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(54) **ELECTROLYTIC PROCESS FOR COATING METAL SURFACES TO PROVIDE HIGH WEAR RESISTANCE**

(57) Process for coating a metal article, which comprises: providing an electrolytic bath comprising a suspension of boron carbide particles, having an average size from 0.01 μm to 2 μm , in an aqueous solution comprising: at least one nickel (II) salt; at least one phosphorous compound selected from: phosphoric acid, phosphorous acid, hypophosphorous acid or salts thereof; at least one surfactant; immersing in the electrolytic bath a cathode comprising the article to be coated and an an-

ode, and carrying out an electrodeposition by passing direct current in the electrolytic bath; subjecting the thus coated metal article to a heat treatment. In such a way a coating layer comprising a phosphorus/nickel alloy matrix and boron carbide particles having an average size from 0.01 μm to 2 μm is obtained. The coating layer thus obtained has very high wear resistance, also at high temperatures, and high hardness (up to 1500 HV), and at the same time high thickness uniformity.

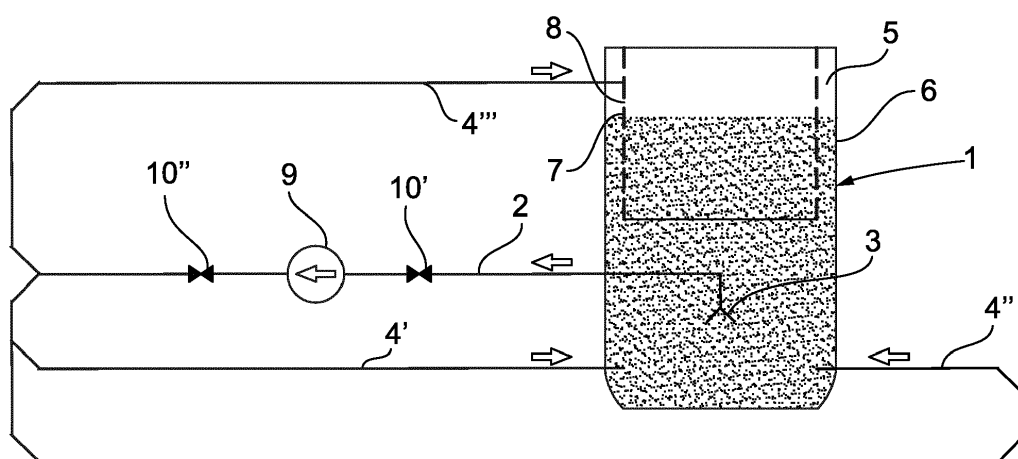


Fig. 2

Description

[0001] The present invention relates to an electrolytic process for coating metal surfaces. More particularly, the present invention relates to an electrolytic process for coating metal surfaces with a layer comprising a nickel/phosphorus alloy matrix and boron carbide particles, in order to provide high wear resistance.

[0002] The need to manufacture metal articles having high surface wear resistance is deeply felt. Generally, the coatings of metal articles are conventionally made by chromium plating, namely electrolytic deposition of a chromium layer having a thickness of the order of 100 μm . Although the chromium plating has low costs, it does not always allow to obtain high-uniformity coatings, especially in the case of surfaces with complex geometry (for example, groovings or other deep embossings) wherein, due to the tip effect, excessive thicknesses are obtained on the tips and pour thickness are obtained in the grooves of the embossings. Furthermore, the use of hexavalent chromium gives serious problems as for the environmental sustainability, due to the high toxicity of this metal, as well as causing high costs in terms of energy and the disposal thereof.

[0003] Another type of coating suitable for conferring wear resistance is that one which uses tungsten carbide, which allows to obtain surfaces with high hardness (Vickers hardness of about 1300 HV), but very high costs, such that to limit the use to specific industrial applications.

[0004] The patent application EP 1 067 220 A2 discloses a process for manufacturing a coating with boron carbide into a nickel-phosphorus matrix, wherein the article to be coated is subjected to electrodeposition into an electrolytic bath comprising two or more nickel salts, in particular a mixture of nickel sulfate and nickel chloride, at least one complexing agent, at least one phosphorus salt, a detensioning agent and boron carbide in the powder form having a particle dimension from 3 to 6 μm . The cathode consists of the material to be coated, while the anode consists of electrolytic nickel. The electrolytic process is carried out at a temperature from 40°C to 70°C with a current density from 1 to 10 A/dm², under stirring. The article thus coated is then subjected to a heat treatment, in particular at a temperature from 250°C to 400°C.

[0005] The Applicant considered the technical problem to manufacture a coating of metal surfaces which allows to obtain high wear resistance, and at the same time high performances in terms of corrosion resistance against oxygen or other chemical agents, with controlled and uniform thicknesses, also in the presence of surfaces having a complex geometry. Furthermore, the Applicant considered the problem to develop a process of electrolytic coating which allows the use of insoluble anodes, namely anodes that remain unchanged during the process, without significant consumption of the material constituting such anodes, thus allowing the use of insoluble anodes commonly used in the conventional chromium plating processes.

[0006] These and other objectives, which will be further illustrated below, were achieved by the Applicant thought the process as defined hereinafter in the present description and attached claims, which allows to obtain a coating layer comprising a nickel/phosphorus (Ni/P) alloy matrix and boron carbide particles having an average size from 0.01 μm to 2 μm .

[0007] Therefore, according to a first aspect, the present invention relates to a process for coating a metal article, which comprises:

- providing an electrolytic bath comprising a suspension of boron carbide particles, having an average size from 0.01 μm to 2 μm , preferably from 0.05 μm to 1 μm , in an aqueous solution comprising:

at least one nickel (II) salt;

at least one phosphorous compound selected from: phosphoric acid, phosphorous acid, hypophosphorous acid or salts thereof;

at least one surfactant;

- immersing in the electrolytic bath a cathode comprising the article to be coated and an anode, and carrying out an electrodeposition by passing direct current in the electrolytic bath;
- subjecting the thus coated metal article to a heat treatment.

