July 24, 1962 T. BERZINS 3,045,334

ALLOY AND COMPOSITE METAL PLATE

Filed Oct. 1, 1958

FIG. 1

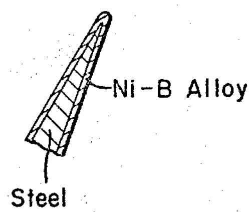


FIG. 2

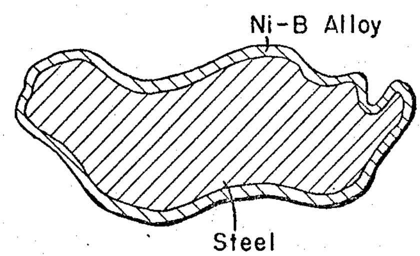


FIG. 3

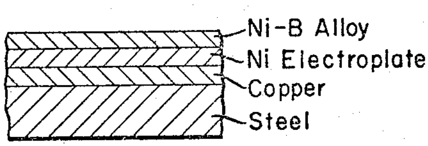


FIG. 4

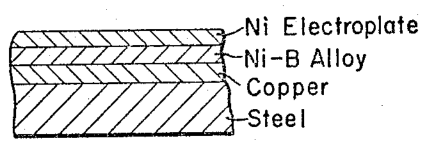
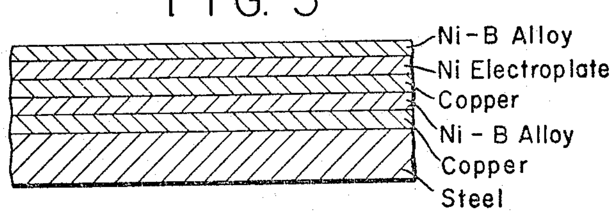


FIG. 5



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ALLOY AND COMPOSITE METAL PLATE
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This invention relates to chemical plating and more particularly it relates to the chemical plating of new nickel-boron and cobalt-boron alloys from new aqueous chemical plating baths.

This application is a continuation-in-part of my copending application Serial No. 669,290, filed July 1, 1957, now abandoned, which is a continuation-in-part of application Serial No. 634,142, filed January 15, 1957 (now abandoned). This application is also related to my copending applications filed of even date herewith and identified as Serial No. 764,490 and Serial No. 765,017.

The chemical plating or deposition of metals or alloys by chemical reduction of metal ions on the surface of the article to be plated has been known for some time. Heretofore, cobalt and nickel deposits have been obtained by a chemical reduction process in which an alkali metal hypophosphite is employed as the reducing agent. Such deposits are not pure metal but contain around 5% to 7% phosphorus.

It is another object of this invention to produce a new series of nickel-boron and cobal-boron alloys which have particularly desirable properties as metal plates or coatings on various materials.

It is another object of this invention to provide a new chemical plating process for the deposition of nickel and cobalt in the form of their boron-containing alloys from an aqueous solution on the surface of a material which catalyzes the plating or deposition of the nickel or cobalt from the solution.

It is still another object of this invention to provide new equeous chemical plating solutions from which new, hard, adherent, corrosion- and wear-resistant coatings of nickel-boron or cobalt-boron alloys can be chemically deposited on certain catalytically active materials.

Other objects of the invention will become apparent from the following detailed description of the invention.

The above objects may be accomplished by producing a new plating solution consisting essentially of an aqueous alkaline solution of a nickel or cobalt salt, a borohydride, and an agent which by forming a comlex compound with nickel or cobalt will maintain the same in solution. New nickel-boron or cobalt-boron alloys may be chemically deposited from such plating solutions onto the surfaces of objects to be plated by placing into contact with the solutions such objects the surface of which is composed of nickel, cobalt, iron, steel, aluminum, zinc, palladium, platinum, copper, brass, manganese, chromium, molybdenum, tungsten, titanium, tin, silver, carbon or graphite. These materials function catalytically to cause a reduction of the nickel or cobalt ions to nickel-boron or cobalt-boron alloys by the borohydride present and thereby deposit such alloys in a uniform layer on these metal surfaces.

