



(86) **Date de dépôt PCT/PCT Filing Date:** 2015/09/18
(87) **Date publication PCT/PCT Publication Date:** 2016/03/24
(45) **Date de délivrance/Issue Date:** 2022/12/13
(85) **Entrée phase nationale/National Entry:** 2017/03/15
(86) **N° demande PCT/PCT Application No.:** US 2015/050910
(87) **N° publication PCT/PCT Publication No.:** 2016/044708
(30) **Priorité/Priority:** 2014/09/18 (US62/052,437)

(51) **Cl.Int./Int.Cl.** **C25D 5/14** (2006.01),
C25D 3/04 (2006.01), **C25D 3/12** (2006.01)
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(54) **Titre : REVETEMENT NANOSTRATIFIE OU GAINAGE DE NICKEL-CHROME PRESENTANT UNE DURETEE ELEVEE**
(54) **Title: NICKEL-CHROMIUM NANOLAMINATE COATING OR CLADDING HAVING HIGH HARDNESS**

(57) **Abrégé/Abstract:**

Electrodeposited nanolaminate materials having layers comprised of nickel and/or chromium with high hardness and processes for making them are disclosed. The uniform or substantially uniform appearance, chemical resistance, and high hardness of embodiments of the nanolaminate NiCr materials described herein render them useful for a variety of purposes including wear (abrasion) resistant barrier coatings or claddings for use in decorative as well as demanding physical, structural and chemical environments.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



WIPO | PCT



(10) International Publication Number
WO 2016/044708 A1

(43) International Publication Date
24 March 2016 (24.03.2016)

(51) International Patent Classification:

C25D 5/02 (2006.01) *C25D 5/14* (2006.01)
C25D 5/08 (2006.01)

(21) International Application Number:

PCT/US2015/050910

(22) International Filing Date:

18 September 2015 (18.09.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/052,437 18 September 2014 (18.09.2014) US

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(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- with amended claims (Art. 19(1))

(54) Title: NICKEL-CHROMIUM NANOLAMINATE COATING OR CLADDING HAVING HIGH HARDNESS

(57) Abstract: Electrodeposited nanolaminate materials having layers comprised of nickel and/or chromium with high hardness and processes for making them are disclosed. The uniform or substantially uniform appearance, chemical resistance, and high hardness of embodiments of the nanolaminate NiCr materials described herein render them useful for a variety of purposes including wear (abrasion) resistant barrier coatings or claddings for use in decorative as well as demanding physical, structural and chemical environments.



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5 This application claims priority to U.S. Provisional Patent Application No. 62/052,437, filed September 18, 2014. In addition, the disclosures of U.S. Provisional Patent Application No. 61/802,112, filed March 15, 2013, and International Application PCT/US2014/030381, filed March 17, 2014 are also relevant to the subject-matter of the present application.

Electrodeposition is recognized as a low-cost method for forming a dense coating or cladding on a variety of conductive materials, including metals, alloys, conductive polymers and the like. Electrodeposition has also been successfully used to deposit nanolaminated coatings or claddings 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. in a variety of engineering applications.

Electrodeposition has also been demonstrated as a viable means for producing laminated and nanolaminated coatings, claddings, 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 or claddings 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.

The present disclosure is directed, among other things, to the production of NiCr nanolaminated materials having a high hardness. The materials have a variety of uses including, but not limited to, the preparation of coatings or claddings that protect an underlying substrate, and which may also increase its strength. In one embodiment hard NiCr coatings or claddings and materials are wear/abrasion resistant and find use as wear resistant coatings or claddings in tribological applications. In another embodiment the hard NiCr coatings or claddings prevent damage to the underlying substrates. Where the NiCr materials are applied

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as a coating or cladding that is more noble than the underlying material upon which it is placed, it may function as a corrosion resistant barrier coating or cladding.

DESCRIPTION

1.1 Overview

5 The present disclosure is directed to methods of producing laminate materials, and to coatings or claddings comprising layers each comprising nickel or nickel and chromium. The materials, which are prepared by electrodeposition, have a Vickers hardness greater than about 750 without the addition of other elements or heat treatments.

