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(54) **NICKEL-CHROMIUM NANOLAMINATE
COATING HAVING HIGH HARDNESS**

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ABSTRACT

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The present disclosure describes electrodeposited nanolaminate materials having layers comprised of nickel and/or chromium with high hardness. The uniform appearance, chemical resistance, and high hardness of the nanolaminate NiCr materials described herein render them useful for a variety of purposes including wear (abrasion) resistant barrier coatings for use both in decorative as well as demanding physical, structural and chemical environments.

NICKEL-CHROMIUM NANOLAMINATE COATING HAVING HIGH HARDNESS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional application 61/802,112, filed Mar. 15, 2013, which application is incorporated herein by reference in its entirety.

BACKGROUND

[0002] Electrodeposition is recognized as a low-cost method for forming a dense coating on a variety of conductive materials, including metals, alloys, conductive polymers and the like. Electrodeposition has also been successfully used to deposit nanolaminated coatings on non-conductive material such as non-conductive polymers by incorporating sufficient materials into the non-conductive polymer to render it sufficiently conductive or by treating the surface to render it conductive, for example by electroless deposition of nickel, copper, silver, cadmium etc. a variety of engineering applications.

[0003] Electrodeposition has also been demonstrated as a viable means for producing laminated and nanolaminated coatings, materials and objects, in which the individual laminate layers may vary in the composition of the metal, ceramic, organic-metal composition, and/or microstructure features. Laminated coatings and materials, and in particular nanolaminated metals, are of interest for a variety of purposes, including structural, thermal, and corrosion resistance applications because of their unique toughness, fatigue resistance, thermal stability, wear (abrasion resistance and chemical properties).

SUMMARY

[0004] The present disclosure is directed to the production NiCr nanolaminated materials having a high hardness. The materials have a variety of uses including, but not limited to, the preparation of coatings that protect an underlying substrate, and which may also increase its strength. In one embodiment hard NiCr coatings and materials are wear/abrasion resistant and find use as wear resistant coatings in tribological applications. In another embodiment the hard NiCr coatings prevent damage to the underlying substrates. Where the NiCr materials are applied as a coating that is more noble than the underlying material upon which it is placed, it may function as a corrosion resistant barrier coating.

DESCRIPTION

1.1 Overview

[0005] The present disclosure is directed to the method of producing laminate materials and coatings comprising layers each comprising nickel or nickel and chromium. The materials, which are prepared by electrodeposition, have a Vickers hardness value up to about 750 without the addition of other elements or heat treatments.

[0006] In one embodiment the disclosure is directed to an electrodeposition processes for forming a multilayered nickel and chromium containing coating on a substrate or mandrel comprising:

[0007] (a) providing one or more electrolyte solutions comprising a nickel salt and/or a chromium salt;

[0008] (b) providing a conductive substrate or mandrel for electrodeposition;

[0009] (c) contacting at least a portion of the substrate or mandrel with one of said one or more electrolyte solutions; and

[0010] (d) passing a first electric current through the substrate or mandrel, to deposit a first layer comprising either nickel or an alloy thereof on the surface; and passing a second electric current through the substrate, to deposit second layer comprising a nickel-chromium alloy on the surface;

[0011] (e) repeating step (d) two or more times thereby producing a multilayered coating having first layers of nickel or an alloy thereof and second layers of a nickel-chromium alloy on at least a portion of the surface of the substrate or mandrel.

[0012] The method may further comprise the step of separating said substrate or mandrel from the coating, where the coating forms an object comprised of the laminate material.

[0013] The high hardness coating produced by the process typically has alternating first and second layers. The first layers are each from about 25 nm to about 75 nm thick, and comprises from about 92% to about 99% nickel, with the balance typically comprising chromium. The second layers are each from about 125 nm to about 175 nm thick, and typically comprise from about 10% to about 21% chromium by weight with the balance typically comprising nickel.

1.2 Definitions

[0014] “Laminate” or “laminated” as used herein refers to materials that comprise a series of layers, including nanolaminated materials.

[0015] “Nanolaminate” or “nanolaminated” as used herein refers to materials that comprise a series of layers less than 1 micron.

[0016] All compositions given as percentages are given as percent by weight unless stated otherwise.