To avoid reaction between the nickel or cobalt salts and the borohydride present in the solution and the precipitation of finely divided nickel or cobalt borides in the mass of the plating solution, and to confine the deposition of the nickel or cobalt and the boron present in the solution to the chemical reduction of the nickel or cobalt ions and some of the boron in borohydride ions to metallic nickel-boron or cobalt-boron alloys on the surfaces of the objects to be plated, the activity of the nickel, cobalt and borohydride ions is controlled in the plating solutions. The activity of the borohydride ions

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is controlled by adjusting the free alkali content, as measured by the hydroxyl ion content, of the bath. The activity of the metal ions is controlled by the addition of an agent which forms with the nickel or cobalt ion a complex ion that is soluble in the plating solution. These nickel or cobalt complex ion-forming agents are often referred to as complexing agents or sequestering agents.

In using borohydride as the reducing agent in the process of this invention it is also essential to combine the bath ingredients in such a manner as to avoid reaction between the nickel or cobalt salts and the borohydride. It is necessary to first add to the aqueous solution of the nickel or cobalt salt a complexing agent to form a nickel complex salt in the aqueous solution and then thoroughly alkalinize the solution before addition thereto of the borohydride. If the borohydride is added before the nickel or cobalt complexions are formed in the alkaline solution, it will react instantaneously to form a precipitate of finely divided nickel or cobalt borides. Such borides cannot again be easily brought into solution. It is preferred to dissolve the nickel salt, e.g., nickel-chloride, together with the complexing agent in water and then add thereto an aqueous solution of NaOH. The borohydride, e.g., sodium borohydride, is dissolved in a small amount of an aqueous solution of NaOH. These two solutions are then carefully mixed with stirring.

The initiation of the plating process can be speeded up, particularly when working at temperatures below about 70° C., by contacting the surface of the material to be plated with a more electro-negative metal such as aluminum, while in contact with the plating solution. Since nickel and cobalt and their alloys with boron are good catalysts for the reduction of the nickel or cobalt ions to metallic nickel or cobalt in the presence of the borohydride ions, once the initial deposit of these metals is obtained upon a surface, the plating will continue as long as the solution remains workable.

Non-metallic materials such as glass and various plastics are in general noncatalytic. However, the surface of noncatalytic materials can be sensitized to be catalytic by producing a film of one of the catalytic materials on these surfaces. This can be accomplished by a variety of techniques known to those skilled in the art. A preferred procedure involves dipping articles of glass or plastic in a solution of stannous chloride and then contacting the treated surface with a solution of palladium chloride. A monolayer of palladium is thus produced. The article can then be chemically plated with nickel-boron or cobalt-boron alloys by the process of this invention.

The term "catalytic surface" as used in connection with my chemical plating process refers to the surface of any article composed of the aforesaid catalytic materials or coated therewith, or to the surface of noncatalytic material which has been sensitized by producing a film of said catalytic materials on its surface.

The borohydride reducing agent may consist of any water-soluble borohydride having a good degree of solubility and stability in aqueous solutions. Sodium and potassium borohydrides are preferred. In addition, substituted borohydrides in which not more than three of the hydrogen atoms of the borohydride ion have been replaced can be utilized. Sodium trimethoxyborohydrides, $NaB(OCH_3)_3H$, is illustrative of the compounds of this type.

Since the oxidation of borohydride ions by water is very rapid in acid and neutral solutions, alkaline plating solutions are used. Due to the alkalinity of the solution, the sequestering agent has to form sufficiently strong complexes with the metal ions to prevent the precipitation of nickel or cobalt hydroxide or basic salts. Furthermore, the complex metal ions must be soluble in the plating solution and be so stable that they will not react with borohydride in the bulk of solution but only at a catalytic surface.

The nickel- or cobalt-complexing or sequestering agents suitable for use in accordance with this invention include ammonia and organic complex-forming agents containing one or more of the following functional groups: primary amino group ($-NH_2$), secondary amino group (>NH), tertiary amino group (>N—), imino group (=NH), carboxy group (—COOH), and hydroxy group (—OH). Preferred agents include ethylene diamine, diethylene triamine, triethylene tetramine, ethylenediamine tetraacetic acid, citric acid, tartaric acid, and ammonia. Related polyamines and N-carboxymethyl derivatives thereof may also be used. Cyanides may not be employed since the plating process will not function in their presence.

