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(54) **ZINC-NICKEL ELECTROLYTE AND
METHOD FOR DEPOSITING A
ZINC-NICKEL ALLOY THEREFROM**

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(57) **ABSTRACT**

A method for depositing a zinc-nickel alloy from a zinc-nickel electrolyte to which an additive has been added in order to broaden the usable current density range. An electrolyte suitable for this method is also presented. The additive is an aromatic or aliphatic carboxylic acid, salt, or derivative. The additive provides for the use of ammonium-free electrolytes.

ZINC-NICKEL ELECTROLYTE AND METHOD FOR DEPOSITING A ZINC-NICKEL ALLOY THEREFROM

BACKGROUND OF THE INVENTION

[0001] The invention concerns a method for depositing a zinc-nickel alloy from an electrolyte.

[0002] Metal substrates are electroplated in order to improve corrosion protection. Because zinc-nickel alloys have better corrosion protection than pure zinc coatings there is strong interest in these alloys in many fields.

[0003] The zinc-nickel alloys typically contain nickel from about 10% to about 16%, since this amount affords the best possible corrosion protection. To deposit the zinc-nickel alloys, essentially two different electrolytes are used in the prior art. One consists of the alkaline zinc-nickel alloy baths and the other consists of the slightly acidic baths containing ammonium and chlorides. However, these baths have considerable disadvantages.

[0004] The alkaline baths have the disadvantage that the deposition rates are low, and there are problems in depositing coatings directly from these baths onto cast iron or hardened steel. Another disadvantage is that these electrolytes contain high concentrations of highly environmentally stressful complex-forming substances, which result the problematic and expensive purification and disposal of highly contaminated wastewater.

[0005] In particular, the ammonium-containing slightly acid electrolytes have the considerable disadvantage that the ammonium ions also severely contaminate wastewater. Because of this, there can be problems in removing metals from the wastewater. Because ammonium concentration in wastewater is often subject to strict government regulations, expensive wastewater treatments have are required. Strong ammonium-containing baths, however, are particularly useful for the processing of rack goods and mass-produced articles and are needed to achieve the deposition of a zinc-nickel alloy on profiled workpieces.

[0006] There have been attempts in the prior art to develop ammonium-free baths for deposition of zinc-nickel alloys. However, these are not comparable to the ammonium-containing baths in their efficiencies. For instance, it is possible to deposit zinc-nickel alloys that contain 10-16% nickel from such baths. The advantage of using such baths lies in the fact that it is free of ammonium and in addition may not require any complexing substances, as is the case with the alkali zinc-nickel baths. Such a bath therefore has the obvious advantage that there is no buildup of substances that contaminate the wastewaters and that have to be removed from them in an expensive and costly way.

[0007] However, these baths have the disadvantage that at high current densities the deposited layer is very brittle and has high internal stress, tending to flake off. In the range of low current densities the layers disadvantageously have a nickel content that is too high, which causes the layer to be black. In addition, the fraction of nickel in the layer varies considerably, so that the layer can contain up to 50% nickel. Thus it is not possible to deposit a uniform layer over a wide range of current densities. These limitations are evident through standard test methods, such as the Hull cell test. Overall there is the disadvantage that the usable current

density range for the ammonium-free baths is extremely low and, because of this, unacceptable restrictions arise in electroplating, in that only geometrically very simple workpieces can be electroplated in this way and certain electroplating techniques such as barrel electroplating cannot be used.

SUMMARY OF THE INVENTION

[0008] Among the objects of the present invention, therefore, is the provision of a process for deposition of a zinc-nickel alloy onto a variety of workpieces at a broader current density range than is available.

[0009] Briefly, therefore, the present invention is directed to a process for deposition of a zinc-nickel alloy onto a substrate in which an electrolyte, which is characterized by a first current density range within which a deposited coating of the alloy is substantially continuous, glossy, and provides corrosion protection, is prepared comprising a source of Zn ions and a source of Ni ions. A current density broadening agent is incorporated into the electrolyte to modify the electrolyte such that it is characterized by a second current density range within which a deposited coating of said alloy is substantially continuous, glossy, and provides corrosion protection and which is broader than the first current density range. The current density broadening agent is selected from the group consisting of an aromatic carboxylic acid, an aromatic carboxylic acid salt, an aromatic carboxylic acid derivative, an aliphatic carboxylic acid, an aliphatic carboxylic acid salt, an aliphatic carboxylic acid derivative, and combinations thereof. An external source of electrons is supplied to the electrolyte to electrolytically deposit the zinc-nickel alloy onto the substrate.