1.3 Nanolaminate NiCr Coatings

1.3.1 Nanolaminate NiCr Materials and Coatings and Methods of Their Preparing

[0017] Electrodeposition has been demonstrated as a viable means for producing nanolaminated metal materials and coatings in which the individual laminate layers may vary in the composition or structure of the metal components. In addition, electrodeposition permits the inclusion of other components, such as ceramic particles and organic-metal components.

[0018] Multi-laminate materials having layers with different compositions can be realized by moving a mandrel or substrate from one bath to another and electrodepositing a layer of the final material. Each bath represents a different combination of parameters, which may be held constant or varied in a systematic manner. Accordingly, laminated materials may be prepared by alternately electroplating a substrate or mandrel in two or more electrolyte baths of differing electrolyte composition and/or under differing plating conditions (e.g., current density and mass transfer control). Alternatively, laminated materials may be prepared using a single electrolyte bath by varying the electrodeposition parameters such as the voltage applied, the current density, mixing rate, substrate or mandrel movement (e.g., rotation) rate, and/or

temperature. By varying those and/or other parameters, laminated materials having layers with differing metal content can be produced in a single bath.

[0019] The present disclosure provides a process for forming a multilayered nickel and chromium containing coating on a substrate or mandrel by electrodeposition comprising:

[0020] (a) providing one or more electrolyte solutions (baths) comprising a nickel salt and/or a chromium salt;

[0021] (b) providing a conductive substrate or mandrel suitable for electrodeposition;

[0022] (c) contacting at least a portion of the substrate or mandrel with one of said one or more electrolyte solutions;

[0023] (d) passing a first electric current through the substrate or mandrel, to deposit a first layer comprising either nickel or an alloy thereof on the substrate or mandrel; and passing a second electric current through the substrate, to deposit second layer comprising a nickel-chromium alloy on the surface; and

[0024] (e) repeating step (d) two or more times thereby producing a multilayered coating having first layers of nickel or an alloy thereof and second layers of a nickel-chromium alloy on at least a portion of the surface of the substrate or mandrel.

[0025] Where separate baths are employed to deposit the first and second layers step (d) includes contacting at least a portion of the substrate or mandrel that having the first layer deposited on it with a second of said one or more electrolyte solutions (baths) prior to passing a second electric current through the substrate, to deposit second layer comprising a nickel-chromium alloy on the surface.

[0026] Where the electroplated material is desired as an object that is "electroformed" or as a material separated from the substrate or mandrel, the method may further comprise a step of separating the substrate or mandrel from the electroplated coating. Where a step of separating the electroplated material from the substrate or mandrel is to be employed, the use of electrodes (mandrel) that do not form tight bonds with the coating are desirable, such as titanium electrode (mandrel).

[0027] In one embodiment, where a single bath is used to deposit the first and second layers, providing one or more electrolyte solutions comprises providing a single electrolyte solution comprising a nickel salt and a chromium salt, and passing an electric current through said substrate or mandrel comprises alternately pulsing said electric current for predetermined durations between said first electrical current density and said second electrical current density; where the first electrical current density is effective to electrodeposit a first composition comprising either nickel or an alloy of nickel and chromium; and the second electrical current density is effective to electrodeposit a second composition comprising nickel and chromium; the process is repeated to producing a multilayered alloy having alternating first and second layers on at least a portion of said surface of the substrate or mandrel.

[0028] Regardless of whether the laminated material is produced by electroplating in more than one bath (e.g., alternately plating in two different baths) or in a single baths, the electrolytes employed may be aqueous or non-aqueous. Where aqueous baths are employed they may benefit from the addition of one or more, two or more, or three or more complexing agents, which can be particularly useful in complexing chromium in the +3 valency. Among the complexing agents that may be employed in aqueous baths are one or

more of citric acid, ethylenediaminetetraacetic acid (EDTA), triethanolamine (TEA), ethylenediamine (En), formic acid, acetic acid, hydroxyacetic acid, malonic acid, or an alkali metal salt or ammonium salt of any thereof. In one embodiment the electrolyte used in plating comprises a Cr^{+3} salt (e.g., a tri-chrome plating bath). In another embodiment the electrolyte used in plating comprises either Cr^{+3} and one or more complexing agents selected from citric acid, formic acid, acetic acid, hydroxyacetic acid, malonic acid, or an alkali metal salt or ammonium salt of any thereof. In still another embodiment the electrolyte used in plating comprises either Cr^{+3} and one or more amine containing complexing agents selected from EDTA, triethanolamine (TEA), ethylenediamine (En), or salt of any thereof.