Cobalt and nickel may be employed in the form of any water-soluble salt which is not antagonistic to the plating process. Cyanides and thiocyanates fall in the latter category. Salts of oxidizing acids are not desirable since they consume borohydrides and thus impair its proper utilization in the reduction process. Chlorides, sulfates, formates, acetates and other salts whose anions are substantially inert with respect to the other ingredients in the chemical plating bath are satisfactory.

In carrying out the plating process, the article to be plated and normally formed of a catalytic material is properly prepared by mechanical cleaning, degreasing and acid pickling, according to the standard practice in electroplating processes. The cleaned article is then immersed in a suitable volume of the hot aqueous plating solution. Almost imediately, hydrogen bubbles can be observed forming on the catalytic surface of the article immersed and escaping in a steady stream from the bath, while the surface of the article is slowly coated with a metallic plate. The plating is continued until the metal ions are depleted from solution, or until the evolution of hydrogen gas stops, indicating that all the borohydride is consumed in the plating process.

The nickel-boron or cobalt-boron alloy plates deposited on metal surfaces in accordance with the process of this invention are new alloys of great utility. These alloy plates have been found to contain between about 1–8% by weight of boron.

Additionally, these alloy plates are structurally quite distinct from alloys obtained by conventional plating processes. While the plates are difficult to analyze, it has been recently determined, through X-ray diffraction and X-ray microscopy techniques, that the boron is imbedded in an amorphous matrix of the metal plated in both nickel- or cobalt-boron plating processes. The matrix metal is essentially amorphous to X-rays (CuK_α radiation e.g.) showing only about 5–10% crystalline nickel or cobalt.

All alloy plates that are prepared in accordance with the present invention contain about 92–99% of nickel or cobalt and about 1–8% boron. Approximately 5–10% of the metal is present as crystalline nickel or cobalt; the remainder of the metal is structurally unorganized and noncrystalline. The boron and crystalline metal are uniformly dispersed and distributed throughout the matrix.

Accordingly, throughout the specification and claims, any reference to amorphous matrix of nickel or cobalt designates an amorphous, structurally unorganized metal insofar as crystallinity is detectable by X-ray examination using CuK_α radiation.

After heat treatment for one hour at 600° C., the X-ray diffraction patterns of nickel-boron plates show the presence of crystalline Ni_3B and additional crystalline nickel, indicating that boron and nickel have chemically reacted and that the small amount (5–10%) of crystalline nickel has grown.

It has been further found that the amount of crystalline nickel present in the amorphous matrix is as high as about 10% of the total nickel content present and possibly higher. The amount of crystalline cobalt present in the amorphous matrix of cobalt is frequently lower, sometimes comprising less than 5%.

The process of using amine-boranes as disclosed in my copending application Serial No. 764,490 identified above, is another method for producing alloy plates having the above characteristics.

The nickel-boron alloy plates to this invention are bright, very hard, exceptionally uniform in thickness, relatively free from porosity, and have a high degree of corrosion resistance as compared to electroplated nickel.

The hardness of the nickel-boron alloy plates of this invention is approximately equal to the hardness of commercial chromium electroplates. The hardness of these nickel-boron alloy plates as determined with a 10 gram load on a Vickers hardness measuring device is as follows:

	Vickers hardness No.
Nickel-boron alloy as plated	780–810
Nickel-boron alloy heated at 325° C. for one hour	890–910
Nickel-boron alloy heated at 440° C. for one hour	570
Nickel-boron alloy heated at 600° C. for one hour	520
Nickel-phosphorus alloy plated from nickel salt-sodium hypophosphite bath of U.S. Patent No. 2,658,841, as plated (Kanigen plate)	450
Nickel electroplate produced from Watts nickel electroplating bath as described in the textbook "Modern Electroplating" published by J. Wiley and Sons, Inc., New York, N.Y., 1953, as plated	325

The nickel-boron alloy plates of this invention show considerable oxidation resistance at elevated temperatures and can be used to protect high temperature construction materials against oxidation. These plates are less porous than commercial nickel electroplates; e.g., 0.1 mil thick nickel-boron plate is less porous than 0.8 to 1.0 mil thick conventional nickel electroplate. Consequently, they offer better corrosion protection than two to four times thicker nickel electroplate, as seen by accelerated corrosion tests. Thus, my nickel-boron plates can be used, and with better results, wherever conventional nickel electroplates are used for corrosion protection.

