March 27, 1973 K. PARKER 3,723,078
ELECTROLESS ALLOY COATINGS HAVING METALLIC
PARTICLES DISPERSED THERETHROUGH
Original Filed Oct. 25, 1968

FIG. 1

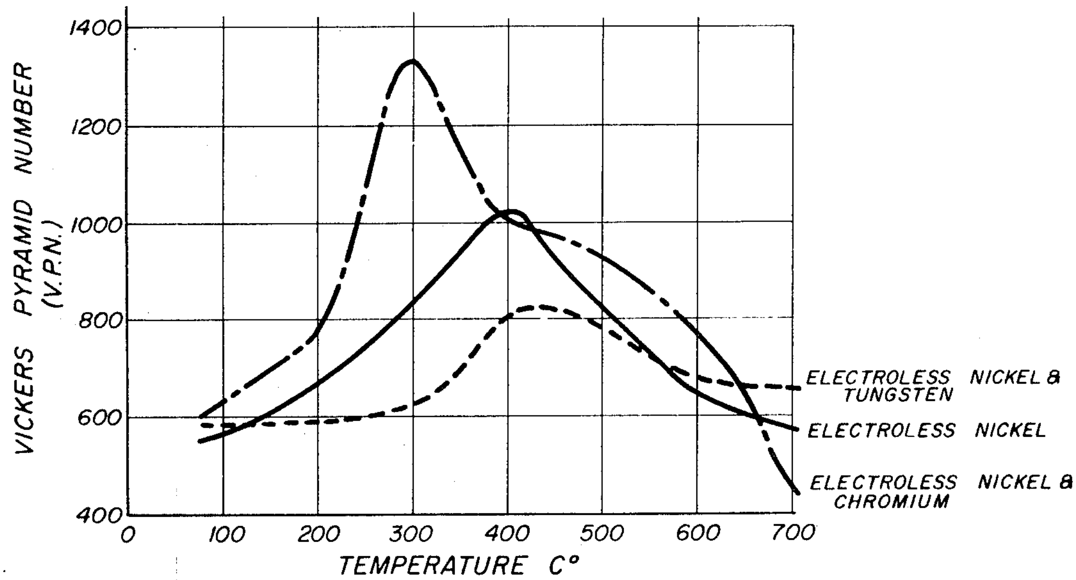
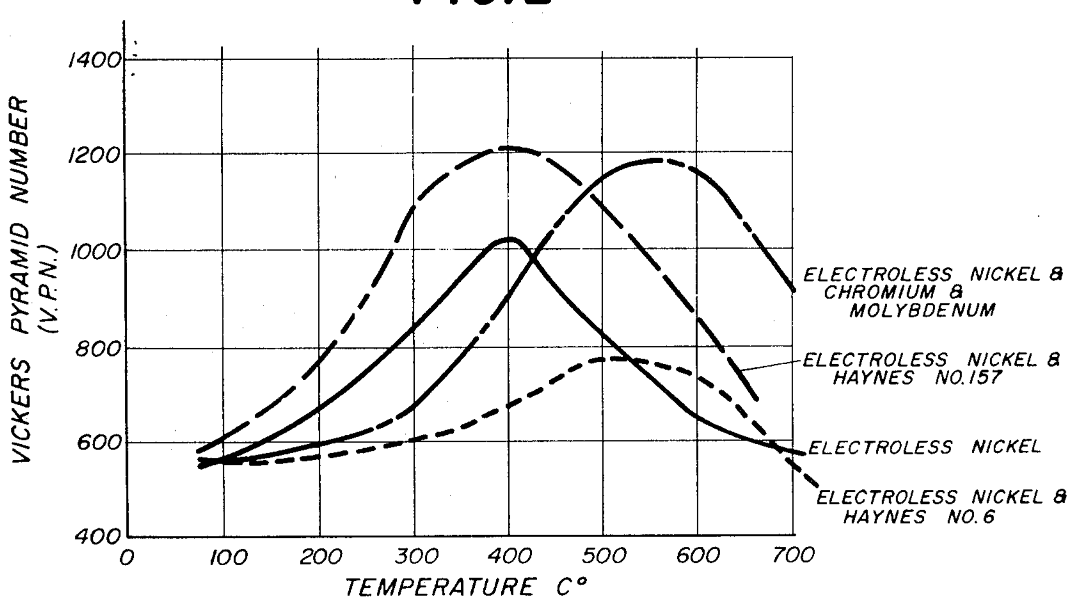


FIG. 2



INVENTOR
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ELECTROLESS ALLOY COATINGS HAVING METALLIC PARTICLES DISPERSED THERETHROUGH

