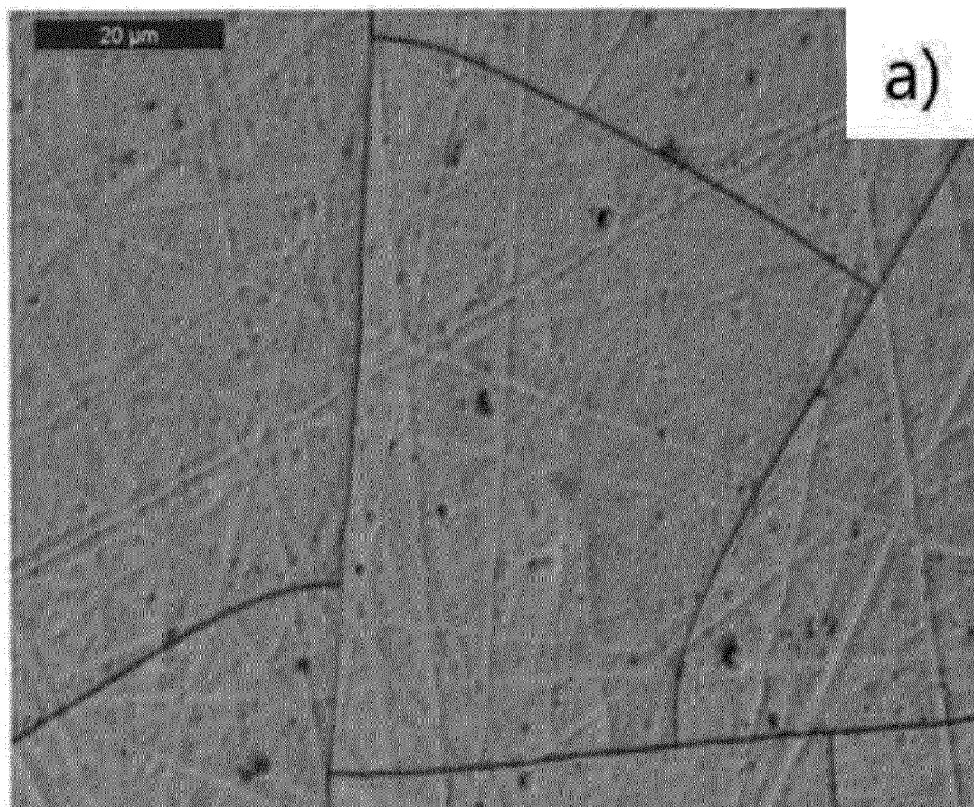


FIG. 2

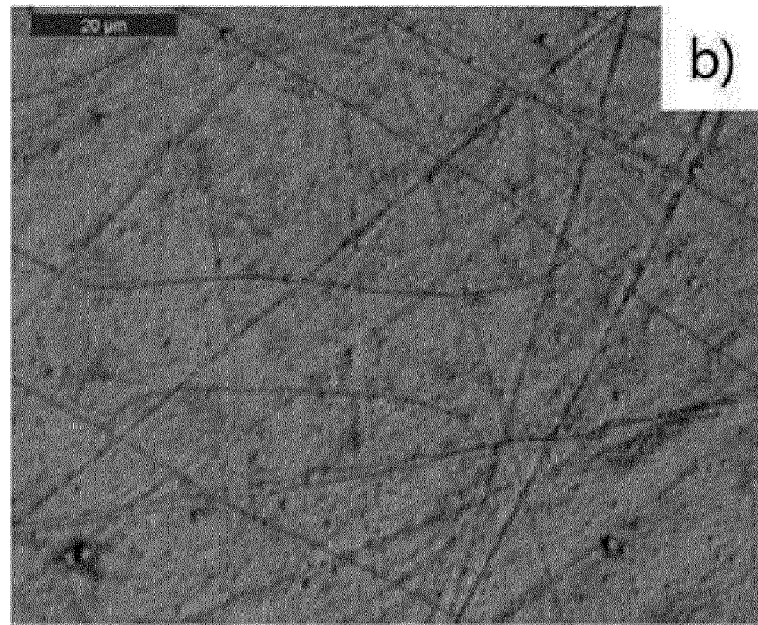


FIG. 3

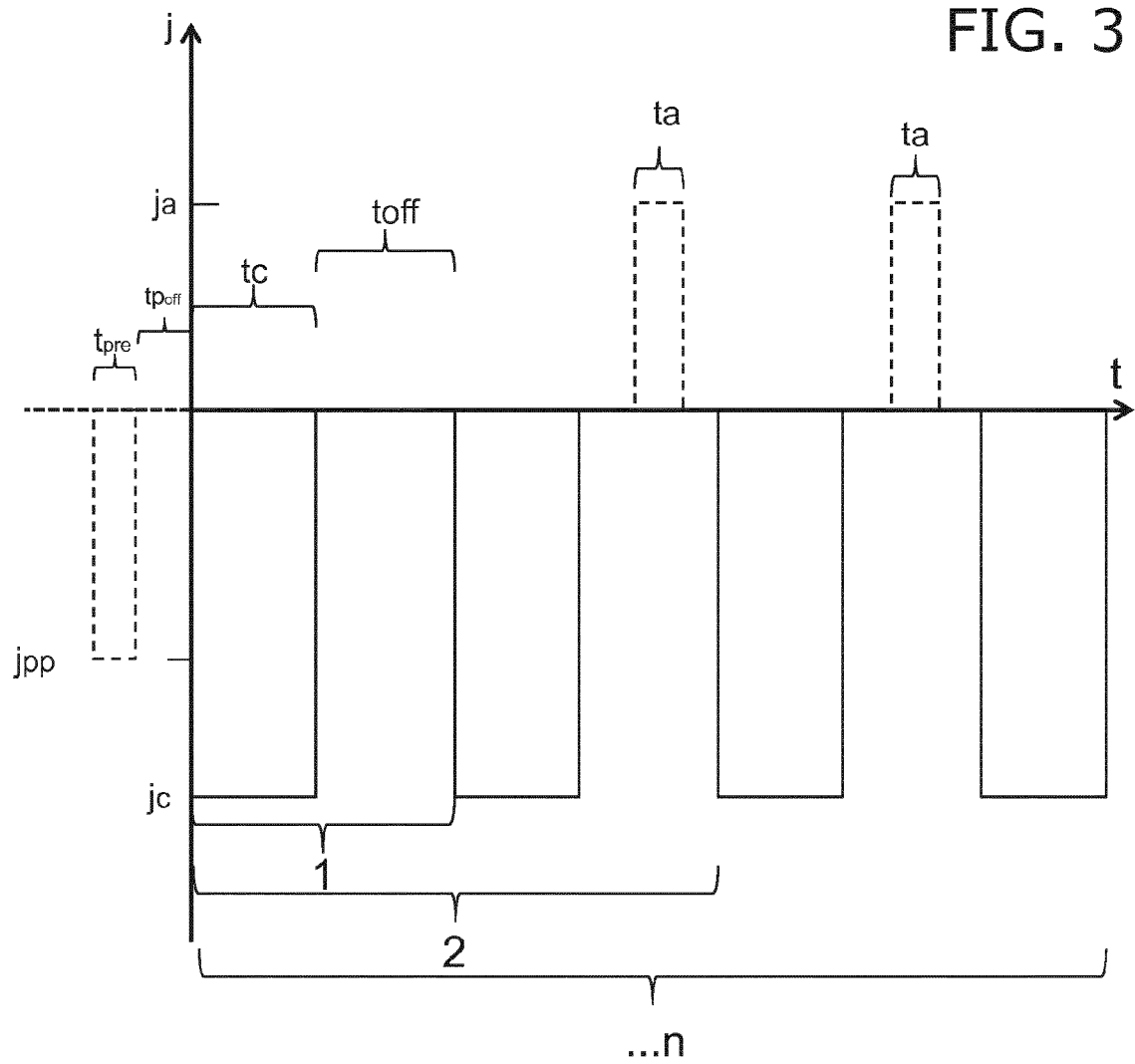


FIG. 4

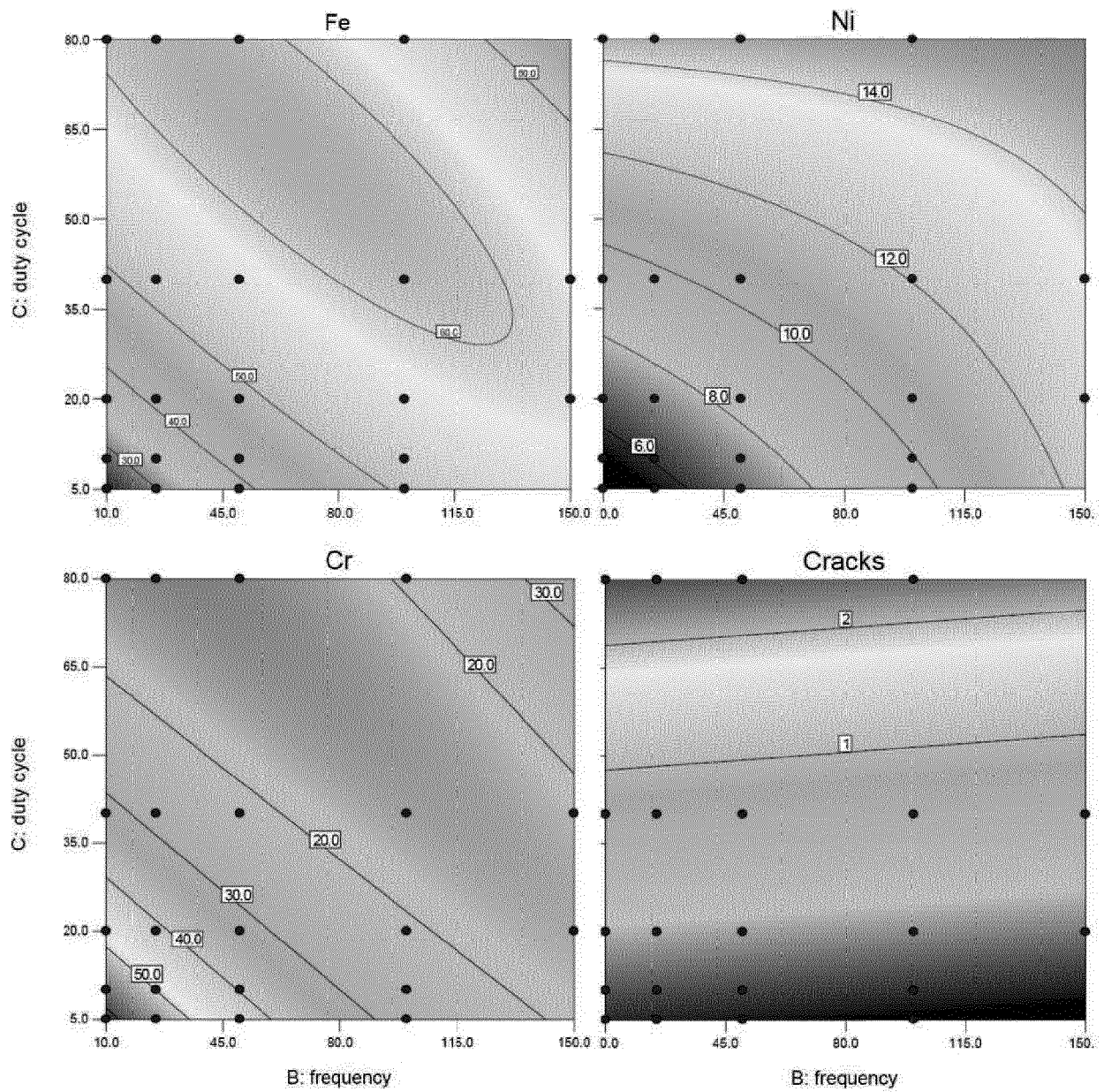