In my plating processes the plating takes place at a uniform rate wherever there is contact between the part being plated and the plating solution. In other words, the throwing power of the bath is infinite, and there is no substantial variation in the plate thickness even for the most complicated shapes. Thus, my nickel-boron plates are uniform in recesses, as well as on exposed parts of the object being plated, and there is no build-up of coating on points or edges. These conditions are difficult or impossible to achieve by electroplating. Because of the uniformity and the protective qualities of these nickel-boron plates, my plating process is ideally suitable for plating objects of irregular or complicated shapes which are difficult or impossible to plate by conventional methods (e.g., complex fabricated assemblies; parts having screw threads, indentations, or holes which must be uniformly plated with the protective deposit; and the interior of vessels, tubes, and pipes).

Additionally, plates produced as disclosed herein are useful as ornamental designs, since a non-catalytic surface may be selectively sensitized by the use of stannous chloride and palladium chloride as described above. Similarly, these metal plates may be deposited in predetermined patterns that serve as electrical conductors. Circuit patterns may thus be selectively plated on the activated areas of an inexpensive sheet of material that is normally non-catalytic.

Nickel plates obtained by electroplating and by chemical plating were compared with the "ferroxyl" test for porosity. The following nickel plates were compared:

nickel-boron plate, nickel-phosphorus plate (obtained by Kanigen process), and electroplated nickel (standard Watts bath). In performing the "ferroxyl" test, nickel plated steel samples were contacted for one minute with filter paper soaked in the "ferroxyl" test solution. This test solution was prepared by dissolving five grams of pure agar-agar in one liter of water containing one gram of NaCl and one gram of $K_3Fe(CN)_6$. The presence of a pore in the nickel plate is indicated by the appearance of a blue spot on the "ferroxyl" test paper. The results of "ferroxyl" tests showed that nickel plated by chemical reduction was less porous than electroplated nickel, e.g., 0.1 mil thick nickel-boron alloy produced by this invention was less porous than 0.4–0.8 mil thick electrodeposit. The porosity of nickel-boron plates was comparable to that of nickel-phosphorus (Kaniegn) plates.

It was found that a thin nickel-boron strike before or after electroplating decreased the porosity of electroplated nickel markedly. The results of "ferroxyl" tests indicated that a 0.02–0.005 mil thick nickel-boron strike made 0.2–0.4 mil thick nickel electroplates practically non-porous, while, without a nickel-boron strike, a thickness of 1.0–1.5 mil was required to eliminate porosity of nickel electroplates. Thus, a thin nickel-boron strike, particularly when used as an overcoat, seals the pores in nickel electroplates very effectively.

Nickel-boron plates also exhibited a higher corrosion resistance than conventional nickel electroplates. It was observed that a thin nickel-boron strike before, and particularly after, electroplating increased the corrosion resistance of electroplated nickel to a considerable extent. Thus, 0.2–0.4 mil thick nickel electroplate, in combination with 0.02–0.03 mil thick nickel-boron strike, protected steel against corrosion in 1% NaCl solution better than 1 mil thick nickel electroplate alone. The corrosion protection of copper electroplates, in combination with thin nickel-boron undercoats or overcoats, was compared to that of standard copper-nickel electroplates. The "Corrodkote" test was used in making this comparison. This test involves coating samples with a corrosive paste containing 0.035 gram cupric nitrate, 0.165 gram ferric chloride, 1.0 gram ammonium chloride, 30 grams kaolin, and 50 ml. water, and exposing the coated samples at 25° C. and 92% relative humidity for twenty hours. Steel samples were electroplated with copper and nickel to the following thicknesses:

(1) 0.2 mil Cu+0.2 mil Ni
(2) 0.35 mil Cu+0.40 mil Ni
(3) 0.6 mil Cu+0.60 mil Ni
(4) 1.0 mil Cu+1.0 mil Ni

These electroplated samples, corresponding to ASTM-AES A166 specifications, were used as standards in "Corrodkote" corrosion tests. Copper was plated from commercial copper cyanide high-speed copper plating baths. Nickel plating was done by a commercial nickel plating process.

Steel samples, electroplated with copper in thicknesses ranging from 0.2 mil to 1.0 mil and having about 0.18 mil thick Ni-B overcoat or undercoat, were prepared. The "Corrodkote" test was made with these samples and with the aforementioned standard samples under the same conditions. In this test copper-nickel electroplates were cracked and corroded to a considerable extent, while the copper electroplates with nickel-boron overcoats remained practically unattacked.