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Original application Oct. 25, 1968, Ser. No. 770,573, now Patent No. 3,562,000, dated Feb. 9, 1971. Divided and this application Sept. 28, 1970, Ser. No. 75,829
Int. Cl. B32b *15/00*
U.S. Cl. 29—194 37 Claims

ABSTRACT OF THE DISCLOSURE

There are disclosed herein processes for electroless metallizing workpieces to provide thereon an electroless plating metal coating incorporating therein metallic particles, workpieces produced by such processes and plating baths which are useful in the practice of such processes and for producing such workpieces. These processes generally comprise contacting the workpieces with an electroless metallizing bath consisting of an aqueous solution of an electroless metal plating salt and a chemical reducing agent therefor and a quantity of metallic particles, wherein said particles are essentially insoluble in said bath and inert and non-catalytic and non-poisonous with respect thereto and non-displacing with respect to the electroless plating metal ions in said bath, the particles being present in said bath in an amount by weight no greater than about ten times the weight of the electroless plating metal in said bath expressed as free metal, and maintaining the particles in suspension throughout the bath during the metallizing of the workpiece; the metallizing bath may contain nickel ions or cobalt ions or mixtures thereof as a source of metal and may contain hypophosphite anion or an alkylborazane or a borohydride as the reducing agent, or may contain copper ions as a source of metal with formaldehyde as the reducing agent; the metallic particles are selected from chromium, molybdenum, tungsten, boron, titanium, vanadium, zirconium, niobium, tantalum and alloys thereof; the metallic particles have dimensions in the range from about 0.1 micron to 50 microns; these metallic particles may be maintained in suspension in the bath by mechanical agitation, by passing the bath including the particles over the workpiece, by passing streams of minute bubbles of gas through the bath, by agitation and movement of the workpiece within the bath, or by slowly rotating the workpiece in conjunction with the rapid circulation of the bath; additionally, the electroless plating metal coating having the metallic particles incorporated therein may be heat-treated by heating to a temperature in the range from about 200° C. to about 1,300° C. for at least one-quarter hour to bond said electroless metal coating and said metallic particlesss at the interfaces thereof.

This application is a division of copending application Ser. No. 770,573, filed Oct. 25, 1968 now Pat. 3,562,000, dated Feb. 9, 1971 for Processes of Electrolessly Depositing Metal Coatings Having Metallic Particles Dispersed Therethrough.

The present invention is directed to workpieces having an electroless plating metal coating deposited thereon, the coating having incorporated therein metallic particles.

It is the principal object of the present invention to provide an article of manufacture comprising a workpiece, a metal coating carried by the workpiece and formed of electroless plating metal having dispersed therethrough metallic particles, the particles being essentially insoluble in the electroless plating bath and inert and non-catalytic and non-poisonous with respect thereto and non-displacing with respect to the electroless plating metal ions in the electroless plating bath, the particles having dimensions on the order of from about 0.1 micron to about 50 microns and constituting by volume from about 5% to about 65% of the coating.

Another object of the present invention is to provide an article of manufacture as set forth in which the particles are selected from the group consisting of chromium, molybdenum, tungsten, boron, titanium, vanadium, airconium, hafnium, niobium, tantalum, and alloys thereof.

Another object of the present invention is to provide an article of manufacture as set forth wherein the metal coating carried by the workpiece is formed of electroless nickel.

Still another object of the present invention is to provide an article of manufacture of the type set forth in which the metal coating carried by the workpiece is formed of electroless cobalt.

Still another object of the present invention is to provide a workpiece of the type set forth in which the metal coating is formed of electroless copper.

Still another object of the present invention is to provide an article of manufacture of the type set forth wherein the electroless plating metal and the metallic particles dispersed therethrough are heat treated and bonded at least at the interfaces thereof.

A further object of the present invention is to provide a workpiece of the type set forth wherein the electroless metal coating is formed of nickel. The invention both as to its organization and method of operation, together with further objects and advantages thereof, will best be understood by reference to the following specification and to the several illustrative examples and the appended drawings wherein:

FIG. 1 shows a series of curves illustrating the hardness-temperature relationship of several electroless nickel coatings including various metallic particles as compared to electroless nickel coatings lacking any metallic particles; and

FIG. 2 shows a further series of curves illustrating the hardness-temperature relationship of electroless nickel coatings including still other types of metallic particles as compared with electroless nickel coatings lacking any metallic particles.