[0010] The present invention is further directed to a process for deposition of a zinc-nickel alloy onto a substrate in which an electrolyte is prepared. The electrolyte comprises a source of Zn ions, a source of Ni ions, and an additive selected from the group consisting of an aromatic carboxylic acid, an aromatic carboxylic acid salt, an aromatic carboxylic acid derivative, an aminocarboxylic acid, an aminocarboxylic acid salt, an aminocarboxylic acid derivative, an hydroxy(poly)carboxylic acid, an hydroxy(poly)carboxylic acid salt, an hydroxy(poly)carboxylic acid derivative, and combinations thereof. An external source of electrons is supplied to the electrolyte to electrolytically deposit the zinc-nickel alloy onto the substrate.

[0011] The present invention is still further directed to an electrolyte for electrolytic deposition of a Zn-Ni alloy which comprises a source of Zn ions, a source of Ni ions, and a current density broadening agent selected from the group consisting of an aromatic carboxylic acid, an aromatic carboxylic acid salt, an aromatic carboxylic acid derivative, an aliphatic carboxylic acid, an aliphatic carboxylic acid salt, an aliphatic carboxylic acid derivative, and combinations thereof.

[0012] Other objects and features will be in part apparent and in part pointed out hereinafter.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] The invention is based on the surprising effect that the addition to a bath of a current density broadening agent

results in the ability to deposit zinc-nickel alloys from a zinc-nickel electrolyte over a broad current range. The current density broadening agent comprises an aliphatic carboxylic acid, its salts and/or its derivatives or at least one additional aromatic and/or aliphatic carboxylic acid, its salts and/or its derivatives. Here the aromatic carboxylic acids or their derivatives are added to the electrolyte preferably as sodium and/or potassium salt.

[0014] The known disadvantages from the prior art are advantageously circumvented by the method in accordance with the invention. For example, it is possible to operate over a broad current density range without the disadvantages connected with the degradation of the properties of the deposited layer that are known from the prior art arising. Profiled workpieces may be electroplated outside of the formerly narrow usable current density range. In this way it is possible even to coat geometrically more complexly shaped workpieces with a uniform glossy zinc-nickel alloy.

[0015] The aromatic and/or aliphatic carboxylic acid, its salt and/or its derivative in this case is preferably chosen so that a shift of the usable current density range into higher and/or lower ranges is possible in a targeted fashion. Thus, in accordance with the invention there is the possibility, in each case according to the choice of the relevant aromatic and/or aliphatic carboxylic acid, its salts and/or its derivatives, of shifting the usable current density range so that the deposition of an alloy coating that satisfies requirements is possible both in higher and also in lower current density ranges.

[0016] The standard bath for deposition of zinc-nickel alloys typically comprises divalent zinc, divalent nickel, chloride, boric acid, surfactants, and brighteners. The surfactants may be anionic or nonionic surface-active substances, similar to those that are used in a conventional acid zinc electrolyte. Ethoxylated alcohols or nonylphenols are examples of useful surfactants. Benzal acetone is useful added as a brightener additive. Aldehydes and ketones can also be added as brighteners, similar to those that are used in a conventional acid zinc electrolyte.

[0017] Some baths may contain a carboxylic acid component, such as for example sodium acetate as a pH buffer. The process and electrolyte compositions according to the present invention comprise at least one additional aromatic and/or aliphatic carboxylic acid in the case that a carboxylic acid is otherwise present in the bath a purpose which is different than the objects of the present invention. The alloys deposited in accordance with the invention preferably have a nickel content of about 10% to about 16%. However, it is understood alloys of greater or lesser nickel content may be deposited if desired.

[0018] The invention advantageously allows one to operate with an ammonium-free electrolyte so that the above disadvantages of wastewater contamination and related costs are avoided. The advantages of the method in accordance with the invention therefore show up in particular in the deposition of a zinc-nickel alloy from a preferably ammonium-free bath which comprises a slightly acidic and chloride-containing zinc-nickel electrolyte.

[0019] In one embodiment of the method in accordance with the invention, nicotinic acid, its salts and/or derivatives are added to the electrolyte as an aromatic carboxylic acid.