The process of this invention therefore permits the plating of steel or copper, or other metals as above described, with much thinner coatings of nickel than heretofore considered practical. Moreover, such thin coatings of nickel-boron will be harder, more corrosion resistant, less porous, and longer lasting than previously known relatively thick electrodeposited nickel coatings.

Further features of this invention comprising the new nickel-boron or cobalt-boron alloy plates, included in certain laminated structures, will be more clearly apparent

by reference to the following description when taken in connection with the accompanying drawings, in which

FIGURE 1 is a cross-sectional view of a portion of a steel razor blade plated in accordance with this invention;

FIGURE 2 is a cross-sectional view of another embodiment of a steel object plated in accordance with this invention;

FIGURES 3, 4 and 5 are cross-sectional views of laminated metal structures produced in accordance with this invention.

Referring to FIGURE 1, the portion of the steel razor blade plated with the nickel-boron alloy illustrates the exceedingly uniform plate obtained by the chemical reduction plating process of this invention particularly around the sharp edge of the blade. Such uniform plate can even be obtained when plating objects of greatly varying contour as shown in FIGURE 2.

FIGURE 3 illustrates an embodiment in which a steel sheet is plated with copper, then with a nickel electroplate and finally with a nickel-boron alloy overcoat. Such use of a nickel-boron alloy overcoat permits the plating of a very thin nickel electroplate so that the total nickel and nickel-boron alloy thickness is considerably less than heretofore considered necessary for a nickel electroplating. Furthermore, no final plate of chromium, as is usually employed, will be necessary in view of the hardness and corrosion-resistance of the nickel-boron alloy overcoat. If a chromium plating is desired because of the color, the nickel-boron or cobalt-boron alloy plate of this invention will readily accept a chromium plate from a conventional chromium plating bath.

FIGURE 4 illustrates a laminated plated structure in which the copper plated steel is first plated with a nickel-boron alloy as an undercoat for a final nickel electroplate. This structure permits the use of thin nickel plates which will be superior from a standpoint of permanence than much thicker electroplates of nickel.

FIGURE 5 shows a laminated structure in which a nickel-boron alloy plate is used between copper undercoats to eliminate porosity and softness of copper plates and another nickel-boron alloy over-plate over nickel electroplate to impart a final corrosion-resistance, hardness, and non-porosity to the electroplated nickel. Alternatively a nickel-boron alloy plate may be plated directly on steel followed by a copper or nickel electroplate.

The following are illustrative examples of bath compositions and working conditions for nickel and cobalt plating solutions.

EXAMPLE I

Sequestering Agent: Ethylenediamine

Nickel chloride ($NiCl_2 \cdot 6H_2O$)	grams/liter	20
Ethylenediamine (98%)	do	45
Sodium hydroxide (NaOH)	do	40
Sodium borohydride ($NaBH_4$)	do	0.67
Temperature of the plating solution	°C	97

Preparation of the plating bath.—The given amount of sodium hydroxide was dissolved in 500 ml. of cold water. A small portion (about 50 ml.) of this solution was used to dissolve sodium borohydride; the rest of the solution was mixed with the solution of nickel chloride and ethylenediamine which was prepared by dissolving the given amount of these chemicals in a separate 500 ml. portion of distilled water. The solution of sodium borohydride was then added to this mixture. The solution was transferred to the plating vessel (alkali resistant glass beaker) and heated to the given temperature.

Clean samples of copper, brass and steel were immersed in the plating bath and kept there for thirty minutes. Bright, adherent and uniform nickel-boron plates were obtained on all the samples immersed in the plating bath. The amount of nickel-boron alloy deposited in thirty minutes was 3.9–4.6 mg./cm.^{2}.

EXAMPLE II

The composition and preparation of the plating bath was the same as described for Example I. Samples of the following materials were immersed in the plating bath: iron, cast iron, stainless steel, manganese, tungsten, chromium, molybdenum, titanium, tin, silver, and graphite. After thirty minutes, the samples were removed from the bath. All the samples showed a gain of weight and the presence of nickel plate.