In accordance with the present invention, there is provided a workpiece or body having an outer surface that is to carry the desired electroless plating metal coating, the outer surface typically being one that will be subject to contact with corrosive fluids such as acids and the like or that will be subject to sliding or rubbing contact with another surface, whereby it will be subjected to substantial wearing and bearing pressures. First, the surface of the workpiece is cleaned using any one of several well known cleaning methods appropriate to the metal substrate, after which the workpiece is contacted with an electroless metallizing bath containing a quantity of metallic particles, the particles being essentially insoluble in the plating bath and inert and non-catalytic and non-poisonous with respect thereto and non-displacing with respect to the electroless plating metal ions in the bath, the particles being present in the bath in an amount by weight no greater than about ten times the weight of the electroless plating metal in the bath expressed as free metal.

A suitable bath for the practice of this process is, for example, a conventional chemical nickel plating bath of the nickel cation-hypophosphite anion type in which the metallic particles are suspended. During the plating process, the metallic particles are maintained in suspension throughout the bath by mechanical agitation or other such means, whereby after a suitable period of time there is produced on the surface of the workpiece a coating of the electroless plating metal, such as nickel for example, having uniformly dispersed therethrough a quantity of the metallic particles. Thereafter, the workpiece may be subjected to a heat-treatment step in order to alloy or bond the electroless plating metal and the metallic particles at the interfaces thereof thereby imparting desirable characteristics to the coating.

The coatings provided in accordance with the processes set forth herein lend to the workpiece various desirable properties; for example, some of these coatings will increase the corrosion resistance of the workpiece as against such corrosive fluids as acids and the like and against oxidation at high temperatures; additionally, other of these coatings provide a surface which is intrinsically harder than the surface of the workpiece itself, thereby increasing the resistance to wear and abrasion. Other desirable properties may similarly be achieved by employing such coatings on the surface of the workpiece as will be more fully explained hereinafter.

While the processes used to produce the articles of manufacture of the present invention are fundamentally independent of the composition of the workpiece, ordinarily the workpiece is formed of an industrial metal such as steel or iron for example, although the workpiece may be formed of other metallic and non-metallic materials. Where non-metallic materials are utilized as workpieces, these workpieces must first be subjected to a pretreatment step in order to prepare the surface so that it may subsequently receive the electroless metallized coating that is inherently produced in the metallizing process described herein. When the metallizing metal is nickel, the pretreatment on plastics and non-conducting surfaces may be that as disclosed in U.S. Pat. No. 2,690,401, granted on Sept. 8, 1954, to Gregoire Gutzeit, Wm. J. Crehan and Abraham Kreig, and in U.S. Pat. No. 2,690,402 granted on Sept. 28, 1954, to Wm. J. Crehan.

The processes used to produce the articles of manufacture of the present are particularly beneficial in providing electroless plating metal coatings on workpieces formed of such materials as aluminum, magnesium, copper, nickel, titanium, or beryllium, whereby desirable surface properties may be imparted to the workpiece without the necessity of a high heat-treatment step.

It will be understood that a large number of metallizing processes of the electroless type may be utilized including electroless nickel processes, electroless cobalt processes and electroless copper processes. The articles of manufacture of the present invention are preferably produced by electroless nickel processes, specifically those using hypophosphite anions as the electroless reducing agent. Furthermore, the electroless metallizing process in the case of electroless nickel is independent of the particular composition of the nickel plating bath of the nickel cation-hypophosphite anion type that is employed in the chemical nickel plating step, whereby a wide variety of these conventional chemical nickel plating baths may be employed.

The plating bath disclosed in U.S. Pat. No. 2,822,294, granted on Feb. 4, 1958, to Gregoire Gutzeit, Paul Talmey and Warren G. Lee, is recommended due to its simplicity and economy. More particularly, this plating bath is of the nickel cation-hypophosphite anion type, also containing lactic anion and propionic anion, and having a pH in the acid range 3.5 to 6.0. A typical example of this chemical nickel plating bath useful in the present invention is as follows:

EXAMPLE 1

$NiSO_4 \cdot 6H_2O$	0.08 mole/liter.
$NaH_2PO_2 \cdot H_2O$	0.23mole/liter.
Lactic acid	0.30 mole/liter.
Propionic acid	0.03 mole/liter.
Lactic acid	1 part per million.
pH	4.6.

A quantity of the above plating bath was placed in a plating vessel provided with a magnetic stirrer and a hot plate for heating and agitating the bath, respectively. Thereafter, there was added chromium powder (−325 mesh) in an amount equal to 0.5% by weight of the solids in the plating bath, the chromium powder being maintained in suspension by the stirrer. A clean steel workpiece was then placed in the plating bath while the temperature of the plating bath was maintained in the general range from about 85° C. to 95° C. and while the chromium particles were maintained in agitated suspension. After about an hour, there was present on the exposed surface of the workpiece an electroless plating metal coating of approximately 12.5 microns in thickness comprising electroless nickel and a quantity of chromium particles uniformly dispersed therethrough. The coating that is inherently produced by this particular plating bath essentially comprises by weight about 77% nickel, 8% phosphorus and about 15% chromium.