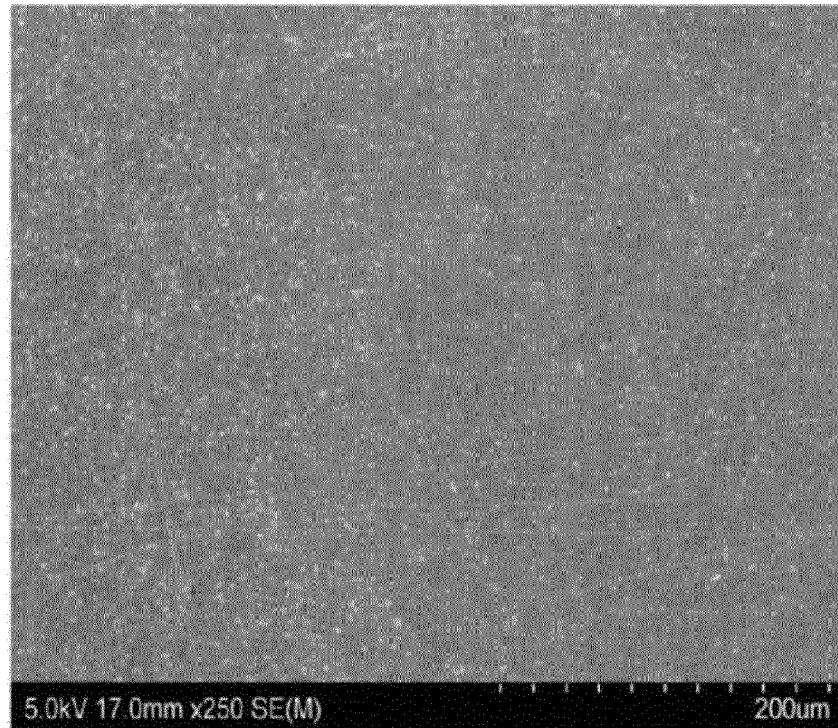
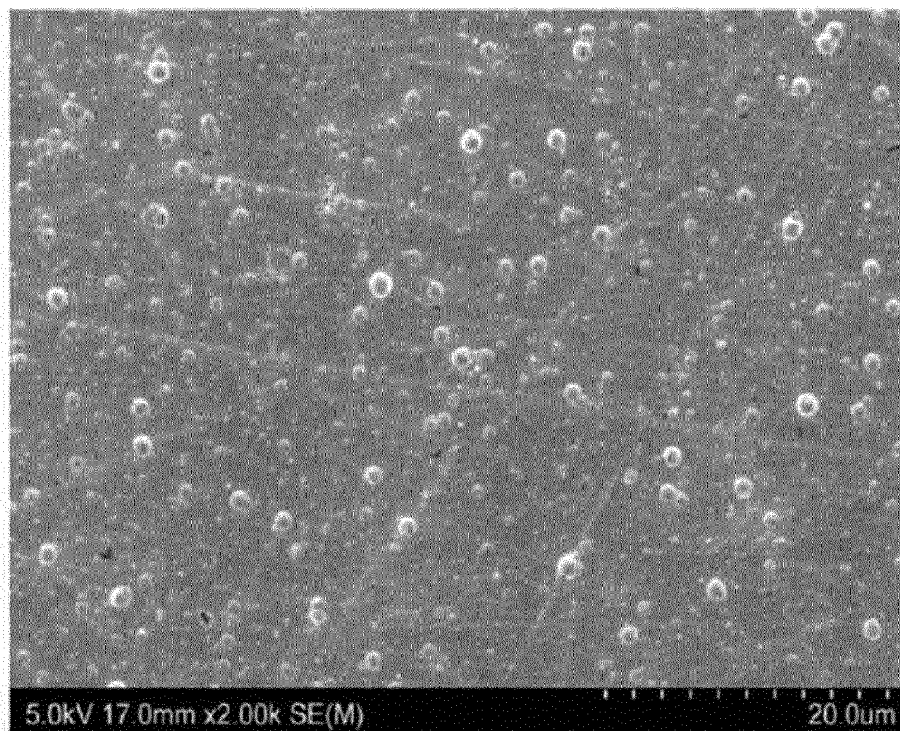


FIG. 5

a)



b)





EUROPEAN SEARCH REPORT

 Application Number
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1 The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 30 August 2017	Examiner Telias, Gabriela
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EUROPEAN SEARCH REPORT

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ANNEX TO THE EUROPEAN SEARCH REPORT
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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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