EXAMPLE III

The composition and preparation of the plating bath was the same as described for Example I. The surface of a polystyrene rod was roughened and cleaned with steel wool and foaming cleanser. The rod was then immersed for thirty seconds in chromic-sulfuric acid cleaning solution, rinsed and placed in the plating bath. After ten minutes of plating only a few spots of the polystyrene sample were covered with nickel plate. The surface of a second polystyrene rod cleaned by the aforementioned procedure was sensitized in the following manner: The sample was (*a*) dipped in stannous chloride solution at 25° C. for one minute (70 g. of $SnCl_2$+40 ml. of conc. HCl in 1000 ml. water), (*b*) rinsed with water, (*c*) dipped in palladium chloride solution at 25° C. for one minute (0.1 g. of $PdCl_2$+1 ml. of conc. HCl in 1000 ml. water), (*d*) rinsed with water. The sensitized sample of polystyrene was then placed in the plating bath. After ten minutes of plating, a uniform nickel plate was obtained on this sample.

EXAMPLE IV

Sequestering Agent: Triethylenetetramine

Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	grams/liter	33
Triethylenetetramine	do	87
Sodium hydroxide (NaOH)	do	40
Sodium borohydride ($NaBH_4$)	do	1
Temperature	° C.	97

The plating bath was prepared in the same way as for Example I. Clean samples of steel and copper were immersed for thirty minutes in the bath. Bright and adherent nickel-boron plates were obtained. The amount of nickel-boron alloy deposited in thirty minutes was about 1 mg./cm.^{2}.

EXAMPLE V

Sequestering Agent: Sodium Potassium Tartrate

Nickel chloride ($NiCl_2 \cdot 6H_2O$)	grams/liter	20
Sodium potassium tartrate ($NaKC_4H_4O_6 \cdot 4H_2O$)	do	65
Sodium hydroxide (NaOH)	do	40
Sodium borohydride ($NaBH_4$)	do	0.67
Temperature	° C.	97

The plating bath was prepared in the same way as for Example I. Clean copper wire was immersed for fifteen minutes in this plating bath. Bright and adherent nickel-boron plate was obtained on the copper wire. The amount of nickel-boron alloy deposited in fifteen minutes was about 0.25 mg./cm.^{2}.

EXAMPLE VI

Sequestering Agent: Ethylenediaminetetraacetate

Cobalt chloride ($CoCl_2 \cdot 6H_2O$)	grams/liter	10
Disodium salt of ethylenediaminetetraacetic acid (formula weight: 372.3)	do	35
Sodium hydroxide (NaOH)	do	40
Sodium borohydride ($NaBH_4$)	do	0.5
Temperature	° C.	92

The plating bath was prepared in the same way as for Example I. Clean samples of copper, brass, and steel were immersed for thirty minutes in the plating bath. Semi-bright, adherent and uniform cobalt-boron plates were obtained on all the samples immersed in the plating bath. The amount of cobalt-boron alloy deposited in thirty minutes was 0.35–0.40 mg./cm.^{2}.

EXAMPLE VII

Plating baths were prepared as follows.—Varying quantities of nickel chloride ($NiCl_2 \cdot 6H_2O$) and ethylene diamine (98%) were dissolved in such quantities of water as to produce a series of 500 ml. solutions as set forth in the table below. NaOH was dissolved in 500 ml. water. 50 ml. of the aqueous solution of NaOH was used to dissolve therein varying quantities of sodium borohydride as set forth below. The other 450 ml. of NaOH solution was added to the aqueous solution of nickel chloride and ethylenediamine. The sodium borohydride solution was then added to the alkaline solution of nickel chloride and ethylenediamine. The resulting solution, having a clear violet color was heated in a glass breaker to a temperature of either 95° C. or 98° C. as noted.

Copper sheets were immersed in the heated solutions for a period of one-half hour. Bright, smooth, uniform coatings of nickel-boron were formed on the copper sheet. The nickel-boron plates were stripped from the copper by placing the plated copper in 2 molar HNO_3 having a temperature of 40° C. The metal ions in the HNO_3 solution were then separated from the boric acid by passing the solution through a column packed with a phenolic cation-exchange resin containing methylene sulfonic polar groups ("Amberlite" I.R. 120(H), manufactured by Rohm and Haas Chemical Company, Philadelphia, Pa.). The boric acid content of the acid solutions was then determined tetrimetrically in the presence of mannitol, using a pH meter to indicate the end-point. See H. Kramer, Anal. Chem. 27, 144 (1955). The boron content of the plates is shown in the following tabulated results.