The surface of the coated workpiece was a dull light gray in color having a slightly rough surface. This coating as plated had a hardness in the nickel-phosphorus chromium alloy area of 610 V.P.N. (Vickers Pyramid Number) and a Taber Wear Index (TWI) value of 4.6. The Taber Wear Index is defined as the loss of weight in milligrams per 100 revolutions of two CS–10 rubber wheels under a 1000 grams load, a TWI of 5 representing a loss in thickness of about 0.25 micron of coating. By contrast, an electroless nickel coating on a test panel made in accordance with Example 1 but without the addition of the chromium particles thereto has a V.P.N. value of 560 as plated, and a TWI value of 15, whereby it is apparent that the coating of the present invention incorporating therein chromium particles improves the hardness and wear resistance of the coating by a factor of 3.

In the chemical nickel plating bath of Example 1, the absolute concentration of hypophosphite in the bath expressed in mole/liter may vary within the range from about 0.15 to about 1.20 and the ratio between the nickel cations and hypophosphite anions in the bath expressed in molar concentrations may vary within the range from about 0.20 to about 1.60. The lactic acid serves as a complexing agent and may be derived from lactic acid or salts thereof. The absolute concentration of lactic ions in the bath expressed in mole/liter being within the range from about 0.25 to about 0.60. The bath also includes an exalting additive, namely, the propionic acid, which has a concentration in the bath expressed in mole/liter in the range from about 0.025 to about 0.60. Other exalting additives may be used in place of the propionic acid, the exalting additive being selected from the group consisting of simple short chain saturated aliphatic monocarboxylic acids, dicarboxylic acids including 3 to 5 carbon atoms, dibasic acids and amino acids and salts thereof. Details of the composition of such a bath and the method of using same are set forth in the aforementioned U.S. Pat. No. 2,822,294 and the disclosure thereof is incorporated herein by reference.

The chromium particles useful in the process of Example 1 may have a particle size in the range from about 0.1 micron to about 50 microns, in order to obtain good suspension of the particles in the plating bath and in order to obtain uniform distribution of said particles in the coating. Smaller particles inhibit the plating action due to close packing, while larger particles cannot easily be dispersed and suspended in the plating bath. The concentration of the chromium particles in the plating bath should not exceed above ten times the weight of the nickel metal present in the bath expressed as nickel metal, although smaller concentrations of the chromium particles may be utilized, it being clear that the volume of chromium particles in the coating will be a function of the concentration and the size of the chromium particles in the plating bath as well as the effectiveness of the dispersion thereof. In Example 1, the chromium particles comprise about 20% by volume of the metal coating although it will be understood that the volume of the chromium particles may vary from as little as 5% to as much as 65% of the volume of the coating.

The thickness of the coating is primarily dependent upon the plating time and in Example 1 after about 1 hour the thickness was found to be 12.5 microns. Other thicknesses of the coating may be provided by varying the plating time, temperature and pH and the coating may have a thickness in the range from about 1 micron to about 250 microns.

The electroless meltallizing processes disclosed herein, such as the process described in Example 1, may be carried out in a continuous system where it is desirable to practice this invention on a commercial scale. Generally, such a system involves the periodic or continuous regeneration of the plating bath by the addition thereto of appropriate ingredients for the purpose of maintaining substantially constant the composition of the bath. Furthermore, it is necessary to maintain substantially constant the pH of the bath by the periodic or continuous addition of either a soluble alkali hydroxide or a soluble alkaline salt, or by the addition of a buffer salt or a combination of buffers. The system is made continuous by providing a regular plating chamber maintained at the plating temperature in which the plating operation is carried out and to which is attached a relatively large reservoir containing a much larger proportion of the bath solution maintained at a lower temperature to avoid thermal decomposition. The bath solution is circulated at a low rate from the reservoir to the plating chamber after being pre-heated, and back again to the reservoir during which time plating may continue. When it is necessary to replenish exhausted ingredients and adjust the pH, the necessary ingredients may be added to the reservoir while the system is in operation without disrupting the plating operation, and further without causing random chemical reduction of the nickel ions in the bath with the resultant decomposition of the bath. The precise means for carrying out such a continuous system and methods whereby such a system may be practiced is disclosed in U.S. Pat. No. 2,658,839 granted Nov. 10, 1953 to Paul Talmey and William J. Crehan, the disclose of that patent being incorporated herein by reference.