[0029] The temperature at which the electrodeposition process is conducted may alter the composition of the electrodeposit. Where the electrolyte(s) employed are aqueous, the electrodeposition process will typically be kept in the range of about 18° C. to about 45° C. (e.g., 18° C. to about 35° C.) for the deposition of both the first and second layers. Both potentiostatic and galvanostatic control of the electrodeposition of the first and second layers is possible regardless of whether those layers are applied from different electrolyte baths or from a single bath. In one embodiment, a single electrolyte bath is employed and the first electrical current ranges from approximately 10 mA/cm² to approximately 100 mA/cm² for the deposition of the first layers. In that embodiment the second electrical current ranges from approximately 100 mA/cm² to approximately 500 mA/cm² for the deposition of the second layers.

[0030] Plating of each layer may be conducted either continuously or by pulse or pulse reverse plating. In one embodiment, the first electrical current is applied to the substrate or mandrel in pulses ranging from approximately 0.001 second to approximately 1 seconds. In another embodiment, the second electrical current is applied to the substrate or mandrel in pulses ranging from approximately 1 second to approximately 100 seconds. In another embodiment, wherein alternating Ni and Cr containing layer are electrodeposited, the electrodeposition may employ periods of DC plating followed by periods of pulse plating.

[0031] In one embodiment, plating of the nearly pure nickel layer may be conducted either by direct current or by pulse plating. In one such embodiment, the first electrical current is applied to the substrate or mandrel in pulses ranging from approximately 0.001 second to approximately 1 seconds. In another embodiment, the second electrical current is applied to the substrate or mandrel in pulses ranging from approximately 1 second to approximately 100 seconds. In another embodiment, wherein alternating Ni and Cr containing layer are electrodeposited, the electrodeposition may employ periods of DC plating followed by periods of pulse plating.

[0032] To ensure adequate binding of NiCr coatings to substrates it is necessary to preparing the substrate for the electrodeposition (e.g., the surface must be clean, electrochemically active, and the roughness determined to be in an adequate range). In addition, depending on the substrate it may be desirable to employ a strike layer, particularly where the substrate is a polymer or plastic that has previously been rendered conductive by electroless plating or by chemical conversion of its surface, as in the case for zincate processing of aluminum, which is performed prior to the electroless or electrified deposition. Where a strike layer is applied, it may be chosen from an of a number of metals including, but not

limited to, copper nickel, zinc, cadmium, platinum etc. In one embodiment, the strike layer is nickel or a nickel alloy from about 100 nm to about 1000 nm or about 250 nm to about 2500 nm thick. In another embodiment, a first layer applied to a substrate may act as a strike layer, in which case it is applied so that it is directly in contact with a substrate, or in the case of a polymeric substrate rendered conductive by electroless deposition of a metal, directly in contact with the electroless metal layer. Accordingly, in one embodiment a first layer is in contact with the substrate or mandrel. In another embodiment, the second layer is in contact with the substrate or mandrel.

[0033] The hard nanolaminate materials, such as coatings, produced by the processes described above will typically comprise alternating first and second layers in addition to any strike layer applied to the substrate. The first layers each having a thickness independently selected from about 25 nm to about 75 nm, from about 25 nm to about 50 nm, from about 35 nm to about 65 nm, from about 40 nm to about 60 nm, or from about 50 nm to about 75 nm. The second layers having thickness independently from about 125 nm to about 175 nm, from about 125 nm to about 150 nm, from about 135 nm to about 165 nm, from about 140 nm to about 160 nm, or from about 150 nm to about 175 nm.

[0034] First layers may typically comprise greater than about 92%, 93%, 94%, 95%, 96%, 97%, 98% or 99% nickel. The balance of first layers may be chromium, or may be comprised of one or more, two or more, three or more, or four or more elements selected independently for each first layer from C, Co, Cr, Cu, Fe, In, Mn, Nb, Sn, W, Mo, and P. In one embodiment the balance of the first layers are each an alloy comprising chromium and one or more elements selected independently for each layer from C, Co, Cu, Fe, Ni, W, Mo and/or P.