10 Some embodiments are directed to an electrodeposition process for forming a multilayered nickel and chromium containing coating or cladding on a substrate or mandrel comprising:

- (a) providing an electrolyte solution 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 the
- 15 electrolyte solution;
- (d) passing a seed layer plating current through the substrate or mandrel to deposit a nickel and chromium containing seed layer on the substrate or mandrel, where the seed layer comprises greater than about 90% nickel by weight;
- (e) passing a first electric current through the substrate or mandrel to deposit a nickel-
- 20 chromium alloy first layer comprising from about 5 to about 35% chromium by weight;
- (f) passing a second electric current through the substrate to deposit a nickel and chromium containing second layer comprising greater than about 90% nickel by weight; and
- (g) repeating steps (e) and (f) four or more times, thereby producing a multilayered coating or cladding having a seed layer and alternating first layers and second layers on the
- 25 surface of the substrate or mandrel.

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

30 The high hardness coating or cladding produced by the process typically has alternating first and second layers. In some embodiments, the first layers are each from about 125 nm to about 175 nm thick, and comprise from about 5% to about 35% chromium by weight with the

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balance typically comprising nickel, and the second layers are each from about 25 nm to about 75 nm thick, and comprise greater than about 90% nickel by weight, with the balance typically comprising chromium. In other embodiments, the percentages of chromium and nickel percentages in the first and second layers may vary outside of the above ranges, and the first and second layers may each be thicker or thinner than the above first- and second-layer thicknesses.

1.2 Definitions

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

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

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

1.3 Nanolaminate NiCr Coatings and Claddings

1.3.1 Nanolaminate NiCr Materials and Coatings or Claddings and Methods of Their Preparation

Electrodeposition has been demonstrated as a viable means for producing nanolaminated metal materials and coatings or claddings 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.

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.

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

Embodiments of the present disclosure provide processes for forming a multilayered nickel and chromium containing coating or cladding on a substrate or mandrel by

5 electrodeposition comprising:

- (a) providing an electrolyte solution 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 the electrolyte solution;
- 10 (d) passing a seed layer plating current through the substrate or mandrel to deposit a nickel and chromium containing seed layer on the substrate or mandrel, where the seed layer comprises greater than about 90% nickel by weight;
- (e) passing a first electric current through the substrate or mandrel to deposit a nickel-chromium alloy first layer comprising from about 5 to about 35% chromium by weight;
- 15 (f) passing a second electric current through the substrate to deposit a nickel and chromium containing second layer comprising greater than about 90% nickel by weight; and
- (g) repeating steps (e) and (f) four or more times, thereby producing a multilayered coating or cladding having a seed layer and alternating first layers and second layers on the surface of the substrate or mandrel.

20 Embodiments of the processes herein may additionally comprise a step of separating the substrate or mandrel from the coating or cladding.

Embodiments of the method may additionally comprise, prior to passing said first electric current, a step of dynamically manipulating, at the cathode diffusion layer, the concentration and speciation of chromium ions via applying a seed layer plating current through
 25 the substrate; and depositing a nickel-chromium alloy first layer having a surface roughness (arithmetical mean roughness or Ra) of less than 0.1 micrometer (*e.g.*, less than 0.09, 0.08, 0.07, or 0.05 microns) and comprising from about 5% to about 35% chromium by weight (*e.g.*, about 5% to about 10%, about 10% to about 20%, about 10% to about 25%, or about 20% to about 35%).

30 Where separate baths are employed to deposit the first and second layers, step (f) includes contacting at least a portion of the substrate or mandrel having the first layer deposited on it with a second of said one or more electrolyte solutions (baths) prior to passing a second

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electric current through the substrate, to deposit a second layer comprising a nickel-chromium alloy on the surface.

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
 5 separating the substrate or mandrel from the electroplated coating or cladding. Where a step of separating the electroplated material from the substrate or mandrel is to be employed, the use of electrodes (mandrel), such as titanium electrodes (mandrel), that do not form tight bonds with the coating or cladding may be employed.