Electroless metallizing baths such as disclosed herein and specifically disclosed in Example 1, have the tendency too slow down rapidly with time due to the fact that the anions of the metal plating salt dissolved in the plating bath combine with the hydrogen cations to form an acid, which, in turn, lowers the pH of the bath, and the reducing power of the hypophosphite anions is decreased as the pH is lowered reducing the efficiency of the bath. In addition, there occurs a random chemical reduction of the nickel cations in the plating bath causing the formation of a black precipitate which results in decomposition of the plating bath. Although various exaltants and buffers have been devised to overcome this problem, decomposition still occurs especially in a continuous system such as described above. This problem may be overcome by the addition of trace amounts of water soluble additives of dipolar molecular characteristics. The anion and cation of the dipolar molecule dissociate and the anion forms a water insoluble product with the various suspensoids in the bath forming a product which is hydrophobic or water-repellent. Sulfhydric compounds perform this function since these compounds have at least one functional group with an affinity for metals and a hydrophobic radical characterized by forming oriented water-repellent coatings on metal surface. Hence, a trace amount of sulfide ions having a concentration in the range of from 1 to about 10 parts per million stabilizes electroless metallizing plating baths of the character described herein, the preferred range being from aboout 1 to about 5 parts per million. At a concentration beyond 10 parts per million, however, these elements are catalytic poisons interfering with the metallic reduction reaction. Examples of elements which will perform quite well as stabilizers when added to the bath include lead, tellurium, tin, and cadmium. Other elements which will perform satisfactorily include copper, bismuth, selenium, tungsten, thorium,

titanium, zinc, manganese and rhenium. These stabilizers may conveniently be provided in the form of metallic salts which dissociate when added to the bath. Organic thiocompounds which are soluble under plating conditions and which hydrolyze with respect to the sulphur content at a rate to maintain a sulfide ion concentration as indicated may similarly be utilized. The lead content of the nickel plating bath of Example 1 therefore, performs the function of stabilizing the bath during the plating operation. Other types of stabilizers may be advantageously utilized in connection with the present invention, suitable such stabilizers being disclosed in U.S. Pat. No. 2,762,723 granted Sept. 11, 1956 to Paul Talmey and Gregoire Gutzeit, the disclosure of that patent being incorporated herein by reference.

Summarizing with respect to Example 1 above, there is described a process of "electroless" plating of a nickel-alloy coating on a steel workpiece, the coating containing chromium particles uniformly dispersed therethrough. The expression "electroless plating" as used herein refers to the plating of metal coatings without the application of an external electrical current by a chemical reduction of the electroless plating metal utilizing a chemical reducing agent for the metal, thereby to accomplish a process of electroless metallizing.

Alkaline nickel plating baths may be utilized advantageously in the present invention, and particularly when coating certain plastics and certain metals such as aluminum and magnesium, examples of suitable alkaline baths being set forth in U.S. Pat. No. 3,211,578 granted on Oct. 12, 1965 to Gregoire Gutzeit, the disclosure thereof being incorporated herein by reference.

The metallic particles utilized in the processes to produce the article of manufacture of the present inventiono must be essentially insoluble in the plating bath, that is such particles must have a very low solubility therein on the order of no more than about 0.01 mole/liter. In addition, these metallic particles must be inert and non-catalytic and non-poisonous with respect to the bath and non-displacing with respect to the electroless plating metal ions in said bath. For example, some metal powders are catalysts for the nickel reduction reaction and will therefore cause spontaneous decomposition of the bath. Such metallic particles as iron, nickel, cobalt, palladium, platinum, ruthenium, rhodium, silver and gold are catalysts for the nickel reduction reaction and will therefore result in spontaneous decomposition of the bath when utilized as the metallic particles in said bath. Other metals such as antimony, bismuth, copper, cadmium, indium, lead, tin, mercury and zinc are catalytic poisons of the nickel reduction reaction and will therefore prevent plating when present in more than trace amounts. Various electropositive metals such as beryllium, aluminum, manganese and magnesium will cause a displacement reaction with the electroless plating metal ions in solution, especially nickel ions. These metallic particles become nickel coated and then act as catalytic nucleii for a spontaneous decomposition of the bath.

Those metals mentioned above which will cause a displacement reaction to occur with the electroless plating metal ions, such as aluminum, may be utilized as the material of the workpiece to be plated. In this instance a displacement reaction occurs on the surface thereof almost instantaneously upon immersion in the bath such that the workpiece receives a nickel coating thereon which may then be electroless plated in accordance with the processes disclosed herein to produce the articles of manufacture of this invention.

The metallic particles may be maintained in suspension throughout the bath by the mechanical agitation of the bath with the particles therein such as by the use of a magnetic or electric stirrer as illustrated in Example 1. Another method for maintaining the metallic particles in suspension consists of pumping a mixture of the plating solution including the metallic particles through the plating vessel, the bottom of the plating vessel being dish-shaped and symmetrical, whereby a uniform stream of the plating bath with the metallic particles suspended therein is passed or flooded across the surfaces of the workpiece being coated.