It has been discovered that the addition of nicotinic acid, its salts, or derivatives improves the layer properties of the deposited coating, with some properties being considerably improved in the ranges of greater current densities. For example, the addition of nicotinic acid to baths operated in the range of greater current densities surprisingly led to reduction or even complete prevention of the cracking and flaking of the layer that occurs without this addition. Also, scorching phenomena are diminished.

[0020] These improvements are noted in experiments with a slightly acidic, ammonium-free, chloride-containing baths to deposit zinc-nickel alloys. Preferably, the nicotinic acid or its salt and/or its derivatives are added to the electrolyte in an amount of at least about 0.25 g/L. More preferably, the nicotinic acid or its salt and/or its derivatives are added to the electrolyte in an amount of from about 0.25 g/L to about 1 g/L. Still more preferably, the amount is about 0.75 g/L.

[0021] In accordance with another embodiment of the invention, salicylic acid, its salts and/or its derivatives are added to the electrolyte as aromatic carboxylic acid. Acetylsalicylic acid, for example, can be used as the salicylic acid derivative. Surprisingly, it turned out that the addition of salicylic acid leads to an improved deposition in the range of lesser current density ranges. For example, the disadvantageous effects and darkening of the alloy layer that otherwise arise are eliminated. The zinc-nickel alloy deposited in this way is, furthermore, detectably more uniform over the entire current density range. Thus, variations, for example, in the alloy composition essentially do not occur, which has an advantageous effect on the quality of the deposited coating.

[0022] Preferably, the salicylic acid, its salts and/or its derivatives are added to the electrolyte in an amount from about 0.5 to about 1.5 g/L. It proved to be particularly advantageous to add about 1 g/L salicylic acid, its salts and/or its derivatives to the electrolyte.

[0023] According to a particularly preferred embodiment of the method in accordance with the invention, both nicotinic acid and salicylic acid, their salts and/or their derivatives are added to the zinc-nickel electrolyte. The addition of both these aromatic carboxylic acids or their salts and/or their derivatives results in it being possible to operate over a particularly broad current density range, since the layer properties are improved both in the range of lesser and greater current densities by the addition of both substances. The overall effect due to the addition of both substances is better than the relevant separate effects. Here the nicotinic acid and the salicylic acid are preferably added in an amount of about 0.75 g/L and 1 g/L, respectively. The zinc-nickel electrolyte in this case is preferably a slightly acid, ammonium-free, chloride containing electrolyte.

[0024] According to another embodiment, at least one aliphatic carboxylic acid, its salts and/or its derivatives are added to the electrolyte in addition to or instead of the salts of carboxylic acid that are typically already used in practice, for example sodium acetate. It surprisingly turned out that the use of other different aliphatic carboxylic acids, their salts and/or their derivatives leads to particularly intensive avoidance of the formation of basic nickel compounds and to improved pH correction and thus to a considerable improvement of the deposition of a layer in ranges of lesser

current densities. The zinc-nickel alloys thus deposited are glossy and detectably more uniform over the entire current density range.

[0025] Preferably aminocarboxylic acids, their salts and/or derivatives and/or hydroxy(poly)carboxylic acids, their salts and/or derivatives are added to the electrolyte as aliphatic carboxylic acids. Aminoacetic acid is a preferred aminocarboxylic acid, and 2-hydroxypropanoic acid is a preferred hydroxy(poly)carboxylic acid. The addition of aminoacetic acid or 2-hydroxypropanoic acid, their salts and derivatives considerably improves the layer properties of the deposited coatings, particularly for rack goods. This effect can be enhanced, particularly in baths for electroplating rack goods, by agitation of the baths, for example by moderate flooding.

[0026] Typically electrolyte temperatures over 38° C. were employed up to now, and electrolyte temperatures of less than 35° C. were avoided, even during interruptions in operation, because of the salt concentration. In contrast, it has also been discovered that the process for the deposition of zinc-nickel alloys according to the present invention may advantageously be performed at electrolyte temperatures of less than about 35° C. Surprisingly, the reduction of temperature leads to the deposited zinc-nickel coating adhering better to the base material and there being a lower tendency for the layer to flake off. Operation at these reduced temperatures, process costs are lower since less energy is used. Moreover, because the deposited coating shows less tendency to flake off in the range of greater current densities, the deposition of zinc-nickel coatings can be performed over a broader range of current density. It is to be noted that the process in accordance with the invention may be performed temperatures higher than 35° C., as may be required by specific processes, without disadvantages resulting from this. For example, in barrel plating very good results can be achieved at temperatures of about 40° C.