[0008] Such process allows to obtain the metal article coated with a layer comprising a nickel/phosphorus (Ni/P) alloy matrix and boron carbide particles having an average size from 0.01 μm to 2 μm , which are present in an very high amount, generally from 10% to 50% by volume, preferably from 5% to 45% by volume, with respect to the total volume of the coating. The coating layer thus obtained has a very high wear resistance, also at high temperatures, and high hardness (up to 1500 HV), and at the same time high thickness uniformity.

[0009] The metal article to be coated can be formed at least partially by one metal, for example, selected from: steel, aluminum, copper, brass, cast iron, and others. The process in accordance with the present invention can be advantageously used for coating metal articles in various technical fields, in particular for coating cylinders for the production of

corrugated cardboard, or for coating the internal surface barrel of firearms, that has groovings with an extremely precise geometry and where the abrasive action of bullets is very height, with the develop of high amounts of heat.

[0010] The boron carbide particles have an average size from 0.01 μm to 2 μm , preferably from 0.05 μm to 1 μm .

[0011] The boron carbide particles in suspension are present in an amount preferably from 1 g/l to 20 g/l, more preferably from 5 to 15 g/l.

[0012] Preferably, the aqueous solution comprises at least one Ni(II) salt with an anion containing sulfur, for example nickel (II) sulfate. More preferably, this is nickel (II) sulfamate ($\text{Ni}(\text{SO}_3\text{NH}_2)_2$). The use of nickel (II) sulfamate is particularly preferred as it allows to increase the electrodeposition rate, with a substantial improvement in terms of productivity and cost of the process.

[0013] As an alternative or in addition to the Ni(II) salt with an anion containing sulfur, the aqueous solution can comprise at least another Ni(II) salt, preferably selected from: nickel (II) carbonate, nickel (II) acetate. It is also possible to use nickel (II) chloride, although this is not particularly preferred if the cathode is a nickel cathode, as the presence of chloride ions causes the consumption of the nickel electrode due to anodic attack.

[0014] Preferably, the aqueous solution comprises Ni (II) ions in a total concentration of from 0.3 moles/l to 3.0 moles/l, more preferably from 0.5 moles/l to 1.5 moles/l.

[0015] Preferably, the aqueous solution comprises a Ni(II) salt with an anion containing sulfur, and a second salt selected from nickel (II) carbonate and nickel (II) acetate, the concentration of the first salt being comprised between 0.3 moles/l and 1.8 moles/l, more preferably between 0.5 moles/l and 1.4 moles/l; the concentration of the second salt being comprised between 0.02 moles/l and 1.0 moles/l, more preferably between 0.05 moles/l and 0.6 moles/l.

[0016] As far as the phosphorus compound is concerned, this is selected from: phosphoric acid, phosphorous acid, hypophosphorous acid or salts thereof. As salts, for example, alkali metal salts (for example potassium, sodium) or alkaline-earth metal salts (for example magnesium, calcium) can be used.

[0017] According to a preferred aspect, the phosphorus compound is a phosphorous acid/hypophosphorous acid mixture, or salts thereof, preferably in a weight ratio comprised between 0.8:1 and 1.2:1. It is believed that such mixture allows to further enhance the characteristics of the final coating, thus achieving an optimal compromise between crystalline phase and amorphous phase in the coating material and therefore between hardness and corrosion resistance thereof.

[0018] The amount of phosphorous compound to be added to the electrolytic bath is mainly selected depending on the type of nickel/phosphorus alloy to be obtained, namely a so-called "low-phosphorus" alloy, namely in general with an amount of phosphorus from 1 to 8% by weight, extremes included (with respect to the weight of the Ni/P alloy), or a so-called "high-phosphorus" alloy, namely in general with an amount of phosphorus higher than 8% and lower than or equal to 16% by weight (with respect to the weight of the Ni/P alloy). The obtaining of a high-phosphorus phosphorus/nickel alloy allows to significantly increase the corrosion resistance of the coating, in particular resistance to the corrosion due to the contact with water with a high content of salt, for example sea water. However, a low-phosphorus phosphorus/nickel alloy has a lower corrosion resistance, but is characterized by a higher hardness with respect to a high-phosphorus alloy.

[0019] According to a preferred aspect, the aqueous solution comprises at least one iodide of an alkali metal, preferably potassium iodide. It is believed that the presence of iodide in the electrolytic bath allows to further enhance the corrosion resistance of the coating, in particular the corrosion resistance in salt fog, a particularly severe test for any material. Preferably, the iodide of an alkali metal is present in the solution in an amount comprised between 0.1 and 10 g/L, more preferably between 0.5 and 3g/L.

[0020] The aqueous solution comprises at least one surfactant, which has mainly the function to facilitate the deposition of the boron carbide particles, particularly when these particles have reduced tank sizes so tending to form agglomerates that remain in suspension or deposit to the bottom of the electrolytic tank instead of depositing on the metal surface together with the Ni/P alloy. Preferably, the surfactant is a cationic, non-ionic or amphoteric surfactant, as these, being positively charged or being neutral, do not undergo the electrostatic repulsive action from the cathode where the deposition of boron carbide occurs.

[0021] The cationic surfactant is preferably selected from tetraalkylammonium salts $\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{N}^+\text{X}^-$ wherein R_1 is an $\text{C}_8\text{-C}_{24}$ alkyl, while $\text{R}_2, \text{R}_3, \text{R}_4$, equal to or different from each other, are $\text{C}_1\text{-C}_6$ alkyls; X^- is an anion, preferably chloride ion or bromide ion. Particularly preferred are the alkyltrimethylammonium salts, such as, for example: cetyltrimethylammonium bromide, hexadecyltrimethylammonium bromide, cetyltrimethylammonium chloride.