Another method for maintaining the metallic particles in suspension is to provide a symmetrical plating bath having dispersed in the bottom thereof a spider including a number of very small gas orifices therein. In this manner very fine air bubbles may be introduced into the plating bath through the orifices, the air bubbles serving to hold metallic particles in suspension throughout the plating solution. In addition to air, other gases such as nitrogen or any one of the noble gases may be utilized. Ultrasonic energy may also be used for dispersion.

A further method of maintaining the particles in suspension is to agitate and move the workpiece within the plating solution thereby causing currents in the plating solution which tend to hold the particles in suspension.

Yet another method for maintaining the metallic particles in suspension consists of slowly agitating the workpiece while at the same time rapidly circulating the plating solution throughout the bath such as by using a pump or the like thereby causing the bath solution with the metallic particles to pass across or flood the surface of the workpiece while the workpiece produces mild agitation.

The coating produced by the process of Example 1 is particularly useful when applied to workpieces having surfaces that are to be employed in sliding application, such as slide bearings, motor housings, shafts and the like. In addition, especially where the coating is subsequently heat-treated as will be illustrated hereinafter, the coating of Example 1 greatly increases the corrosion resistance of workpieces against corrosion due to acids and other such fluids. Hence workpieces having such corrosion-resistant coatings on their surfaces are particularly useful as liners for vessels which are to carry acidic solutions and the like. It will be understood, however, that the incorporation of metallic particles in the electroless deposited plating metal coating affects other properties of the coating in addition to the hardness and corrosion resistance thereof. Other physical, chemical and electrochemical properties affected include the coefficient of friction, the oxidation stability of the coating, the reflectivity and/or gloss thereof and other such properties.

FIG. 1 of the drawings shows a series of curves illustrating the hardness-temperature relationship involved in the heat treatment of various nickel coatings including metallic particles as contrasted with heat-treated nickel coatings lacking any metallic particles dispersed therein. Each curve was constructed by computing the V.P.N. hardness value after heat treatment for one hour at various temperatures within the range of 200° C. to about 700° C. The curve representing the hardness-temperature relationship with respect to the electroless nickel coating including chromium particles has a hardness of about 630 V.P.N. at 100° C. which increases rapidly to a peak of 1330 V.P.N. at 300° C. as contrasted to a coating of electroless nickel lacking any metallic particles which has a hardness of 560 V.P.N. at 100° C. and a maximum hardness of 1020 V.P.N. at a temperature of 400° C.

Where the heat-treatment of the coating including the metallic particles is carried out in the temperature range of about 600° C. to about 1300° C., the metallic particles are not only bonded to the electroless plating metal by wetting the surface thereof, but the particles are alloyed wtih the electroless plating metal at least at the interfaces thereof. Heat treatment in the range of from about 1,200° C. to about 1,300° C. for a period of from about one hour to about sixteen hours results in homogenization of the structure and solutionizing of the alloyed particles. The heat-treatment step is carried out in an oven under vacuum conditions, or in an inert or reducing atmosphere, such as an atmosphere consisting of argon or hydrogen

gas. The vacuum condition, or the inert or reducing atmospheres are employed during the heating step in order to prevent surface oxidation.

The resistance of the coating of Example 1 to corrosion due to acids is also particularly manifested when the coating is heat-treated following immersion in the electroless metallizing bath. The following is an example of the heat-treatment of the novel coating of Example 1.

EXAMPLE 2

The steel workpiece having a coating thereon produced as in Example 1 was gradually heated in an oven to 600° C. for a period of one hour. From test coupons exposed to a solution of 10% sulfuric acid at room temperature for 17 hours, the corrosion rate was computed to be 22 mdd. whereas the corrosion rate of a coating produced in accordance with Example 1 but without the addition of the chromium particles was computed to be 91 mdd. The corrosion rate is derived by calculating the weight loss of the coupons expressed in terms of milligrams per square decimeter per day (mdd.). The corrosion rate may similarly be computed by calculating the weight loss when exposed to a solution of 10% hydrochloric acid at 180° F. for from 1 to 3 hours. The weight loss was 33% lower for the coating produced in Example 2 than for a nickel coating without metallic particles disposed therein.

Utilizing the bath described in Example 1, other metallic particles may similarly be utilized in producing coatings having the desired physical and chemical properties indicated.