In embodiments where a single bath is used to deposit the first and second layers,
 10 providing one or more electrolyte solutions comprises providing a single electrolyte solution comprising a nickel salt and a chromium salt. The step of passing an electric current through the 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
 15 comprising an alloy of nickel and chromium, and the second electrical current density is effective to electrodeposit a second composition comprising nickel or a composition (*e.g.*, an alloy) comprising nickel and chromium. The process is repeated to produce a multilayered alloy having alternating first and second layers on at least a portion of the surface of the substrate or mandrel.

20 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 bath, 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
 25 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 some embodiments, the electrolyte used in plating comprises a Cr^{+3} salt (*e.g.*, a tri-chrome plating bath). In other embodiments, the electrolyte used in plating comprises either
 30 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 other embodiments, the electrolyte used in plating comprises either Cr^{+3} and one or more amine containing complexing agents selected from EDTA, TEA, En, or a salt of any thereof.

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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.

5 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 some embodiments, a single electrolyte bath is employed and the first electrical current ranges from about 100 to about 300 mA/cm² for the deposition of the first layers, and the second electrical current ranges from about 20 to about 60
10 mA/cm² for the deposition of the second layers. In such embodiments, the first electrical current is applied to the substrate or mandrel for about 50 milliseconds to about 500 milliseconds, and the second electrical current is applied to the substrate or mandrel for about 50 milliseconds to about 500 milliseconds. In other embodiments, wherein alternating Ni and/or Ni/Cr containing layers are electrodeposited, the electrodeposition may employ periods
15 of DC plating followed by periods of pulse plating. In embodiments, plating of a nearly pure nickel layer may be conducted either by direct current or by pulse plating.

In such embodiments, the first electrical current is applied to the substrate or mandrel in a pulse ranging from about 50 milliseconds to about 500 milliseconds at a current density of about 100 to about 300 mA/cm², and the second electrical current is applied to the substrate or
20 mandrel in a pulse ranging from about 50 milliseconds to about 500 milliseconds at a current density from about 20 to about 60 mA/cm². In such embodiments, the resulting coating or cladding has layers of substantially pure nickel alternated with layers of nickel and chromium.

Prior to applying the first and second layers, a seed layer comprising greater than about 90% nickel by weight (*e.g.*, about 90.00 up to about 100, about 90 to about 92, about 92 to
25 about 95, about 94 to about 98, about 95 up to about 100, about 96 to about 100, about 97.00 to about 99.99, about 98.00 to about 99.99, about 99.00 to about 99.99) is applied to the substrate or mandrel. Where a strike layer is also applied, the strike layer is applied prior to the seed layer.

To ensure adequate binding of NiCr coatings or claddings to substrates, it is necessary
30 to prepare the substrate for electrodeposition (*e.g.*, the surface must be clean and 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

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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 any of a number of metals including, but not limited to, copper, nickel, zinc, cadmium, platinum etc. In some embodiments, the strike layer is nickel or a nickel alloy from about 100 nm to about 1,000 nm or from about 250 nm to about 2,500 nm thick. In other embodiments, where the substrate is a non-conductive polymeric material rendered conductive by electroless deposition of a metal, the metal composition deposited by the electroless plating may act as a strike layer.

The hard nanolaminate materials, such as coatings and claddings, produced by the processes described above will typically comprise alternating first and second layers in addition to a seed layer and any strike layer applied to the substrate. The first layers each have a thickness independently selected from the following ranges: 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 each have a thickness independently selected from the following ranges: from about 75 nm to about 225 nm, from about 100 to about 200 nm, 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.

First layers may typically comprise a percent of chromium by weight selected from one of the following ranges: from about 7 to about 32%, from about 10 to about 30%, from about 12 to about 28%, from about 10 to about 32%, from about 10 to about 18%, from about 10 to about 16%, from about 9 to about 17%, from about 9 to about 19%, from about 20 to about 32%, from about 10 to about 20%, from about 15 to about 30%, from about 16 to about 25%, and from about 18 to about 27%. The balance of first layers may be nickel, or may comprise nickel and one or more, two or more, three or more, or four or more additional elements selected independently for each second layer, e.g., from elements such as C, Co, Cu, Fe, In, Mn, Mo, P, Nb, Ni and W. In some embodiments, the balances of the first layers each independently comprise nickel and one or more, two or more, or three or more, elements selected independently for each layer from C, Co, Cr, Cu, Mo, P, Fe, Ti, and W (e.g., C, Co, Cr, Cu, Mo, P, Fe, and W, or alternatively, Co, Cr, Cu, Mo, Fe, and W).