[0022] The non-ionic surfactant is preferably selected from: polyoxyethylene $\text{C}_8\text{-C}_{24}$ -alkyl ethers, polyoxypropylene $\text{C}_8\text{-C}_{24}$ -alkyl ethers, oxyethylene/oxypropylene copolymers $\text{C}_8\text{-C}_{24}$ -alkyl ethers, polyoxyethylene $\text{C}_6\text{-C}_{24}$ -alkylphenyl ethers, glucosides $\text{C}_8\text{-C}_{24}$ -alkyl ethers. The non-ionic surfactant is capable of increasing in a particularly effective way the wettability of the particles of boron carbide, slowing the sedimentation and promoting particles to be kept in suspension. Furthermore the non-ionic surfactant is particularly effective to prevent the packing of the boron carbide on the bottom of the tank. Therefore, the use of such surfactant is advantageous both during the deposition step and in those steps wherein the plant does not work and so the solution is maintained at rest.

[0023] The amphoteric surfactant, having zwitterionic hydrophilic groups, is preferably selected from: $\text{C}_8\text{-C}_{24}$ -alkyl betaines, $\text{C}_8\text{-C}_{24}$ -alkylamidopropyl betaines, $\text{C}_8\text{-C}_{24}$ -alkylamphodiacetates, $\text{C}_8\text{-C}_{24}$ -alkylamphodipropionates. As the bo-

boron carbide is free of electrical charge, an amphoteric surfactant is preferably used because it provides the boron carbide particles with a charge, thus increasing the amount of said particles in the coating layer obtained by electrolytic deposition.
[0024] The surfactants at least partially fluorinated, preferably cationic, non-ionic or amphoteric surfactants, are particularly preferred. These generally have formula:



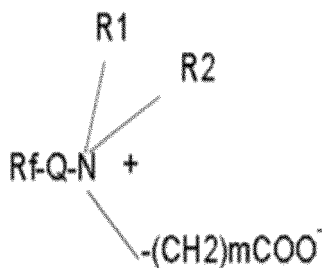
where:

Rf is a C₂-C₂₀ perfluoroalkyl group, linear or branched;
 Q is a non-fluorinated bifunctional group, for example -(CH₂)_nCH(OH)CH₂-NH(CH₂)₃-, -(CH₂)_nCH(OCOCH₃)CH₂-, -(CH₂)_nSCH₂CH(OH)CH₂- or -SO₂NH(CH₂)₃-, where n is 1 or 2;
 T is a hydrophilic cationic, non-ionic or amphoteric group.

[0025] For example, T can be selected from:

cationic groups of formula -N⁺R₃X⁻, where R, equal to or different from each other, are C₁-C₄ alkyls, X⁻ is an anion, preferably chloride or bromide ion;
 polyethylene oxide groups -(CH₂CH₂O)_mH, where m is an integer from 1 to 20;
 amphoteric groups, such as, for example: -N⁺(CH₃)₂CH₂COO⁻, -N⁺(CH₃)₂O⁻, -SCH(COO⁻)CH₂CONH(CH₂)₃N⁺(CH₃)₃.

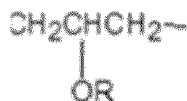
[0026] According to another preferred aspect of the invention, the amphoteric surfactant has general formula



wherein:

Rf is a linear or branched perfluorinated alkyl group of formula -C_nF_{2n+1} wherein n is an integer comprised between 4 and 20, preferably between 6 and 14, extremes included, more preferably n is 4 or 6;
 Q is selected from:

- i) a group of formula -(C_pH_{2p})-, linear or branched, where p is an integer comprised between 1 and 50, preferably between 2 and 10, extremes included;
- ii) a group of formula -(C_pH_{2p})_q-C₆H₄-(C_{p1}H_{2p1})_r- wherein q and r are each independently 0 or 1, p₁ is an integer comprised between 1 and 50, extremes included, and p is as defined above;
- iii) a group of formula -(C_pH_{2p})_q-C₆H₄-(CH₂CH₂O)_D- where p and q are as defined above, and D is an integer comprised between 1 and 40, extremes included;
- iv) a group of formula



wherein R is selected from hydrogen and a linear or branched C₁-C₅ alkyl group, preferably R is -CH₃ or H, more preferably R is H;
 R₁ and R₂, equal to or different from each other, are selected from: a linear or branched C₁-C₅ alkyl group, a Rf-Q- group as defined above, or, together with the N atom to which they are bounded, form a piperidine, morpholine or N-alkyl (C₁-C₄) piperazine ring;

m is an integer comprised between 1 and 10, preferably comprised between 2 and 3, extremes included.

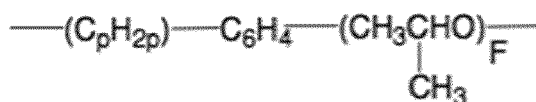
[0027] According to another preferred aspect of the invention, the non-ionic surfactant has general formula:



wherein:

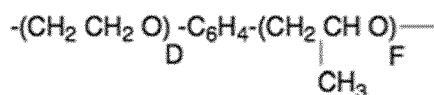
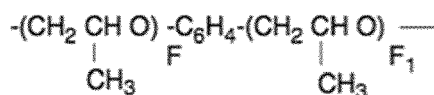
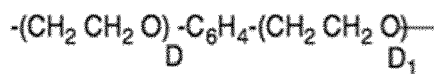
Rf is a perfluorinated alkyl group, linear or branched, having formula $-\text{C}_n\text{F}_{2n+1}$ wherein n is an integer comprised between 4 and 20, preferably comprised between 6 and 14, extremes included, more preferably n is 4 or 6;
Q is selected from:

- i) a group of formula $-(\text{C}_p\text{H}_{2p})-$, linear or branched, wherein p is an integer comprised between 1 and 50, preferably comprised between 2 and 10, extremes included;
- ii) a group of formula $-(\text{C}_p\text{H}_{2p})_q-\text{C}_6\text{H}_4-(\text{C}_{p_1}\text{H}_{2p_1})_{r_1}-$ wherein q and r are each independently 0 or 1, p_1 is an integer comprised between 1 and 50, extremes included, and p is as above defined;
- iii) a group of formula $-(\text{C}_p\text{H}_{2p})_q-\text{C}_6\text{H}_4-(\text{CH}_2\text{CH}_2\text{O})_D-$ wherein p and q are as defined above, and D is an integer comprised between 1 and 40, extremes included;
- iv) a group of formula



wherein p is as above defined and F is an integer comprised between 1 and 40, extremes included;

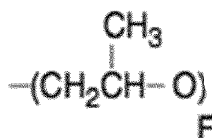
v) a group selected from:



wherein D and F are as above defined, D_1 and F_1 are integer, each independently comprised between 1 and 40, extremes included;

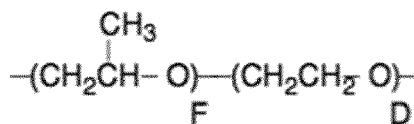
vi) a group of formula $-(\text{CH}_2\text{CH}_2\text{O})_D-$ where D is as above defined;

vii) a group of formula



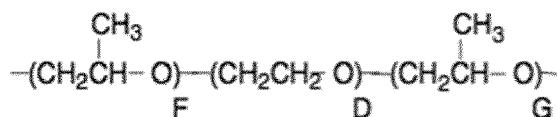
wherein F is as above defined;

viii) an ethylene oxide and propylene oxide block copolymer of formula



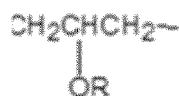
where F and D are as above defined;

ix) an ethylene oxide-propylene oxide-ethylene oxide block copolymer of formula



where F and D are as above defined, G is an integer comprised between 1 and 40, extremes included;

x) a group of formula



where R is selected from hydrogen and a C₁-C₅ alkyl group, linear or branched, preferably R is -CH₃ or H, more preferably R is H;

Y is an hydrogen or a C₁-C₁₀ alkyl group, linear or branched, preferably Y is -CH₃ or H.

[0028] The concentration of said at least one surfactant is preferably comprised between 0.01 g/l and 2 g/l, more preferably between 0.05 g/l and 1 g/l.

[0029] Preferably the aqueous solution has a pH from 0.5 to 4, more preferably from 1.5 to 3. In order to obtain pH values within the above mentioned ranges, a strong acid is preferably added to the aqueous solution, in particular an aqueous solution of sulfuric acid. In certain cases, in order to maintain the pH within the selected range, the addition of a buffering agent may be advantageous, for example a boric/borate acid or acetic acid/acetate system.

[0030] Preferably, the aqueous solution further comprises at least one detensioning agent, which has the function to reduce tensions which are generated within the coating mainly due to the presence of phosphorous, tensions which can cause a deterioration of the coating layer, with the formation of cracks and possible detachments thereof.

[0031] The detensioning agents is preferably selected from: saccharin; thiocarbamic acid, possibly N or N,N' substituted by C₁-C₄ alkyls, or derivatives thereof, such as salts or C₁-C₄ esters, preferably N,N'-diethyl-carbamic acid or salts or esters thereof; thiocompounds (for example thiourea, ammonium sulphocyanide, potassium sulphocyanide).

[0032] The concentration of the detensioning agent is preferably comprised between 0.2 g/l and 10 g/l, more preferably between 4 g/l and 8 g/l.

[0033] Preferably, the aqueous solution further comprises at least one complexing agent, which is preferably selected from the carboxylic acids or derivatives thereof, such as, for example: citric acid, lactic acid, malic acid, malonic acid, succinic acid, glycolic acid, or mixtures thereof. The lactic acid is particularly preferred.

[0034] The concentration of the complexing agent is preferably comprised between 0.05 moles/l and 2 moles/l, more preferably between 0.5 moles/l and 1 moles/l.

[0035] If the obtaining of a particularly high corrosion resistance is desirable, it is preferable that the final coating has a high amount of phosphorous. Therefore, in such cases, it is preferable to work with a bath at high concentrations of phosphorous in the absence of the detensioning agent and/or of the complexing agent, as said agents generally tend to reduce the content of phosphorus in the bath, as well as reducing the deposition ratio.

[0036] As far as this latter aspect is concerned, the Applicant noted that the presence of boron carbide particles in the electrolytic bath affects the deposition ratio of the coating layer, thus causing a slowing of the rate at which said deposition occurs. Therefore, according to a preferred aspect, before carrying out the electrodeposition in the presence of boron carbide particles, the article is preventively coated with a first coating layer by electrodeposition in a first electrolytic bath consisting of an aqueous solution, free of boron carbide particles, comprising:

at least one nickel (II) salt;

at least one phosphorus compound selected from: phosphoric acid, phosphorous acid, hypophosphorous acid or salts thereof. In this way a first deposition of a first coating layer free of boron carbide particles and a following

deposition of a second coating layer containing boron carbide particles, is carried out.

[0037] Advantageously, such deposition sequence enables a first fast deposition of the first layer free of boron carbide, while the second deposition, which is slower, enables to give the desired wear and corrosion resistance properties to the surface of the article. In such a way, an overall saving of time with respect to that one necessary for an single deposition in the presence of boron carbide, with evident advantages for the overall productivity of the process, is obtained.

[0038] As for the way to carry out the electrochemical process object of the present invention, said process can be carried out according to conventional modes, provided that a constant and homogeneous movement of the electrolytic bath is ensured, mainly in order to maintain in suspension the boron carbide particles without causing perturbations in the process of electrolytic deposition. Particularly, it is appropriate to avoid the formation of preferential routes for the flow of the suspension into the electrolytic bath, which could cause a lack of homogeneity in the coating layer.