EXAMPLE 3

To an electroless metallizing bath consisting of the components described in Example 1 was added 1% by weight of the solids in the bath of molybdenum powder having an average particle size of 3 microns. A steel workpiece was then placed in the plating bath while the molybdenum particles were maintained in agitated suspension throughout the plating bath, and while the temperature of the bath was maintained in the range of from 93° C. to 98° C. After an hour, there was present on the surface of the workpiece an electroless metal coating comprising electroless nickel and a quantity of molybdenum particles uniformly dispersed therethrough, said coating having a thickness of 15 microns. The coating that is inherently produced by this plating bath comprises by weight about 57.5% nickel, 5% phosphorus and 35% molybdenum.

The surface of the coated workpiece was a dull light gray in appearance having a slightly rough surface, the coating possessing the valuable properties described with respect to the coating of Example 1.

The hardness and corrosion resistance of the electroless nickel coating incorporating therein molybdenum particles as described in Example 3 are improved by heat-treatment of the coating following the plating thereof.

EXAMPLE 4

A test coupon having the coating thereon produced in Example 3 was gradually heated in an oven at about 600° C. for a period of one hour. The coupons were immersed in 10% sulfuric acid for 17 hours and at the end of that time the corrosion rate was computed and found to be 25 mdd. as compared with a value of 133 for a coating produced in accordance with Example 3 but without the molybdenum particles and similarly heated to 600° for one hour.

The process of Example 1 is similarly useful for producing an electroless nickel coating having both chromium and molybdenum particles uniformly dispersed therethrough.

EXAMPLE 5

To an electroless metallizing bath consisting of the components described in Example 1, was added 1.0% by weight of the solids in the bath of a mixture consisting of chromium particles and molybdenum particles in equal amounts by weight. After one hour of plating, a coating having a thickness of 12.5 microns was deposited on the surface of the steel workpiece. The corrosion rate when calculated from immersion in a 10% solution of hydrochloric acid at 180° F. for between 1 to 3 hours was calculated to be 2500 mdd. for the coating as produced in Example 5 as compared with a value of 7900 mdd. for the coating produced by the process of Example 1 but without any metallic particles incorporated therein.

The coating of Example 5 may further be improved in terms of its hardness and corrosion resistance by heat-treating said coating as follows:

EXAMPLE 6

The workpiece with the coating of Example 5 thereon was heat-treated in an inert atmosphere oven to 600° C. for a period of 1 hour. The hardness of said coating was found to have a value of 1160 V.P.N. and a corrosion rate of 70 mdd. when calculated from a 10% solution of sulfuric acid at room temperature for 17 hours. By contrast a coating produced in accordance with Example 1 but without the incorporation of any metallic particles has a hardness of 650 V.P.N. and a corrosion rate in 10% sulfuric acid at room temperature of 91 mdd. after heat-treatment at 600° for 1 hour.

As shown in FIG. 2, the hardness of the electroless nickel coating including chromium and molybdenum particles does not surpass the hardness of the electroless nickel coating until heat-treated to a temperature of about 500° C., the peak hardness being 1160 V.P.N. at about 550° C.

Other metallic particles may similarly be used to produce the articles of manufacture of the present invention.

EXAMPLE 7

The plating bath and process of Example 1 was repeated but there was substituted 0.5% by weight of the solids in the bath of tungsten powder with an average particle size of 1 micron in place of the chromium powder utilized in Example 1. A dull coating was deposited on the steel workpiece having a thickness of 12.5 microns after 1 hour of coating time, the coating having a composition consisting of 62.6% nickel, 5.6% phosphorus and 30.2% tungsten.

Heat-treatment of the coating produced in accordance with Example 7 imparts further desirable properties to said coating.

EXAMPLE 8

The workpiece with the coating of Example 7 thereon was further processed and heat-treated by heating same in an oven to 600° C. for a period of 1 hour. The corrosion rate of the resulting coating was found to be 66 mdd. in a 10% sulfuric acid solution after 17 hours at room temperature as contrasted with a value of 91 mdd. for a coating lacking any metallic particles and heat-treated to 600° C. for 1 hour.

As shown in FIG. 1, the hardness of the electroless nickel coating including tungsten does not surpass that of the electroless nickel coating lacking any particles, but does increase by heat-treatment of the coating, the peak hardness being about 819 V.P.N. after heating to 400° C. as compared to about 1,000 V.P.N. for the plain electroless nickel coating.

EXAMPLE 9

The plating bath and the coating process of Example 1 were duplicated except that 0.5% by weight of the solids in the bath of boron powder (1 to 2 microns) was substituted for the chromium powder utilized in Example 1. After one hour of plating, a coating having a thickness of 2.5 microns was deposited on the surface of the workpieces, the coating having a hardness of 605 V.P.N. as plated, as contrasted with a value of 560 V.P.N. for a nickel coating lacking any metallic particles dispersed therein.