[0035] Second layers may typically comprise about 5% to about 40%, about 5% to about 21%, about 10% to about 14%, about 12% to about 16%, about 14% to about 18%, about 16 to about 21%, about 18% to about 21% or about 18% to about 40% chromium. The balance of second layers may be nickel, or may be comprised of nickel and one or more, two or more, three or more, or four or more elements selected independently for each second layer from C, Co, Cu, Fe, In, Mn, Mo, P, Nb, Ni and W. In one embodiment the balance of the second layers is an alloy comprising nickel and one or more elements selected independently for each layer from C, Co, Cr, Cu, Mo, P, Fe, Ti and W.

[0036] In one embodiment, for an element to be considered as being present, it is contained in the electrodeposited material in non-trivial amounts. In such an embodiment a trivial amount may be less than about 0.005%, 0.01%, 0.05% or 0.1% by weight. Accordingly, non-trivial amounts may be greater than 0.005%, 0.01%, 0.05% or 0.1% by weight. Laminated or nanolaminated materials including coatings prepared as described herein comprise two or more, three or more, four or more, six or more, eight or more, ten or more, twenty or more, forty or more, fifty or more, 100 or more, 200 or more, 500 or more or 1000 or more alternating first and second layers. In such embodiments, the first and second layers are counted as pairs of first and second layers. Accordingly, two layers each having a first layer and second layer, consists of a total of four laminate layers (i.e., each layer is counted separately).

[0037] In addition to the methods of preparing hard NiCr materials, the present disclosure is directed to hard NiCr

materials, including hard NiCr coatings and electroformed NiCr objects prepared by the methods described above.

1.3.2 Properties and Applications of Nanolaminate NiCr Coatings

1.3.2.1 Surface Properties

[0038] The hard NiCr materials described herein have a number of properties that render them useful for both industrial and decorative purposes. The coatings applied are self-leveling and depending on the exact composition of the outermost layer can be reflective to visible light. Accordingly, the hard NiCr materials may serve as a replacement for chrome finishes in a variety of application where reflective metal surfaces are desired. Such applications include, but are not limited to, minors, automotive details such as bumpers or fenders, decorative finishes and the like.

[0039] In one embodiment the laminated NiCr coatings described herein have a surface roughness (arithmetical mean roughness or Ra) of less than 0.1 micrometer (e.g., 0.09, 0.08, 0.07, or 0.05 microns).

1.3.2.2 Hardness

[0040] Through the use of nanolamination it is possible to increase the hardness of NiCr alloys above the hardness observed for homogeneous electrodeposited NiCr compositions (alloys) that have not been heat treated and have the same thickness and average composition as the hard NiCr nanolaminate material. Then laminated NiCr materials have a Vickers microhardness as measured by ASTM E384-11e1 of 550-750, 550-600, 600-650, 650-700, 700-750 or greater than 750 but less than about 900, 950, 1000 or 1100 units without heat treatment. The use of heat treatments in the presence of other elements such as P, C in the first and second layers can increase the hardness of the coating.

[0041] In another embodiment the NiCr materials described herein comprising alternating first and second layers, where the first layers that comprise nickel or comprise a nickel-chromium alloy, and the second layers comprise a nickel-chromium alloy. Such materials have a Vickers microhardness as measured by ASTM E384-11e1 of 550-750, 550-600, 600-650, 650-700, 700-750, 750-800, or 800-850 without heat treatment.

[0042] In one embodiment, the NiCr materials described herein consist of alternating first and second layers, where the first layers consist of a nickel or a nickel-chromium alloy and second layers consist of a nickel-chromium alloy. Such materials have a Vickers microhardness as measured by ASTM E384-11e1 of 550-750, 550-600, 600-650, 650-700, 700-750, 750-800 or 800-850 without heat treatment.

1.3.2.3 Abrasion Resistance

[0043] Due to their high hardness the laminated NiCr materials are useful as a means of providing resistance to abrasion, especially when they are employed as coatings. In one embodiment, the nanolaminate NiCr coatings that have not been heat treated display 5%, 10%, 20%, 30% or 40% less loss of weight than homogeneous electrodeposited NiCr compositions (alloys) that have not been heat treated and have the same thickness and average composition as the hard NiCr nanolaminate material when subject to testing on a Taber Abraser equipped with CS-10 wheels and a 250 g load and operated at room temperature at the same speed for both

samples (e.g., 95 RPM). In another embodiment, the laminated NiCr compositions display a higher abrasion resistance when subject to testing under ASTM D4060 than their homogeneous counterpart (e.g., homogeneous electrodeposited counterpart having the average composition of the laminated NiCr composition).