Second layers may typically comprise a percent of nickel by weight in one of the following ranges: about 90.00 up to about 100%, about 90 to about 92%, about 92 to about 95%, about 94 to about 98%, about 96 up to about 100%, about 97.00 to about 99.99%, about

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98.00 to about 99.99%, and about 99.00 to about 99.99%. The balance of second layers may be chromium, or may be comprised of one or more, two or more, three or more, or four or more additional elements selected independently for each second layer, e.g., from elements such as C, Co, Cr, Cu, Fe, In, Mn, Nb, Sn, W, Mo, and P. In some embodiments, the balances of the second layers each independently comprise chromium and one or more additional elements selected independently for each layer, e.g. from elements such as C, Co, Cu, Fe, Ni, W, Mo and/or P. In the embodiments described herein, for any such additional element to be considered as being present, it must be present in the electrodeposited material in a non-trivial amount, *i.e.*, not less than an amount selected from the following amounts: 0.005%, 0.01%, 0.05% or 0.1% by weight.

Laminated or nanolaminated materials including coatings and claddings 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 1,000 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 a second layer, consists of a total of four laminate layers (*i.e.*, each layer is counted separately).

In addition to the methods of preparing hard NiCr materials, the present disclosure is directed to hard NiCr materials, including hard NiCr coatings or claddings and electroformed NiCr objects, prepared by the methods described above.

1.3.2 Properties and Applications of Nanolaminate NiCr Coatings or Claddings

1.3.2.1 Surface Properties

Embodiments of the hard NiCr materials described herein have a number of properties that render them useful for both industrial and decorative purposes. The coatings or claddings 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 replacements for chrome finishes in a variety of applications where reflective metal surfaces are desired. Such applications include, but are not limited to, mirrors, automotive details such as bumpers or fenders, decorative finishes and the like.

In some embodiments, the laminated NiCr coatings or claddings 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).

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1.3.2.2 Hardness

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
5 NiCr nanolaminate material. Embodiments of the laminated NiCr materials disclosed herein have a Vickers hardness (microhardness) number as measured by ASTM E384-11e1 in a range selected from: 550-750, 550-600, 600-650, 650-700, 700-750, 750-1000, 1000-1100, 1100 to 1200, or 1200 or more; or, alternatively, a hardness number greater than 750, 800, 850, 900, 950, 1000, 1050, 1100, 1150, 1200, or more, without heat treatment. The use of heat treatments
10 in the presence of other elements such as B, P, or C in the first and second layers can increase the hardness of the coating or cladding.

In other embodiments, the NiCr materials described herein comprise alternating first and second layers that consist essentially of nickel or a nickel-chromium alloy. Such materials have a Vickers microhardness as measured by ASTM E384-11e1 of 550-750, 550-600, 600-650,
15 650-700, 700-750, 750-800, 800-850, 850-900, 900-1000, 1000-1100, 1100 to 1200, or 1200 or more without heat treatment.

In some embodiments, the NiCr materials described herein consist of alternating first and second layers that consist of nickel or a nickel-chromium alloy. Such materials have a Vickers microhardness as measured by ASTM E384-11e1 in a range selected from 550-750,
20 550-600, 600-650, 650-700, 700-750, 750-800, 800-850, 850-900, 900-1,000 or 1,000-1,100 without heat treatment.