[0027] The method in accordance with the invention and the electrolyte in accordance with the invention are further illustrated by means of examples.

EXAMPLE 1

[0028] An ammonium-free, slightly acidic, chloride-containing zinc-nickel electrolyte is prepared according to the following composition:

Standard Bath	
Zinc chloride	115 g/L
Nickel chloride (6 H ₂ O)	143 g/L
Potassium chloride	245 g/L
Boric acid	20 g/L
Sodium acetate (3 H ₂ O)	65 g/L
Surfactants	6 g/L
Sodium saccharate	1.5 g/L
Benzylideneacetone (dissolved in ethyl diglycol)	75 mg/L

[0029] The pH is between 5.3 and 5.7.

[0030] The surfactants can be anionic or nonionic surface-active substances, similar to those that are used in a conventional acid zinc electrolyte. Ethoxylated alcohols or nonylphenols are usually used. Benzal acetone is added as a

brightener additive. Aldehydes and ketones can also be added as brighteners, similar to those that are used in a conventional acid zinc electrolyte. For example, besides benzylidene acetone it is also possible to use sodium benzoate, etc. Zinc-nickel alloys that have a nickel content from about 12% to about 16% can be deposited onto a workpiece with this bath.

[0031] Such a bath, however, has the disadvantage that one can operate only in a very limited current density range. These limitations are clearly detectable in a Hull cell test (2 A, 20 min). The Hull cell test systematically covers all of the current density ranges that arise in the electroplating of highly profiled workpieces. The particular shape of the test cell allows evaluation of the galvanic coating even in a relatively large current density range. In each case according to the spacing of the cathode plate from the anode a specific current density is established at the cathode plate, so that even the very first experiment gives insight into the mode of operation of the electrolyte in the various current density ranges. Thus it is possible to estimate by means of a Hull cell test the current density ranges over which an electrolyte can be used without any problem. The electrolytes that are composed in accordance with the embodiment examples were tested with a slightly modified Hull cell in order to estimate the current density range over which the electrolytes operate flawlessly. The Hull cell that was used was set up for a volume of 500 mL. The cathode length was 200 mm.

[0032] The composition of the electrolytes and the test results are summarized in Table 1 in order to provide a representation of the extremely positive effects of this invention.

[0033] The standard bath described above, to which various aromatic carboxylic acids, in this case nicotinic acid and salicylic acid, were added, was used in order to demonstrate the positive effects of the invention. Here it is pointed out that the experimentally determined usable mm ranges of the deposited layer are subject to certain experimental variations, so that they are intended to give only an idea, but are not to be considered as absolute values in a sense limiting the invention. In addition, it should be noted here that the given current density ranges, which can be derived from the results, do not necessarily correspond with the actual current densities that were present, since polarizations and deviations in the conductivity or throwing power of the electrolyte play a role, but do not enter into the calculation. This is why the current density ranges that derive from the usable or unusable mm ranges are intended to give only a rough estimate of the current density ranges in which the electrolyte works flawlessly. However, these values are not to be understood as absolute values in a sense limiting the invention.

TABLE 1

Electrolyte Additive to standard bath of Example 1	Scorching/Bubble Formation		Black LCD Range	
	mm from HCD End	Estimated Current Density (A/dm ²)	mm from LCD End	Estimated Current Density (A/dm ²)
None	32	4.6	90	1.5
1 g/L	42	4.2	5	0.3

TABLE 1-continued

Electrolyte Additive to standard bath of Example 1	Scorching/Bubble Formation		Black LCD Range	
	mm from HCD End	Estimated Current Density (A/dm ²)	mm from LCD End	Estimated Current Density (A/dm ²)
Salicylic acid 0.25 g/L	6	6	51	1.1
Nicotinic acid 0.75 g/L	3	>6	50	1.1
Nicotinic acid 1 g/L	11	5.6	2	0.2
Salicylic acid and 0.25 g/L Nicotinic acid				
1 g/L	3	>6	0	<0.2
Salicylic acid and 1 g/L Nicotinic acid				