1.3.2.4 Corrosion Protection

[0044] The behavior of organic, ceramic, metal and metal-containing coatings in corrosive environments depends primarily on their chemistry, microstructure, adhesion, their thickness and galvanic interaction with the substrate to which they are applied.

[0045] NiCr generally acts as barrier coating being more electronegative (more noble) than substrates to which it will be applied, such as iron-based substrates. As such, NiCr coatings act by forming a barrier to oxygen and other agents (e.g., water, acid, base, salts, and/or H₂S) causing corrosive damage, including oxidative corrosion. When a barrier coating that is more noble than its underlying substrate is maned or scratched, or if coverage is not complete, the coatings will not work and may accelerate the progress of substrate corrosion at the substrate-coating interface, resulting in preferential attack of the substrate. Consequently, coatings prepared from the hard NiCr coatings described herein offer advantages over softer NiCr nanolaminate coatings as they are less likely to permit a scratch to reach the surface of a corrosion susceptible substrate. Another advantage offered by the hard NiCr laminate coatings described herein are their fully dense structure, which lacks any significant pores or micro-cracks that extend from the surface of the coating to the substrate. To avoid the formation of microcracks the first layer can be a nickel rich ductile layer that hinders the formation of continuous cracks from the coating surface to the substrate. To the extent that microcracks occur in the high chromium layers, they are small and tightly spaced. The lack of pores and continuous microcracks more effectively prohibits corrosive agents from reaching the underlying substrate and renders the laminate NiCr coatings described herein more effective as a barrier coating to oxidative damage of a substrate than an equivalent thickness of electrodeposited chromium.

2.0 Certain Embodiments

[0046] 1. A process for forming a multilayered nickel and chromium containing coating on a surface of a substrate or mandrel by electrodeposition comprising:

[0047] (a) providing one or more electrolyte solutions comprising a nickel salt and/or a chromium salt;

[0048] (b) providing a conductive substrate or mandrel for electrodeposition;

[0049] (c) contacting at least a portion of the surface of the substrate or mandrel with one of said one or more electrolyte solutions;

[0050] (d) passing a first electric current through the substrate or mandrel, to deposit a first layer comprising either nickel, or an alloy thereof, on the substrate or mandrel; and passing a second electric current through the substrate, to deposit a second layer comprising a nickel-chromium alloy on the surface;

[0051] (e) repeating step (d) two or more times thereby producing a multilayered coating having first layers of nickel, or an alloy thereof, and second layers of a nickel-chromium alloy on at least a portion of the surface of the

substrate or mandrel; and optionally separating the substrate or mandrel from the coating.

[0052] 2. The process of embodiment 1, wherein:

[0053] said providing one or more electrolyte solutions comprise providing an electrolyte solution comprising a nickel salt and a chromium salt;

[0054] passing an electric current through said substrate or mandrel comprises alternately pulsing said electric current for predetermined durations between said first electrical current and said second electrical current (e.g., pulsing for predetermined durations at a first electrical current value and then at a second electrical current value);

[0055] where said first electrical current is effective to electrodeposit a first composition comprising nickel or an alloy of nickel and chromium; and

[0056] where said second electrical current is effective to electrodeposit a second composition comprising nickel and chromium;

[0057] thereby producing a multilayered alloy having alternating first and second layers, said first layer comprising either nickel, or an alloy thereof, and said second layer comprising a nickel-chromium alloy on at least a portion of the surface of the substrate or mandrel.

[0058] 3. The process of embodiment 1 or embodiment 2, wherein at least one of said one or more electrolyte solutions is an aqueous bath (e.g., aqueous solution) comprising one or more complexing agents.

[0059] 4. The process of embodiment 3, wherein said complexing agent is selected from one or more, two or more, or three or more of citric acid, ethylenediaminetetraacetic acid (EDTA), triethanolamine (TEA), ethylenediamine (En), formic acid, acetic acid, hydroxyacetic acid, malonic acid or an alkali metal or ammonium salt of any thereof.