1.3.2.3 Abrasion Resistance

Due to their high hardness, embodiments of the laminated NiCr materials disclosed herein are useful as a means of providing resistance to abrasion, especially when they are
25 employed as coatings or claddings. When subjected 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), embodiments of the nanolaminate NiCr coatings or claddings disclosed herein 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
30 treated and have the same thickness and average composition as the hard NiCr nanolaminate material. In other embodiments, the laminated NiCr compositions display a higher abrasion resistance when subject to testing under ASTM D4060 than their homogeneous counterpart

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(*e.g.*, homogeneous electrodeposited counterpart having the average composition of the laminated NiCr composition).

1.3.2.4 Corrosion protection

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

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

2.0 Certain Embodiments

1. A process for forming a multilayered coating or cladding on a surface of a substrate or
 30 mandrel by electrodeposition, comprising:
 - (a) providing an electrolyte solution comprising a nickel salt and/or a chromium salt;
 - (b) providing a conductive substrate or mandrel for electrodeposition;

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- (c) contacting at least a portion of the surface of the substrate or mandrel with the electrolyte solution;
- (d) passing a seed layer plating current through the substrate or mandrel to deposit a nickel and chromium containing seed layer on the substrate or mandrel, where the seed layer comprises greater than about 90% nickel by weight;
- (e) passing a first electric current through the substrate or mandrel to deposit a nickel-chromium alloy first layer comprising from about 5 to about 35% chromium by weight;
- (f) passing a second electric current through the substrate to deposit a nickel and chromium containing second layer comprising greater than about 90% nickel by weight;
- (g) repeating steps (e) and (f) four or more times, thereby producing a multilayered coating or cladding having a seed layer and alternating first layers and second layers on the surface of the substrate or mandrel; and
- (h) optionally separating the substrate or mandrel from the coating or cladding.
2. The process of embodiment 1, wherein the seed layer plating current has a density selected from the group consisting of from about 20 to about 60 mA/cm², from about 20 to about 50 mA/cm², from about 30 to about 60 mA/cm², from about 30 to about 50 mA/cm², from about 25 to about 55 mA/cm², from about 20 to about 45 mA/cm², from about 20 to about 35 mA/cm², from about 30 to about 45 mA/cm², from about 30 to about 40 mA/cm², and from about 40 to about 50 mA/cm².
3. The process of embodiment 1 or embodiment 2, wherein the seed layer plating current has a density selected from the group consisting of about 20 mA/cm², about 25 mA/cm², about 30 mA/cm², about 35 mA/cm², about 40 mA/cm², about 45 mA/cm², about 50 mA/cm², about 55 mA/cm², and about 60 mA/cm².
4. The process of any preceding embodiment wherein the seed layer plating current is applied to the substrate or mandrel for a time period selected from the group consisting of about 1 minute to about 10 minutes, about 1 minute to about 5 minutes, about 3 minutes to about 8 minutes, about 5 minutes to about 10 minutes, about 2 minutes to about 6 minutes, about 4 minutes to about 8 minutes, and about 6 minutes to about 10 minutes.
5. The process of any preceding embodiment wherein the seed layer comprises nickel in a weight percent (Ni wt.%) range selected from the group consisting of about 90.00 up to about 100, about 90 to about 92, about 92 to about 95, about 94 to about 98, about 95 up to

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about 100, about 96 to about 100, about 97.00 to about 99.99, about 98.00 to about 99.99, and about 99.00 to about 99.99.