INITIAL COMPOSITION OF PLATING

No.	Solutions in g. mole/liter				Temperature, ° C.	Boron Content, percent
	$NiCl_2$	Ethylenediamine	NaOH	$NaBH_4$		
1	0.1	0.9	1.0	0.013	98	5.0
2	0.1	0.9	1.0	0.020	98	5.4
3	0.1	0.9	1.0	0.026	98	5.5
4	0.1	0.9	0.1	0.026	98	5.7
5	0.1	0.9	1.0	0.026	95	5.3
6	0.1	2.0	1.0	0.020	98	5.0
7	0.1	2.0	1.0	0.026	98	5.4
8	0.05	0.45	1.0	0.026	98	6.0
9	0.025	0.225	1.0	0.013	98	6.4
10	0.025	0.225	1.0	0.020	98	6.6
11	0.2	1.8	1.0	0.026	98	5.6

EXAMPLE VIII

Sequestering Agent: Ammonia

Nickel chloride ($NiCl_2 \cdot 6H_2O$)	grams/liter	24
Ammonium hydroxide 28% aq. sol.	ml./liter	120
Sodium borohydride ($NaBH_4$)	gm./liter	0.4
Temperature of the plating solution	° C.	60

Preparation of the plating bath.—The given amount of nickel chloride was dissolved in water after which 100 ml. of the ammonium hydroxide was added. To this solution of nickel chloride and ammonium hydroxide was added water to a total solution of 980 ml. The given amount of sodium borohydride was dissolved in 20 ml. ammonium hydroxide and this solution added to the nickel chloride-ammonium hydroxide solution. The solution was transferred to the plating vessel (alkali resistant glass breaker) and heated to a temperature of 60° C.

Clean samples of copper were immersed in the plating bath and kept there for thirty minutes. Bright, adherent and uniform nickel-boron plates were obtained on all the samples immersed in the plating bath. The amount of nickel-boron alloy deposited in thirty minutes was 0.6 mg./cm.^{2}.

In general, the boron content of the plates increases slightly when the ratio of sodium borohydride to nickel salt in the bath is increased, but, as seen from the above table, in a particular system the variations in boron content are very small. Other systems containing different complexing agents can reduce the amount of boron deposited in the plate, especially in the instance of cobalt-boron plates. Under varying conditions in cobalt-boron plating baths, the amount of boron in the plate may be as low as about 1%. All of the plates obtained through the practice of the herein-disclosed invention, however, will contain about 1–8% by weight of boron. Nickel-boron plates containing about 3–7% boron are produced by preferred methods and have shown excellent qualities.

Temperature is one of the most important factors affecting the rate of plating. The rate of plating increases rapidly with temperature. At 60° C. the rate of plating is only about one-tenth of that at 90° C. When high rate of plating is desired, the plating bath should be operated as near to the boiling point of the solution as convenient, preferably above 90° C.

The most favorable range of borohydride concentration lies in the range of 0.005 to 0.05 mole per liter. In the case of sodium borohydride this concentration lies between 0.2 to 1.5 grams per liter. Higher concentrations can be used when the plating bath is operated at lower temperatures. At higher temperatures and high concentrations of sodium borohydride, the spontaneous decomposition (i.e., reduction of nickel or cobalt ions by borohydride in the bulk of solution) could occur. Therefore, it is advantageous to replenish the bath with sodium borohydride intermittently rather than use high initial borohydride concentrations.

The concentration of hydroxyl ions in the plating bath may vary from 0.001 to 2.0 moles per liter, the preferable range being from 0.1 to 1.0 mole per liter. Low hydroxyl ion concentration can be used at the lower temperatures; the use of a high hydroxyl ion concentration at high temperatures generally requires a large excess of sequestering agent to prevent the formation of insoluble metal hydroxide or basic salts. Any alkali metal hydroxide can be used to provide hydroxyl ions. When amines or ammonia are used as sequestering agents, the alkali metal hydroxide may be omitted from the composition of the plating solution. The pH of the plating solution is high, usually greater than 11.

The preferable initial concentration of nickel or cobalt salts may vary from 0.02 to 0.2 mole per liter. The use of higher concentrations may result in spontaneous decomposition of the plating solution.