[0034] As the results summarized in Table 1 show, with the standard bath over 3 cm of the deposited layer in the high current density range is not usable (HCD=high current density). The layers deposited with the above described standard bath have, in the high density ranges, significant internal stresses, are very brittle, and exhibit cracks after a little time. Also, the layer flakes off after a little time and is thus unusable. In the low current density ranges (LCD=low current density) the deposited alloy has a completely different appearance than the layer deposited over the other current density ranges. Instead of being silvery white, it is dark gray to black. For this reason up to 9 cm is unusable because of these effects, since the electrolyte does not operate flawlessly in this current density range. In addition, tests showed that the alloy coating has a completely different composition and contains up to 50% nickel instead of 10-16%. The standard electrolyte operates only in a very limited current density range. Only narrow current density ranges from about 1.5 to 4.6 A/dm² are seen as usable. Because of these restrictions in the usable current density ranges, only workpieces with simple geometry can be coated, which greatly restricts the application range. Presumably, barrel plating is also not possible because of these restrictions.

[0035] As the data in Table 1 shows, the addition of 1 g/L salicylic acid in accordance with the invention leads to considerable improvement of deposition in low current density ranges. Instead of up to 9 cm, only up to 0.5 cm is not usable, which leads to a distinct improvement and considerably broadens the usable LCD range.

[0036] Furthermore, the addition of 0.25 g/L nicotinic acid already noticeably improves the deposition in the current density ranges. For instance, the layer has a lesser tendency to flake off and to form cracks. Through the addition of 0.75 g/L nicotinic acid this effect is even more enhanced, as the table shows. Through the addition of nicotinic acid the usable current density range in the HCD range becomes considerably broader.

[0037] The addition of both nicotinic acid and salicylic acid results in it being possible to operate over a particularly broad current density range, since the layer properties of the deposited layer are considerably improved both in the low and in the high current density ranges through the addition of both substances. The overall effect due to the addition of both substances is better than the relevant separate effects. For example, zinc-nickel layers with good quality properties can be deposited in the current density ranges from under 0.2 up to over 6 A/dm² due to the addition of 1 g/L nicotinic acid and 1 g/L salicylic acid. In this bath, compared to the standard bath, the electrolyte operates flawlessly over very broad current density ranges. For this reason even profiled workpieces can be coated by the method in accordance with the invention and the deposited layers are overall qualitatively higher in value because of the detectably higher uniformity. For this reason the electroplating possibilities are also broadened by the method in accordance with the invention or the electrolyte in accordance with the invention, as the case may be, so that even barrel plating becomes possible.

[0038] It was also possible to illustrate by the Hull cell test how the addition in accordance with the invention of nicotinic acid and salicylic acid improve the usable current density range. Crack formation and flaking of the layer is greatly reduced in high current density ranges, and the black discoloration of the layer in the low current density range is also reduced. The deposited layer is clearly more uniform over the entire current density range, as was shown by XRF analysis.

EXAMPLE 2

[0039] Through the variable addition of at least one aliphatic carboxylic acid, its salt and/or derivative the said zinc-nickel electrolytes can be further developed in an advantageous way. The zinc-nickel electrolytes listed below as example Baths A and B proved to be particularly advantageous further developments of a weakly acid zinc alloy electrolyte for the rack plating technology because of the very uniform alloy composition over the entire current density range.

Bath A	
Zinc chloride	115 g/L
Nickel chloride (6 H ₂ O)	143 g/L
Potassium chloride	245 g/L
Boric acid	25 g/L
Aminoacetic acid	45 g/L
Surfactants	6 g/L
Sodium saccharate	2.5 g/L
Brighteners	2 g/L
pH	5.3-5.7
Bath B	
Zinc chloride	115 g/L
Nickel chloride (6 H ₂ O)	143 g/L
Potassium chloride	245 g/L
Boric acid	25 g/L
2-Hydroxypropanoic acid	54 g/L
Surfactants	6 g/L
Sodium saccharate	2.5 g/L
Brighteners	2 g/L
pH	5.3-5.7

[0040] In accordance with one variation of embodiment the temperature of the electrolyte in deposition is under 35° C., since in this way the adhesion properties of the layer are improved. This leads to the layers not flaking off even after some time, which increases the quality of the zinc-nickel alloy layers deposited from the electrolyte in accordance with the invention by the method in accordance with the invention.

[0041] When introducing elements of the present invention or the preferred embodiment(s) thereof, the articles “a”, “an”, “the” and “said” are intended to mean that there are one or more of the elements. The terms “comprising”, “including” and “having” are intended to be inclusive and mean that there may be additional elements other than the listed elements.