6. The process of any preceding embodiment, wherein the first electric current has a density in a range selected from the group consisting of from about 100 to about 300 mA/cm², from about 100 to about 200 mA/cm², from about 200 to about 300 mA/cm², from about 150 to about 250 mA/cm², from about 150 to about 290 mA/cm², and from about 160 to about 280 mA/cm².
7. The process of any preceding embodiment, wherein the first electric current has a density selected from the group consisting of about 160 mA/cm², about 180 mA/cm², about 200 mA/cm², about 220 mA/cm², about 240 mA/cm², and about 260 mA/cm².
8. The process of any preceding embodiment, wherein the first current is applied for a time period selected from the group consisting of about 50 milliseconds to about 500 milliseconds, about 50 milliseconds to about 100 milliseconds, about 100 milliseconds to about 200 milliseconds, about 200 milliseconds to about 300 milliseconds, about 200 milliseconds to about 400 milliseconds, about 300 milliseconds to about 400 milliseconds, about 400 milliseconds to about 500 milliseconds, and about 100 milliseconds to about 400 milliseconds.
9. The process of any preceding embodiment wherein the second electric current has a density in a range selected from the group consisting of from about 20 to about 60 mA/cm², from about 20 to about 50 mA/cm², from about 30 to about 60 mA/cm², from about 30 to about 50 mA/cm², from about 25 to about 55 mA/cm², from about 20 to about 45 mA/cm², from about 20 to about 35 mA/cm², from about 30 to about 45 mA/cm², from about 30 to about 40 mA/cm², and from about 40 to about 50 mA/cm².
10. The process of any preceding embodiment wherein the second electric current has a density selected from the group consisting of about 20 mA/cm², about 25 mA/cm², about 30 mA/cm², about 35 mA/cm², about 40 mA/cm², about 45 mA/cm², about 50 mA/cm², about 55 mA/cm², and about 60 mA/cm².
11. The process of any preceding embodiment wherein the second electric current is applied for a time period selected from the group consisting of: about 50 milliseconds to about 500 milliseconds, about 50 milliseconds to about 100 milliseconds, about 100 milliseconds to about 200 milliseconds, about 200 milliseconds to about 300 milliseconds, about 200

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milliseconds to about 400 milliseconds, about 300 milliseconds to about 400 milliseconds, about 400 milliseconds to about 500 milliseconds, and about 100 milliseconds to about 400 milliseconds.

12. The process of any preceding embodiment, where steps (e) and (f) are repeated greater than
5 10, 20, 50, 100, 200, 400, 500, 1,000, 2,000, 5,000, 7,500, or 10,000 times.
13. The process of any preceding embodiment, where steps (e) and (f) are repeated from about
4 to 10,000 times, from about 5 to 5,000 times, from about 5 to 2,500 times, and from about
5 to 2,000 times.
14. The process of any preceding embodiment wherein one, two, three, four or more of the first
10 layers comprises chromium in a weight percent (Cr wt.%) range selected from the group
consisting of from about 7 to about 32, from about 10 to about 30, from about 12 to about
28, from about 10 to about 32, from about 10 to about 18, from about 10 to about 16, from
about 9 to about 17, from about 9 to about 19, from about 20 to about 32, from about 10 to
about 20, from about 15 to about 30, from about 16 to about 25, and from about 18 to about
15 27.
15. The process of any preceding embodiment wherein each of the first layers comprises
chromium in a weight percent (Cr wt.%) range selected from the group consisting of from
about 5 to about 35, from about 10 to about 30, from about 12 to about 28, from about 10 to
about 32, from about 10 to about 18, from about 10 to about 16, from about 9 to about 17,
20 from about 9 to about 19, from about 20 to about 32, from about 10 to about 20, from about
15 to about 30, from about 16 to about 25, and from about 18 to about 27.
16. The process of any preceding embodiment, wherein one, two, three, four or more of the
second layers comprises nickel in a weight percent (Ni wt.%) range selected from the group
consisting of about 90.00 up to about 100, about 90 to about 92, about 92 to about 95, about
25 94 to about 98, about 95 up to about 100, about 96 up to about 100, about 97.00 to about
99.99, about 98.00 to about 99.99, and about 99.00 to about 99.99.
17. The process of any preceding embodiment, wherein each of the second layers comprises
nickel in a weight percent (Ni wt.%) range selected from the group consisting of about
90.00 up to about 100, about 90 to about 92, about 92 to about 95, about 94 to about 98,
30 about 96 up to about 100, about 97.00 to about 99.99, about 98.00 to about 99.99, and about
99.00 to about 99.99.