[0060] 5. The process of any of embodiments 1-4, wherein said passing said first electric current through said substrate or mandrel and passing said second electric current through said substrate or mandrel are conducted at a temperature ranging from approximately (about) 18° C. to approximately (about) 35° C., or from approximately (about) 18° C. to approximately (about) 45° C.

[0061] 6. The process of any of embodiments 1-5, wherein the first electric current has a range from approximately (about) 10 mA/cm² to approximately (about) 100 mA/cm²

[0062] 7. The process of any of embodiments 1-6, wherein the second electric current has a range from approximately (about) 100 mA/cm² to approximately (about) 500 mA/cm².

[0063] 8. The process of any of embodiments 1-7, wherein the first electrical current is applied to the substrate or mandrel in pulses ranging from approximately (about) 0.001 second to approximately (about) 1.00 seconds.

[0064] 9. The process of any of embodiments 1-8, wherein the second electrical current is applied to the substrate or mandrel in pulses ranging from approximately (about) 0.001 second to approximately (about) 1.00 seconds.

[0065] 10. The process of any of embodiments 1-9, wherein said first layer is in contact with said substrate or mandrel.

[0066] 11. The process of any of embodiments 1-9, wherein said second layer is in contact with said substrate or mandrel.

[0067] 12. The process of any of embodiments 1-11, wherein said first layer has a thickness from about 25 nm to about 75 nm, from about 25 nm to about 50 nm, from about