The amount of sequestering agent to be added to the plating solution depends upon the nature of the sequestering agent and the amount of the metal salt present in the bath. In alkaline solutions, the preferred molar ratio of nickel chloride to ethylenediamine lies between 1:3 and 1:10, the molar ratio of nickel sulfate (or chloride) to triethylenetetramine or sodium potassium tartrate between 1:2 and 1:10, and the molar ratio of cobalt chloride to ethyelenediamine tetraacetic acid between 1:1 and 1:5. A small excess of the sequestering agent increases the rate of plating, but generally decreases the stability of the plating bath. In addition to the aforementioned sequestering agents, ammonium hydroxide and water-soluble citrates may be used to sequester nickel ions, and ammonium hydroxide, tartrates and citrates may be used for sequestering cobalt ions particularly when the bath is operated at the lower temperatures and when lower concentrations of hydroxyl ions and metal salts are used.

Throughout the specification and claims, any reference to parts, proportions and percentages refers to parts, proportions and percentages by weight unless otherwise specified.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A metal-boron alloy plate selected from the group consisting of nickel-boron and cobalt-boron plates, said plate being an amorphous matrix of said metal containing about 1–8% by weight of boron and about 92–99% of said metal, about 5–10% by weight of said metal being in crystalline form, said amorphous matrix of metal being in structurally disorganized form and containing said boron and said crystalline metal as uniform dispersions.

2. A nickel-boron alloy plate, said plate being an amorphous matrix of nickel containing about 3–7% by weight of boron and about 93–97% nickel, about 5–10% by weight of said nickel being in crystalline form, said amorphous matrix of nickel being in structurally disorganized form and containing said boron and said crystalline nickel as uniform dispersions.

3. A laminated plate structure comprising a lamina of a catalytic material selected from the group consisting of nickel, cobalt, iron, steel, aluminum, zinc, palladium, platinum, copper, brass, manganese, chromium, molybdenum, tungsten, titanium, tin, silver, carbon and graphite and bonded thereto a lamina of a plate of claim 1.

4. A laminated plate structure comprising a lamina of a catalytic material selected from the group consisting of nickel, cobalt, iron, steel, aluminum, zinc palladium, platinum, copper, brass, manganese, chromium, molybdenum, tungsten, titanium, tin, silver, carbon and graphite and bonded thereto a lamina of a plate of claim 2.

5. A cobalt-boron alloy plate, said plate being an amorphous matrix of cobalt containing about 1–8% by weight of boron and about 92–99% of cobalt, about 5–10% by weight of said cobalt being in crystalline form, said amorphous matrix of cobalt being in structurally disorganized form and containing said boron and said crystalline cobalt as uniform dispersions.

6. A laminated plate structure comprising a lamina of copper and bonded thereto a lamina of a plate of claim 1.

7. A laminated plate structure comprising a lamina of chromium and bonded thereto a lamina of a plate of claim 1.

8. A laminated plate structure comprising a lamina of electroplated nickel and bonded thereto a lamina of a plate of claim 1.

9. A laminated plate structure comprising a lamina of steel and bonded thereto a lamina of a plate of claim 1.

10. A laminated plate structure comprising a lamina of copper and bonded thereto a lamina of a plate of claim 2.

11. A laminated plate structure comprising a lamina of chromium and bonded thereto a lamina of a plate of claim 2.

12. A laminated plate structure comprising a lamina of electroplated nickel and bonded thereto a lamina of a plate of claim 2.

13. A laminated plate structure comprising a lamina of steel and bonded thereto a lamina of a plate of claim 2.

References Cited in the file of this patent

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,045,334 July 24, 1962

Talivaldis Berzins

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 28, for "another" read -- an --; line 29, for "cobal-boron" read -- cobalt-boron --; line 48, for "comlex" read -- complex --; column 3, line 33, for "imediately" read -- immediately --; column 4, line 8, for "to" read -- of --; column 5, line 16, for "(Kaniegn)" read -- (Kanigen) --; column 8, lines 18 and 70, for "breaker", each occurrence, read -- beaker --.

Signed and sealed this 3rd day of December 1963.

(SEAL)
Attest:

ERNEST W. SWIDER

Attesting Officer

EDWIN L. REYNOLDS

Acting Commissioner of Patents