[0039] For this purpose it is particularly advantageous to carry out the process according to the present invention into an apparatus comprising an electrolytic tank and a system for recycling the electrolytic bath. In particular, the recycling system comprises at least one intake line of the bath provided with an intake head inserted into the tank, at least one supply line of the bath into the tank which leads into a distribution chamber delimited by an external wall of the tank and by an internal wall provided with passing holes through which the bath flows into the tank.

[0040] Preferably, the passing holes are homogeneously distributed along the perimeter of the inner wall, thus making an intake of the bath into the tank as much as possible uniform, without generating preferential flows which would cause nonhomogeneity in the electrolytic deposition of the coating layer.

[0041] The intake head is preferably placed at a certain distance from the bottom of the tank, so as to avoid obstructions of the intake line, especially when the boron carbide particles are deposited on the bottom after a prolonged shutdown of the apparatus.

[0042] Preferably, the recycling system comprises at least two supply lines of the bath into the tank, which lead into the tank in diametrically opposite positions, preferably at the same level in the tank and tangential with respect to the external wall, so as to make a rotary flow of the suspension into the tank. Preferably, the two supply lines lead into the lower part of the tank, in correspondence of the bottom, so that the inlet flows contribute to the mixing of boron carbide particles possibly settled on the bottom.

[0043] Preferably, the recycling system comprises a third supply line placed in correspondence of a different level of the tank with respect to the two above-mentioned supply lines, preferably in the top of the tank, in order to make a better mixing of the suspension into the tank because of convective motions derived from liquid flows placed at several heights.

[0044] The process according to the present invention can be carried out within a wide range of temperatures, generally from 30°C to 90°C, preferably from 40°C to 70°C. Lower temperatures to the above-mentioned ranges would cause a reduction of the electrodeposition efficiency, while higher temperatures would have as a disadvantage an excessive evaporation of the electrolytic bath, with consequent inefficiency from the energetic point of view.

[0045] The electrolytic bath preferably has a pH value from 1 to 5, more preferably from 1.5 to 3.

[0046] The metal article to be coated is immersed in the the electrolytic bath, which acts as cathode, and an anode, preferably an insoluble anode, for example an anode selected from: anodes made of titanium platinized or coated with mix oxides; anodes made of stainless steel (for example AISI 316), possibly coated with a noble metal, for example gold or platinum; nickel anodes.

[0047] The passage necessary to carry out the process of electrodeposition is obtained tank to the connection of the electrodes with a generator of continuous electric energy, so as to obtain a current density in the electrolytic bath generally comprised between 1 and 40 mA/cm², preferably between 5 and 30 mA/cm².

[0048] The process of electrodeposition is carried out for a time so as to obtain the desired thickness of the coating, which is generally comprised between 5 μm and 100 μm, more preferably between 10 μm and 40 μm.

[0049] After the electrodeposition, the article thus coated is subjected to a heat treatment, at a temperature generally comprised between 250°C and 400°C, preferably between 300°C and 375°C, for a time variable within wide limits, for example between 1 and 24 hours, preferably between 6 and 18 hours. The heat treatment mainly has the aim to form the Ni/P alloy, thus removing the hydrogen formed during the electrolytic process, so as to obtain a coating layer stable and homogeneous, thus minimizing defects and internal tensions.

[0050] The present invention will be now further illustrated with reference to the non-limiting figures attached to the present description, wherein:

Figures 1 and 2 represent a scheme of an apparatus for carrying out a process according to the present invention, Figure 1 according to a plan view, Figure 2 according to a side view;

Figure 3 shows the SEM image of a double layer coating, obtained by a deposition in succession;

Figure 4 show the SEM image of the surface of a coating layer made of high-phosphorous Ni-P alloy, free of boron carbide particles.

[0051] With reference to said Figures 1 and 2, the apparatus comprise an electrolytic tank (1), preferably cylindrical-shaped, and a system for recycling the electrolytic bath comprising at least one intake line (2) of the bath provided with one intake head (3) inserted into the tank (1), at least one supply line (4', 4'' and 4''') of the bath into the tank (1) which leads into a distribution chamber (5), preferably present on the top of the tank (1), delimited by an external wall (6) of the tank (1) and by an internal wall (7) provided with passing holes (8) through which the bath flows into the tank (1). The arrows in Figure 1 have the aim to show the direction of the flows of the electrolytic bath.

[0052] In the embodiment according to Figure 1, the apparatus comprises three supply lines of the electrolytic bath into the tank (1), a first one (4') placed in correspondence of the lower portion of the tank (1), a second one (4'') placed at the same height and in the position diametrically opposite with respect to the first one (4'), and a third one (4''') placed in correspondence of the higher portion of the tank (1). The combination of the three inlet flows has the function to create a movement of the electrolytic bath both in circular direction, along the internal wall (7), and in vertical direction, so as to increase the mixing and therefore the homogeneity of the suspension during the electrolytic process and minimizing the risk of flows with preferential directions.

[0053] The recycling system of the electrolytic bath is obviously provided with a pump (9) and a plurality of valves (10', 10'') in order to put into pressure the supply and intake lines and suitably managing the flows of the electrolytic bath into the tank (1).

[0054] The following examples of embodiment are provided only for illustrative purposes of the present invention and they are not to be intended as limitative of the scope of protection defined by the attached claims.

EXAMPLE 1 (low-P Ni/P alloy).

[0055] A water-based electrolytic bath (total volume: 200 ml) consisting of:

NiSO ₄	1.16 moles/l;
H ₃ PO ₃	0.3 moles/l;
lactic acid	0.5 moles/l;
saccharin	1 g/l;
non ionic surfactant	0.35 g/l;

was prepared.

[0056] Boron carbide particles was added to the bath in an amount equal to 10 g/l, having average sizes equal to 0.4 μm. The electrolytic bath had a pH value equal to 2.0.

[0057] The electrodeposition process was carried out into an apparatus as illustrated in Figure 1, maintaining the electrolytic bath at a temperature of about 65°C. The current density was maintained at a pH value of about 20 mA/cm² for three hours. The coating was made on a steel plate, used as a cathode, while a titanium anode coated with mix oxides was used as an anode.