- 35 nm to about 65 nm, from about 40 nm to about 60 nm, or from about 50 nm to about 75 nm.
- [0068] 13. The process of any of embodiments 1-12, wherein said second layer has a thickness from about 125 nm to about 175 nm, from about 125 nm to about 150 nm, from about 135 nm to about 165 nm, from about 140 nm to about 160 nm, or from about 150 nm to about 175 nm.
- [0069] 14. The process of any of embodiments 1-13, wherein said first layer comprises greater than about 92%, 93%, 94%, 95%, 96%, 97%, 98% or 99% nickel by weight and a balance of other elements.
- [0070] 15. The process of any of embodiments 1-14, wherein said second layer comprises about 10% to about 21%, about 10% to about 14%, about 12% to about 16%, about 14% to about 18%, about 16% to about 21%, about 18% to about 21% or about 18% to about 40% chromium by weight and a balance of other elements.
- [0071] 16. The process of embodiment 14, wherein said first layer comprises greater than about 92%, 93%, 94%, 95%, 96%, 97%, 98% or 99% nickel, and the balance of the first layer is chromium.
- [0072] 17. The process of embodiment 15, wherein said second layer comprises about 10% to about 21%, about 10% to about 14%, about 12% to about 16%, about 14% to about 18%, about 16% to about 21%, about 18% to about 21% or about 18% to about 40% chromium, and the balance of the second layer is nickel.
- [0073] 18. The process of any of embodiments 1-15, wherein the first layer and/or the second layer comprises one or more, two or more, three or more or four or more elements selected independently for each layer from the group consisting of C, Co, Cu, Fe, In, Mn, Nb, W, Mo, and P.
- [0074] 19. The process of embodiment 18, wherein said elements selected independently for each layer are each present in a non-trivial amount greater than 0.005%, 0.01%, 0.05% or 0.1% by weight.
- [0075] 20. The process of any of embodiments 1-19, comprising two or more, three or more, four or more, six or more, eight or more, ten or more, twenty or more, forty or more, fifty or more, 100 or more, 200 or more, 500 or more or 1000 or more alternating first layers and second layers.
- [0076] 21. An object or coating comprising a multilayered nickel and chromium containing coating prepared by the method of any of embodiments 1-20.
- [0077] 22. An object or coating comprising a multilayered coating comprising a plurality of alternating first layers of nickel or an alloy comprising nickel, and second layers of an alloy comprising nickel and chromium, and optionally comprising a substrate.
- [0078] 23. The object or coating of embodiment 22, wherein said multilayer coating comprises two or more, three or more, four or more, six or more, eight or more, ten or more, twenty or more, forty or more, fifty or more, 100 or more, 200 or more, 500 or more or 1000 or more alternating first and second layers.
- [0079] 24. The object or coating of any of embodiments 22-23, wherein said first layers have a thickness from about 25 nm to about 75 nm, from about 25 nm to about 50 nm, from about 35 nm to about 65 nm, from about 40 nm to about 60 nm or from about 50 nm to about 75 nm.
- [0080] 25. The object or coating of any of embodiments 22-24, wherein said second layers have a thickness from about 125 nm to about 175 nm, from about 125 nm to about 150 nm, from about 135 nm to about 165 nm, from about 140 nm to about 160 nm or from about 150 nm to about 175 nm.
- [0081] 26. The object or coating of any of embodiments 22-25, wherein said first layer is in contact with said substrate or mandrel.
- [0082] 27. The object or coating of any of embodiments 22-26, wherein said second layer is in contact with said substrate or mandrel.
- [0083] 28. The object or coating of any of embodiments 22-27, wherein said first layer comprises greater than about 92%, 93%, 94%, 95%, 96%, 97%, 98% or 99% nickel.
- [0084] 29. The object or coating of any of embodiments 22-28, wherein each second layer comprises chromium in a range independently selected from about 10% to about 21%, about 10% to about 14%, about 12% to about 16%, about 14% to about 18%, about 16% to about 21%, about 18% to about 21% or 18%-40% chromium.
- [0085] 30. The object or coating of embodiment 28, wherein said first layer comprises greater than about 92%, 93%, 94%, 95%, 96%, 97%, 98% or 99% nickel and the balance of the first layer is chromium.
- [0086] 31. The object or coating of embodiment 29, wherein said second layer comprises greater than about 10% to about 21%, about 10% to about 14%, about 12% to about 16%, about 14% to about 18%, about 16% to about 21%, about 18% to about 21% or about 18% to about 40% chromium and the balance of the second layer is nickel.
- [0087] 32. The object or coating of any of embodiments 22-31, wherein said first and/or second layer comprises one or more, two or more, three or more, or four or more elements selected independently from the group consisting of C, Co, Cu, Fe, In, Mn, Nb, W, Mo, and P.
- [0088] 33. The object or coating of any of embodiments 22-31, wherein each of said elements are present at concentrations of 0.01% or greater.
- [0089] 34. The object or coating of any of embodiments 22-33, comprising two or more, three or more, four or more, six or more, eight or more, ten or more, twenty or more, forty or more, fifty or more, 100 or more, 200 or more, 500 or more or 1000 or more alternating first and second layers.
- [0090] 35. The object or coating of any of embodiments 22-34, wherein said first layers consist of nickel or a nickel chromium alloy and said second layers consist of a nickel-chromium alloy and wherein said coating has a Vickers microhardness as measured by ASTM E384-11e1 of about 550 to about 750, about 550 to about 600, about 600 to about 650, about 650 to about 700, about 700 to about 750, about 750 to about 800 or about 800 to about 850 without heat treatment.
- [0091] 36. The object or coating of any of embodiments 22-34, wherein said substrate comprises one or more metals.
- [0092] 37. The object or coating of embodiment 36, wherein said substrate comprises one or more metals or other elements selected from the group consisting of C, Co, Cu, Fe, In, Mn, Nb, W, Mo, and P.
- [0093] 38. The object or coating of embodiment 37, wherein said substrate is selected from iron or steel.
- [0094] 39. The object or coating of any of embodiments 22-38, wherein said coating has fewer cracks, pores, or microcracks than a monolithic coating of chromium of substantially the same thickness (e.g., an electrodeposited coating of chromium of substantially the same thickness

deposited under conditions suitable for deposition of second layers but consisting of chromium).

[0095] 40. The object or coating of any of embodiments 22-39, wherein said object resists corrosion of said substrate caused by exposure to one or more of water, air, acid, base, salt water, and/or H₂S.

[0096] 41. The object or coating of any of embodiments 36-40, wherein said first layers consists of nickel, or a nickel chromium alloy, and second layers consist of a nickel-chromium alloy, and wherein said coating has a Vickers microhardness as measured by ASTM E384-11e1 of about 550 to about 750, about 550 to about 600, about 600 to about 650, about 650 to about 700, about 700 to about 750, about 750 to about 800 or about 800 to about 850 without heat treatment.

[0097] 42. The process of any of embodiments 1-20, further comprising separating said multilayered coating from said substrate or mandrel to form a multilayered object.