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18. A process for forming a multilayered coating or cladding on a surface of a substrate or mandrel by electrodeposition, comprising:
- (a) providing an electrolyte solution comprising a nickel salt and/or a chromium salt from which nickel and/or chromium can be electrodeposited;
 - 5 (b) providing a conductive substrate or mandrel for electrodeposition;
 - (c) contacting at least a portion of the surface of the substrate or mandrel with the electrolyte solution;
 - (d) passing a seed layer plating current having a density of about 30 to about 50 mA/cm² for a time period of about 1 minute to about 5 minutes through the substrate or mandrel to
10 deposit a nickel and chromium containing seed layer on the substrate or mandrel, where the seed layer comprises greater than about 90% nickel by weight;
 - (e) passing a first electric current having a density of about 100 to about 300 mA/cm² for a time period of about 200 milliseconds to about 400 milliseconds through the substrate or mandrel to deposit a nickel-chromium alloy first layer comprising from about 5 to about
15 35% chromium by weight;
 - (f) passing a second electric current having a density of about 30 to about 50 mA/cm² for a time period of about 200 milliseconds to about 400 milliseconds through the substrate to deposit a nickel and chromium containing second layer comprising greater than about
20 90% nickel by weight;
 - (g) repeating steps (e) and (f) 10 or more times, thereby producing a multilayered coating or cladding having a seed layer and alternating first layers and second layers on the surface of the substrate or mandrel; and
 - (h) optionally separating the substrate or mandrel from the coating or cladding.
19. A process for forming a multilayered coating or cladding on a surface of a substrate or
25 mandrel by electrodeposition, comprising:
- (a) providing an electrolyte solution comprising a nickel salt and/or a chromium salt from which nickel and/or chromium can be electrodeposited;
 - (b) providing a conductive substrate or mandrel for electrodeposition;
 - (c) contacting at least a portion of the surface of the substrate or mandrel with the
30 electrolyte solution;
 - (d) passing a seed layer plating current having a density of about 35 to about 45 mA/cm² for a time period of about 1 minute to about 3 minutes through the substrate or mandrel to

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deposit a nickel and chromium containing seed layer on the substrate or mandrel, where the seed layer comprises greater than about 90% nickel by weight;

- 5 (e) passing a first electric current having a density of about 150 to about 260 mA/cm² for a time period of about 250 milliseconds to about 350 milliseconds through the substrate or mandrel to deposit a nickel-chromium alloy first layer comprising from about 5 to about 35% chromium by weight;
- 10 (f) passing a second electric current having a density of about 35 to about 45 mA/cm² for a time period of about 250 milliseconds to about 350 milliseconds through the substrate to deposit a nickel and chromium containing second layer comprising greater than about 90% nickel by weight;
- (g) repeating steps (e) and (f) 10 or more times, thereby producing a multilayered coating or cladding having a seed layer and alternating first layers and second layers on the surface of the substrate or mandrel; and
- (h) optionally separating the substrate or mandrel from the coating or cladding.
- 15 20. A process according to embodiment 18 or 19, wherein one, two, three, four or more of the first layers comprises chromium in a weight percent (Cr wt.%) range of from about 12 to 26.
21. A process according to any of embodiments 18-20, wherein one, two, three, four or more of the second layers comprises nickel in a weight percent (Ni wt.%) range of at least 95%.

CLAIMS

1. A process for forming a multilayered coating or cladding on a surface of a conductive substrate or mandrel by electrodeposition, comprising:

(a) providing an electrolyte solution comprising a nickel salt and a chromium salt;

(b) providing the conductive substrate or mandrel for electrodeposition;

(c) contacting at least a portion of the surface of the conductive substrate or mandrel with the electrolyte solution;

(d) depositing a seed layer comprising nickel and chromium on the conductive substrate or mandrel by passing a seed layer plating current through the conductive substrate or mandrel for a first time period ranging from 1 minute to 10 minutes to deposit the seed layer comprising nickel and chromium on the substrate or mandrel, the seed layer comprising from about 90% to less than 100% nickel by weight;

(e) depositing a first layer comprising nickel and chromium by passing a first electric current through the substrate or mandrel for a second time period ranging from 50 milliseconds to 500 milliseconds, the first layer comprising from about 5% to about 35% chromium by weight;

(f) depositing a second layer comprising nickel and chromium by passing a second electric current through the substrate or mandrel for a third time period ranging from 50 milliseconds to 500 milliseconds, the second layer comprising from about 90% to less than 100% nickel by weight; and

(g) repeating steps (e) and (f) four or more times, thereby producing a multilayered coating or cladding comprising the seed layer and alternating said first and second layers on the surface of the conductive substrate or mandrel.