[0058] At the end of the electrodeposition process, a coating layer of the plate having a thickness of about 120 μm, containing about 4% by weight of phosphorous, having Vickers hardness equal to 750 HV, is obtained.

EXAMPLE 2 (high-P Ni/P alloy).

[0059] A water-based electrolytic bath (total volume: 200 ml) consisting of:

NiSO ₄	1.16 moli/l;
H ₃ PO ₃	1.0 moli/l;
Lactic acid	0.5 moli/l;
saccharin	1 g/l;
non-ionic surfactant	0.35 g/l;

was prepared.

[0060] Boron carbide particles were added to the bath in an amount equal to 10 g/l, having average sizes equal to 0.4 μm. The electrolytic bath had a pH value equal to 2.0.

[0061] The electrodeposition process was carried out into an apparatus as illustrated in Figure 1, maintaining the electrolytic bath at a temperature of about 65°C. The current density was maintained to a value of about 20 mA/cm² for three hours. The coating was made on a steel plate, used as a cathode, while a titanium anode coated with mix oxides was used as an anode.

EP 3 098 334 A1

[0062] At the end of the electrodeposition process, a coating layer of the plate having a thickness of about 120 μ m, containing about 12% by weight of phosphorous, having Vickers hardness equal to 450 HV, is obtained.

EXAMPLE 3 (low-P Ni/P alloy).

[0063] A water-based electrolytic bath (total volume: 200 ml) consisting of:

Ni sulfamate	1.1 moles/l;
H ₃ PO ₃	0.22 moles/l;
Lactic acid	0.5 moles/l;
saccharin	1 g/l;
fluorinated non ionic surfactant	0.35 g/l;

was prepared.

[0064] Boron carbide particles were added to the bath in an amount equal to 10 g/l, having average sizes equal to 0.4 μ m. The electrolytic bath had a pH value equal to 2.0.

[0065] The electrodeposition process was carried out into an apparatus as illustrated in Figure 1, maintaining the electrolytic bath at a temperature of about 65°C. The current density was maintained at a value of about 20 mA/cm² for three hours. The coating was made on a steel plate, used as a cathode, while a titanium anode coated with mix oxides was used as an anode.

[0066] At the end of the electrodeposition process, a coating layer of the plate having a thickness of about 60 μ m is obtained, containing about 4% by weight of phosphorous, having Vickers hardness equal to 590 HV, is obtained.

ESEMPIO 4 (high-P Ni/P alloy).

[0067] A water-based electrolytic bath (total volume: 200 ml) consisting of:

Ni sulfamate	1.1 moles/l;
H ₃ PO ₃	0.8 moles/l;
Lactic acid	0.5 moles/l;
saccharin	1 g/l;
fluorinated non ionic surfactant	0.35 g/l;

was prepared.

[0068] Boron carbide particles were added to the bath in an amount equal to 10 g/l, having average sizes equal to 0.4 μ m. The electrolytic bath had a pH value equal to 2.0.

[0069] The electrodeposition process was carried out into an apparatus as illustrated in Figure 1, maintaining the electrolytic bath at a temperature of about 65°C. The current density was maintained at a value of about 20 mA/cm² for one hour. The coating was made on a steel plate, used as a cathode, while a 316 L stainless steel anode was used as an anode.

[0070] At the end of the electrodeposition process, a coating layer of the plate having a thickness of about 42 μ m, containing about 12% by weight of phosphorous, having Vickers hardness equal to 700 HV, is obtained.

EXAMPLE 5 (double layer).

[0071] A double layer coating was made (Figure 3), where the first layer was free of boron carbide particles, while the second layer contained boron carbide particles.

[0072] A first water-based electrolytic bath (total volume: 200 ml) consisting of a solution so called "high-ratio" and high-phosphorous, free of boron carbide particles, comprising:

• phosphorous acid	100 g/L
• nickel sulfate (NiSO ₄ * 6H ₂ O)	55 g/L
• sulfuric acid (H ₂ SO ₄)	30 g/L

(continued)

- sodium acetate (CH_3COONa) 120 g/L
- KI 10 g/L,

5 was prepared.

[0073] The electrolytic bath was brought at a pH value equal to 3.0 with NaOH.

[0074] The electrodeposition process was carried out into an apparatus as illustrated in Figure 1, maintaining the electrolytic bath at a temperature of about 60°C. The current density was maintained at a value comprised in the range of 7-10 mA/cm² for one hour. The coating was made on a steel plate, used as a cathode, while a pure nickel anode was used as an anode.

[0075] As far as the first coating layer is concerned, a deposition efficiency of 120 μm/h and a hardness of 750 HV were observed. However, after a heat treatment at 400°C for 1h, it was possible to obtain an enhanced hardness of said first layer equal to about 1100 HV. Furthermore, the coating layer obtained had a weight content of phosphorous equal to about 14%.

[0076] For the deposition of the second coating layer a second electrolytic bath (total volume: 200 ml) was prepared. First of all, an aqueous solution so-called "low-phosphorous", consisting of:

- Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) 75 g/L;
- phosphorous acid 15 g/L;
- sodium hypophosphite 20 g/L;
- sodium acetate (CH_3COONa) 120 g/L;
- KI 10 g/L;

25 was prepared.

[0077] The electrolytic bath was brought at a pH value equal to 2.0 with an aqueous solution of H_2SO_4 .

[0078] Then, a suspension of boron carbide thus prepared was added to the aqueous solution. 1 g/L of a fluorinated non-ionic surfactant was added to 10 g/L of boron carbide and the whole was subjected to stirring for 10 minutes and ultrasonic for 5 minutes. 2 g/L of an amphoteric surfactant having functional groups containing fluorine were added to the mixture thus obtained and the whole was subjected under stirring for 10 minutes.