1. A process for forming a multilayered nickel and chromium containing coating on a surface of a substrate or mandrel by electrodeposition comprising:

- (a) providing one or more electrolyte solutions comprising a nickel salt and/or a chromium salt;
- (b) providing a conductive substrate or mandrel for electrodeposition;
- (c) contacting at least a portion of the surface of the substrate or mandrel with one of said one or more electrolyte solutions;
- (d) passing a first electric current through the substrate or mandrel, to deposit a first layer comprising either nickel or an alloy thereof, on the substrate or mandrel; and passing a second electric current through the substrate, to deposit a second layer comprising a nickel-chromium alloy on the surface;
- (e) repeating step (d) two or more times thereby producing a multilayered coating having first layers of nickel, or an alloy thereof, and second layers of a nickel-chromium alloy on at least a portion of the surface of the substrate or mandrel; and

optionally separating the substrate or mandrel from the coating.

2. The process of claim 1, wherein:

said providing one or more electrolyte solutions comprises providing an electrolyte solution comprising a nickel salt and a chromium salt;

passing an electric current through said substrate or mandrel comprises alternately pulsing said electric current for predetermined durations between said first electrical current and said second electrical current;

where said first electrical current is effective to electrodeposit a first composition comprising nickel or an alloy of nickel and chromium; and

where said second electrical current is effective to electrodeposit a second composition comprising nickel and chromium; thereby producing a multilayered alloy having alternating first and second layers, said first layer comprising either nickel or an alloy thereof, and said second layer comprising a nickel-chromium alloy on at least a portion of the surface of the substrate or mandrel.

3. The process of claim 1, wherein at least one of said one or more electrolyte solutions is an aqueous solution comprising one or more complexing agents.

4. The process of claim 3, wherein said complexing agent is selected from one or more, two or more or three or more of citric acid, EDTA, triethanolamine (TEA), ethylenediamine (En), formic acid, acetic acid, hydroxyacetic acid, malonic acid, or an alkali metal or ammonium salt of any thereof.

5. (canceled)

6. The process of claim 1, wherein the first electric current ranges from approximately 10 mA/cm² to approximately 100 mA/cm², and wherein the second electric current ranges from approximately 100 mA/cm² to approximately 500 mA/cm².

7-13. (canceled)

14. The process of claim 1, wherein said first layer comprises greater than about 92% nickel by weight and a balance of other elements.

15. The process of claim 1, wherein said second layer comprises about 10% to about 21%, chromium by weight and a balance of other elements.

16-17. (canceled)

18. The process of claim 1, wherein the first layer and/or the second layer comprises one to four or more elements selected independently for each layer from the group consisting of C, Co, Cu, Fe, In, Mn, Nb, W, Mo, and P.

19. (canceled)

20. The process of claim 1, comprising fifty or more alternating first layers and second layers.

21. An object or coating comprising a coating prepared by the method of claim 1.

22. An object or coating comprising a multilayered coating comprising a plurality of alternating first layers of nickel, or an alloy comprising nickel, and second layers of an alloy comprising nickel and chromium, and optionally comprising a substrate.

23-27. (canceled)

28. The object or coating of any of claim 22, wherein each first layer comprises greater than about 92% nickel, and wherein each second layer comprises chromium in a range independently selected from 10%-21% chromium.

29-34. (canceled)

35. The object or coating of claim 22, wherein said first layers consist of nickel or a nickel chromium alloy and said second layers consist of a nickel-chromium alloy and wherein said coating has a Vickers microhardness as measured by ASTM E384-11e1 of 550-750, 750-800, or 800-850 without heat treatment.

36. (canceled)

37. The object or coating of claim 22, wherein said substrate comprises one or more elements selected from the group consisting of C, Co, Cu, Fe, In, Mn, Nb, W, Mo, and P.

38-39. (canceled)

40. The object or coating of claim 22, wherein said object resists corrosion of said substrate caused by exposure to one or more of water, air, acid, base, salt water and/or H₂S.

41. The object or coating of claim 37, wherein said first layers consist of nickel, or a nickel chromium alloy, and said second layers consist of a nickel-chromium alloy, and wherein said coating has a Vickers microhardness as measured by ASTM E384-11e1 of 550-750, 750-800, or 800-850 without heat treatment.

42. (canceled)