[0042] In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

[0043] As various changes could be made in the above methods and compositions without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for deposition of a zinc-nickel alloy onto a substrate comprising:

preparing an electrolyte comprising a source of Zn ions and a source of Ni ions, which electrolyte is characterized by a first current density range within which a deposited coating of said alloy is substantially continuous, glossy, and provides corrosion protection;

incorporating a current density broadening agent into the electrolyte to modify the electrolyte such that it is characterized by a second current density range within which a deposited coating of said alloy is substantially continuous, glossy, and provides corrosion protection; and

supplying an external source of electrons to the electrolyte to electrolytically deposit the zinc-nickel alloy onto the substrate;

wherein said second current density range is broader than said first current density range;

wherein the current density broadening agent is selected from the group consisting of an aromatic carboxylic acid, an aromatic carboxylic acid salt, an aromatic carboxylic acid derivative, an aliphatic carboxylic acid, an aliphatic carboxylic acid salt, an aliphatic carboxylic acid derivative, and combinations thereof.

2. The process according to claim 1 wherein the electrolyte is an ammonium-free electrolyte which is slightly acidic.

3. The process according to claim 1 wherein the additive is selected from the group consisting of nicotinic acid, nicotinic acid salts, and nicotinic acid derivatives.

4. The process according to claim 3 wherein the additive is present in the electrolyte at a concentration ranging from about 0.25 to about 1 g/L.

5. The process according to claim 4 wherein the additive is present in the electrolyte at a concentration of about 0.75 g/L.

6. The process according to claim 1 wherein the additive is selected from the group consisting of salicylic acid, salicylic acid salts, and salicylic acid derivatives.

7. The process according to claim 6 wherein the additive is present in the electrolyte at a concentration ranging from about 0.5 to about 1.5 g/L.

8. The process according to claim 7 wherein the additive is present in the electrolyte at a concentration of about 1 g/L.

9. The process according to claim 1 wherein the electrolyte comprises a first additive selected from the group consisting of nicotinic acid, nicotinic acid salts, and nicotinic acid derivatives and a second additive selected from the group consisting of salicylic acid, salicylic acid salts, and salicylic acid derivatives.

10. The process according to claim 1 wherein the additive is selected from the group consisting of aminocarboxylic acids, aminocarboxylic acid salts, and aminocarboxylic acid derivatives.

11. The process according to claim 10 wherein the additive is selected from the group consisting of aminoacetic acid, an aminoacetic acid salt, and an aminoacetic acid derivative.

12. The process according to claim 1 wherein the additive is selected from the group consisting of hydroxy(poly)carboxylic acids, hydroxy(poly)carboxylic acid salts, and hydroxy(poly)carboxylic acid derivatives.

13. The process according to claim 12 wherein the additive is selected from the group consisting of 2-hydroxypropanoic acid, a 2-hydroxypropanoic acid salt, and a 2-hydroxypropanoic acid derivative.

14. The process according to claim 1 wherein the zinc-nickel alloy is deposited on a workpiece while the electrolyte is at a temperature which is no greater than 35° C.

15. A process for deposition of a zinc-nickel alloy onto a substrate comprising:

preparing an electrolyte comprising a source of Zn ions, a source of Ni ions, and an additive selected from the group consisting of an aromatic carboxylic acid, an aromatic carboxylic acid salt, an aromatic carboxylic acid derivative, an aminocarboxylic acid, an aminocarboxylic acid salt, an aminocarboxylic acid derivative, an hydroxy(poly)carboxylic acid, an hydroxy(poly)carboxylic acid salt, an hydroxy(poly)carboxylic acid derivative, and combinations thereof; and

supplying an external source of electrons to the electrolyte to electrolytically deposit the zinc-nickel alloy onto the substrate.

16. The process according to claim 15 wherein the electrolyte is an ammonium-free electrolyte which is slightly acidic.

17. The process according to claim 15 wherein the additive is selected from the group consisting of nicotinic acid, nicotinic acid salts, and nicotinic acid derivatives.

18. The process according to claim 17 wherein the additive is present in the electrolyte at a concentration ranging from about 0.25 to about 1 g/L.

19. The process according to claim 18 wherein the additive is present in the electrolyte at a concentration of about 0.75 g/L.

20. The process according to claim 15 wherein the additive is selected from the group consisting of salicylic acid, salicylic acid salts, and salicylic acid derivatives.