2. The process according to claim 1, wherein the seed layer plating current has a density ranging from about 20 mA/cm² to about 60 mA/cm².

3. The process according to claim 1, wherein the seed layer plating current has a density selected from the group consisting of about 20 mA/cm², about 25

mA/cm², about 30 mA/cm², about 35 mA/cm², about 40 mA/cm², about 45 mA/cm², about 50 mA/cm², about 55 mA/cm², and about 60 mA/cm².

4. The process according to any one of claims 1-3, wherein the seed layer comprises from 90.00% to 99.99% nickel by weight.

5. The process according to any one of claims 1-4, wherein the first electric current has a density ranging from about 100 mA/cm² to about 300 mA/cm².

6. The process according to any one of claims 1-4, wherein the first electric current has a density selected from the group consisting of about 160 mA/cm², about 180 mA/cm², about 200 mA/cm², about 220 mA/cm², about 240 mA/cm², and about 260 mA/cm².

7. The process according to any one of claims 1-4, wherein the second electric current has a density ranging from about 20 mA/cm² to about 60 mA/cm².

8. The process according to any one of claims 1-4, wherein the second electric current has a density selected from the group consisting of about 20 mA/cm², about 25 mA/cm², about 30 mA/cm², about 35 mA/cm², about 40 mA/cm², about 45 mA/cm², about 50 mA/cm², about 55 mA/cm², and about 60 mA/cm².

9. The process according to any one of claims 1-4, where steps (e) and (f) are repeated greater than 50 times.

10. The process according to any one of claims 1-4, where steps (e) and (f) are repeated from 4 to 10,000 times.

11. The process according to any one of claims 1-4, wherein two or more of the first layers comprise from about 7% to about 32% chromium by weight.

12. The process according to any one of claims 1-4, wherein each of the first layers comprises from about 5% to about 35% chromium by weight.

13. The process according to any one of claims 1-4, wherein two or more of the second layers comprise from 90.00% to 99.99% nickel by weight.

14. The process according to any one of claims 1-4, wherein each of the second layers comprises from 90.00% to 99.99% nickel by weight.

15. The process according to any one of claims 1-14, further comprising separating the substrate or mandrel from the coating or cladding.

16. The process according to claim 1, wherein:

depositing the seed layer comprises passing the seed layer plating current having a density of about 30 mA/cm² to about 50 mA/cm² through the conductive substrate or mandrel for a time period of about 1 minute to about 5 minutes;

depositing the first layer comprises passing the first electric current having a density of about 100 mA/cm² to about 300 mA/cm² through the conductive substrate or mandrel for a time period of about 200 milliseconds to about 400 milliseconds;

depositing the second layer comprises passing the second electric current having a density of about 30 mA/cm² to about 50 mA/cm² through the conductive substrate or mandrel for a time period of about 200 milliseconds to about 400 milliseconds; and

steps (e) and (f) are repeated 10 or more times.

17. The process according to claim 1, wherein:

depositing the seed layer comprises passing the seed layer plating current having a density of about 35 mA/cm² to about 45 mA/cm² through the conductive substrate or mandrel for a time period of about 1 minute to about 3 minutes;

depositing the first layer comprising passing the first electric current having a density of about 150 mA/cm² to about 260 mA/cm² through the conductive substrate or mandrel for a time period of about 250 milliseconds to about 350 milliseconds;

depositing the second layer comprises passing the second electric current having a density of about 35 mA/cm² to about 45 mA/cm² through the conductive substrate or mandrel for a time period of about 250 milliseconds to about 350 milliseconds; and

steps (e) and (f) are repeated 10 or more times.

18. The process according to claim 16 or 17, wherein two or more of the first layers comprise from about 12% to 26% of chromium by weight.

19. The process according to claim 18, wherein two or more of the second layers comprise at least 95% nickel by weight.