[0079] The electrodeposition process was carried out into an apparatus as illustrated in Figure 1, maintaining the electrolytic bath at a temperature of about 80°C. The current density was maintained at a value of 2 mA/cm² for one hour. The coating was made in the same electrolytic cell of the first layer by using as a cathode that one coated with the first layer.

[0080] A deposition efficiency of the second layer between 10 and 30 μm/h and an hardness of said second layer of 900 HV were observed. However, after a heat treatment at 400°C for 1 hour, it was possible to obtain an enhanced hardness equal to about 1350 HV. Furthermore, the coating layer obtained has a weight content of phosphorous equal to about 7%.

Claims

1. Process for coating a metal article, which comprises:

- providing an electrolytic bath comprising a suspension of boron carbide particles, having an average size from 0.01 μm to 2 μm, in an aqueous solution comprising:

at least one nickel (II) salt;

at least one phosphorous compound selected from: phosphoric acid, phosphorous acid, hypophosphorous acid or salts thereof;

at least one surfactant;

- immersing in the electrolytic bath a cathode comprising the article to be coated and an anode, and carrying out an electrodeposition by passing direct current in the electrolytic bath;

- subjecting the thus coated metal article to a heat treatment.

2. Process according to claim 1, wherein the boron carbide particles in suspension are present in an amount of from

1 g/l to 20 g/l, preferably from 5 to 15 g/l.

3. Process according to claim 1 or 2, wherein the nickel (II) salt is nickel (II) sulfamate ($\text{Ni}(\text{SO}_3\text{NH}_2)_2$).

4. Process according to anyone of the preceding claims, wherein the aqueous solution comprises Ni(II) ions in a total concentration of from 0.3 moles/l to 3.0 moles/l, preferably from 0.5 moles/l to 1.5 moles/l.

5. Process according to anyone of the preceding claims, wherein said at least one surfactant is a cationic, non-ionic or amphoteric surfactant.

6. Process according to claim 5, wherein said at least one surfactant is a cationic surfactant selected from tetraalkylammonium salts $\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{N}^+\text{X}^-$, wherein R_1 is a C_8 - C_{24} alkyl, whereas R_2 , R_3 , R_4 , equal to or different from each other, are C_1 - C_6 alkyls; X^- is an anion, preferably chloride ion or bromide ion.

7. Process according to claim 5, wherein said at least one surfactant is a non-ionic surfactant selected from: polyoxyethylene C_8 - C_{24} -alkyl ethers, polyoxypropylene C_8 - C_{24} -alkyl ethers, oxyethylene/oxypropylene copolymers C_8 - C_{24} -alkyl ethers, polyoxyethylene C_6 - C_{24} -alkylphenyl ethers, glucosyde C_8 - C_{24} -alkyl ethers.

8. Process according to claim 5, wherein said at least one surfactant is an amphoteric surfactant selected from: C_8 - C_{24} -alkyl betaine, C_8 - C_{24} -alkylamidopropyl betaine, C_8 - C_{24} -alkylamphodiacetates, C_8 - C_{24} -alkylamphodipropionates.

9. Process according to anyone of the preceding claims, wherein said at least one surfactant is a surfactant at least partially fluorinated, preferably cationic, non-ionic or amphoteric.

10. Process according to anyone of the preceding claims, wherein the aqueous solution has a pH from 0.5 to 4, preferably from 1.5 to 3.

11. Process according to anyone of the preceding claims, wherein the anode is an insoluble anode.

12. Process according to anyone of the preceding claims, wherein, before carrying out the electrodeposition in the presence of boron carbide particles, the article is preventively coated with a first coating layer by electrodeposition in a first electrolytic bath consisting of an aqueous solution, free of boron carbide particles, comprising:

at least one nickel (II) salt;

at least one phosphorus compound selected from: phosphoric acid, phosphorous acid, hypophosphorous acid or salts thereof.

13. Process according to any one of the preceding claims, wherein the electrolytic bath is contained into an apparatus comprising an electrolytic tank and a system for recycling the electrolytic bath, the recycling system comprising at least one intake line of the bath provided with an intake head inserted into the tank, at least one supply line of the bath into the tank which leads into a distribution chamber delimited by an external wall of the tank and by an internal wall provided with passing holes through which the bath flows into the tank.

14. Process according to anyone of the preceding claims, wherein the heat treatment is carried out at a temperature comprised from 250°C to 400°C, preferably from 300°C to 375°C.