21. The process according to claim 20 wherein the additive is present in the electrolyte at a concentration ranging from about 0.5 to about 1.5 g/L.

22. The process according to claim 21 wherein the additive is present in the electrolyte at a concentration of about 1 g/L.

23. The process according to claim 15 wherein the electrolyte comprises a first additive selected from the group consisting of nicotinic acid, nicotinic acid salts, and nicotinic acid derivatives and a second additive selected from the group consisting of salicylic acid, salicylic acid salts, and salicylic acid derivatives.

24. The process according to claim 15 wherein the additive is selected from the group consisting of aminocarboxylic acids, aminocarboxylic acid salts, and aminocarboxylic acid derivatives.

25. The process according to claim 24 wherein the additive is selected from the group consisting of aminoacetic acid, an aminoacetic acid salt, and an aminoacetic acid derivative.

26. The process according to claim 15 wherein the additive is selected from the group consisting of hydroxy(poly)carboxylic acids, hydroxy(poly)carboxylic acid salts, and hydroxy(poly)carboxylic acid derivatives.

27. The process according to claim 26 wherein the additive is selected from the group consisting of 2-hydroxypropanoic acid, a 2-hydroxypropanoic acid salt, and a 2-hydroxypropanoic acid derivative.

28. The process according to claim 15 wherein the zinc-nickel alloy is deposited on a workpiece while the electrolyte is at a temperature which is no greater than 35° C.

29. An electrolyte for electrolytic deposition of a Zn-Ni alloy, the electrolyte comprising:

a source of Zn ions;

a source of Ni ions;

a current density broadening agent selected from the group consisting of an aromatic carboxylic acid, an aromatic carboxylic acid salt, an aromatic carboxylic acid derivative, an aliphatic carboxylic acid, an aliphatic carboxylic acid salt, an aliphatic carboxylic acid derivative, and combinations thereof.

30. The electrolyte according to claim 29 wherein the electrolyte is an ammonium-free electrolyte which is slightly acidic.

31. The electrolyte according to claim 29 wherein the additive is selected from the group consisting of nicotinic acid, nicotinic acid salts, and nicotinic acid derivatives.

32. The electrolyte according to claim 31 wherein the additive is present in the electrolyte at a concentration ranging from about 0.25 to about 1 g/L.

33. The electrolyte according to claim 32 wherein the additive is present in the electrolyte at a concentration of about 0.75 g/L.

34. The electrolyte according to claim 29 wherein the additive is selected from the group consisting of salicylic acid, salicylic acid salts, and salicylic acid derivatives.

35. The electrolyte according to claim 34 wherein the additive is present in the electrolyte at a concentration ranging from about 0.5 to about 1.5 g/L.

36. The electrolyte according to claim 35 wherein the additive is present in the electrolyte at a concentration of about 1 g/L.

37. The electrolyte according to claim 29 wherein the electrolyte comprises a first additive selected from the group consisting of nicotinic acid, nicotinic acid salts, and nicotinic acid derivatives and a second additive selected from the group consisting of salicylic acid, salicylic acid salts, and salicylic acid derivatives.

38. The electrolyte according to claim 37 wherein the first additive is present in the electrolyte at a concentration ranging from about 0.25 to about 1 g/L and the second additive is present in the electrolyte at a concentration ranging from about 0.5 to about 1.5 g/L.

39. The electrolyte according to claim 38 wherein the first additive is present in the electrolyte at a concentration of about 0.75 g/L and the second additive is present in the electrolyte at a concentration of about 1 g/L.

40. The electrolyte according to claim 29 wherein the additive is selected from the group consisting of aminocarboxylic acids, aminocarboxylic acid salts, and aminocarboxylic acid derivatives.

41. The electrolyte according to claim 40 wherein the additive is selected from the group consisting of aminoacetic acid, an aminoacetic acid salt, and an aminoacetic acid derivative.

42. The electrolyte according to claim 29 wherein the additive is selected from the group consisting of hydroxy(poly)carboxylic acids, hydroxy(poly)carboxylic acid salts, and hydroxy(poly)carboxylic acid derivatives.

43. The electrolyte according to claim 42 wherein the additive is selected from the group consisting of 2-hydroxypropanoic acid, a 2-hydroxypropanoic acid salt, and a 2-hydroxypropanoic acid derivative.

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