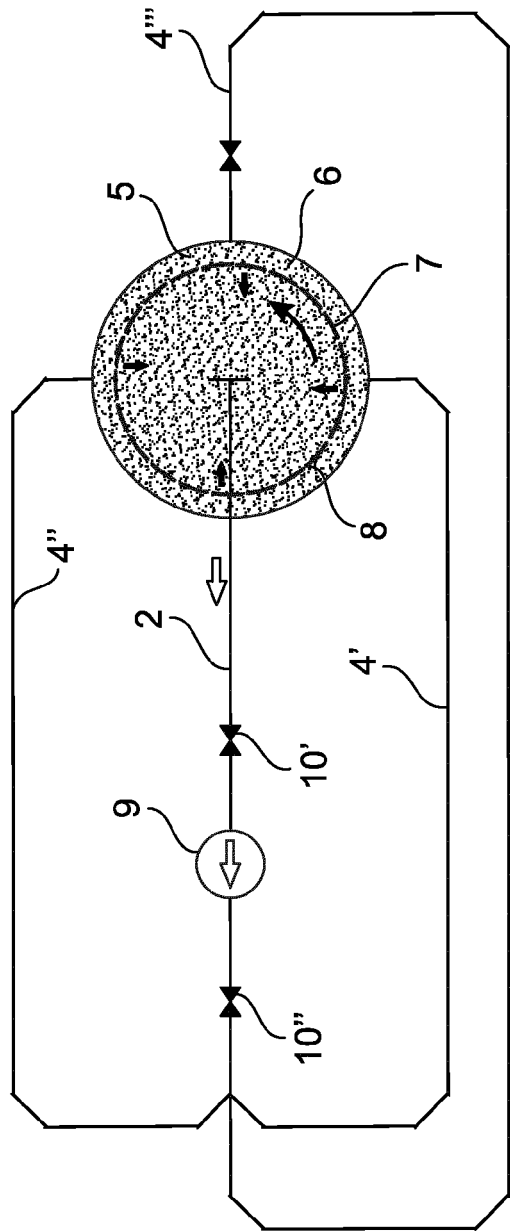


Fig. 1

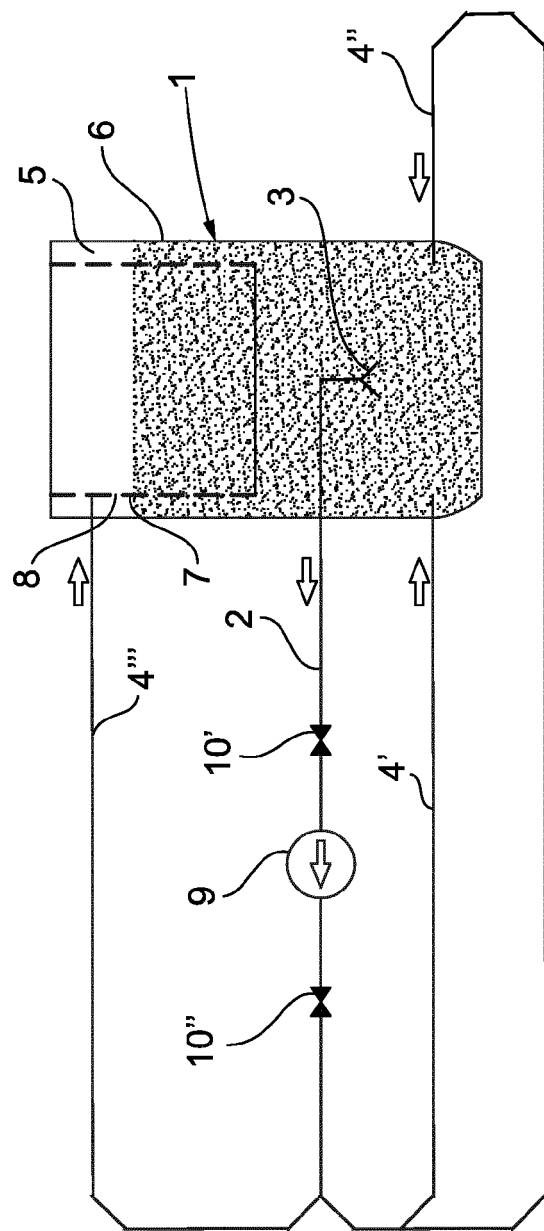


Fig. 2

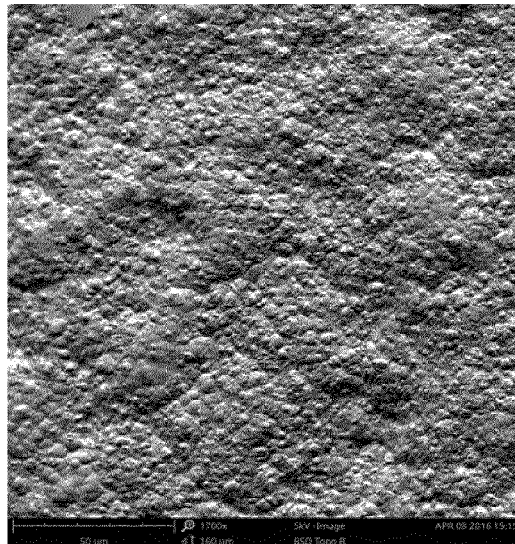


Fig. 3

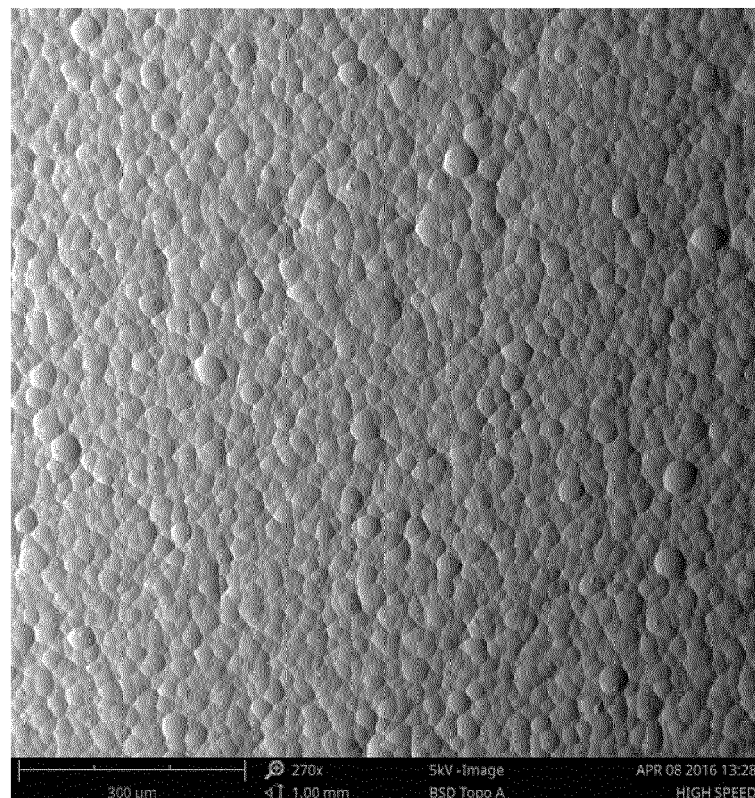


Fig. 4



EUROPEAN SEARCH REPORT

Application Number
EP 16 17 1777

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Place of search The Hague		Date of completion of the search 29 September 2016	Examiner Telias, Gabriela
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EPO FORM 1503 03.82 (P04C01)



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