EXAMPLE 10

The workpiece with the coating of Example 9 was further processed and heat-treated by heating the same in an oven to 500° C., for a period of one hour. The hardness of the coating after heat-treatment was found to have a value of 1047 V.P.N. as contrasted with a value of 825 V.P.N. for a nickel coating lacking any nickel particles dispersed therein similarly heat-treated.

EXAMPLE 11

The plating bath and the coating process of Example 1 were duplicated except that 0.5% by weight of the solids in the bath of titanium powder was substituted for the chromium powder utilized in Example 1. After 1 hour of plating a coating having a thickness of 17.5 microns was deposited on the surface of the workpiece, having similarly good properties with respect to hardness and corrosion resistance as the other coatings produced by the foregoing examples.

EXAMPLE 12

The plating bath and the coating process of Example 1 were duplicated except that 0.5% by weight of the solids in the bath of vanadium powder was substituted for the chromium powder utilized in Example 1. After 1 hour of plating, a coating having a thickness of about 2.5 microns was then deposited on the surface of the workpiece, having similarly good properties with respect to hardness and corrosion resistance as the other coatings produced in the foregoing examples.

The plating bath in the coating process of Example 1 may be duplicated, substituting for the chromium powder utilized in Example 1, 0.5% by weight of the solids in the bath of either zirconium, hafnium, or tantalum powder, as illustrated in Examples 11 and 12 with titanium and vanadium powders respectively. Coatings produced with an electroless nickel incorporating therein either zirconium, hafnium and tantalum or alloys thereof exhibit similarly useful characteristics with respect to hardness, corrosion resistance and the like, and which may also be heat-treated as described in Example 2 above.

EXAMPLE 13

The plating bath and coating process of Example 1 were again duplicated except that in place of the chromium powder utilized in Example 1, there is substituted a mixture including 1.5% chromium, 1.5% molybdenum and 0.4% tungsten. All of said percentages are based upon the weight of the solids in the plating bath. A steel workpiece was then immersed in the plating bath for a period of 1 hour and following deposition of the coating therein, the workpiece was heat-treated by heating said workpiece to a temperature of 600° C. for 1 hour. The corrosion rate of the workpiece was computed to be 28 mdd. in a 10% solution of sulfuric acid as compared to 91 mdd. for a workpiece having a nickel coating but with no metallic particles dispersed therein.

EXAMPLE 14

The procedure of Example 1 was repeated substituting in the place of the chromium powder, a mixture including 1.5% chromium, 1.5% molybdenum, 0.4% tungsten and 0.1% vanadium, all of the percentages being by weight of the solids in the plating bath. A steel workpiece was immersed in the plating bath and the coating continued for a period of 1 hour resulting in a coating having a composition consisting of 59.5% nickel, 5.7% phosphorus and 33.0% of the metallic particles based upon the weight of the coating. The physical and chemical properties of the coating produces compared favorably with coatings produced in accordance with the foregoing examples.

EXAMPLE 15

The plating bath and process of Example 1 was again duplicated except that the plating bath had dispersed therein 1% by weight of the solids in the bath of "Haynes Stellite No. 157" powder, which consists of 21% chromium, 0.07% carbon, 1.60% silicon, 2.40% boron, 4.50% tungsten and the balance being cobalt. A steel workpiece was immersed in a plating bath for a period of 1 hour producing an electroless nickel coating on the steel workpiece having the metallic particles dispersed therethrough. The coating, as plated, had a hardness of 580 V.P.N. which was improped after heating the workpiece including the coating to a temperature of 400° C. for 1 hour to a value of 1209 V.P.N. By contrast a coating produced in accordance with Example 1 but lacking any metallic particles dispersed in the nickel coating had a hardness of 1020 V.P.N. after being heat-treated at a temperature of 400° C. for 1 hour.

As shown in FIG. 2, the electroless nickel coating including "Haynes Stellite No. 157" has a greater hardness than electroless nickel coatings lacking any metallic particles after heat treatment throughout the temperature range of from about 100° C. to about 650° C.

EXAMPLE 16

The plating bath and coating process of Example 1 were duplicated employing 0.5% by weight of the solids in the bath of "Haynes Stellite No. 6" powder in place of the chromium powder utilized in Example 1. "Haynes Stellite No. 6" has the approximate chemical composition of 28.0% chromium, 1.0% carbon, 1.0% silicon, 1.0% manganese, 3.0% iron, 3.0% nickel, 4.0% tungsten with the balance being cobalt. There resulted from 1 hour of plating, a coating having a thickness of about 17.5 microns and composed of 85% nickel, 9% phosphorus and 6% of the alloy metallic particles. The workpiece as plated had a hardness of 570 V.P.N. as compared to 560 V.P.N. for a nickel coating lacking any metallic particles dispersed therein.

EXAMPLE 17

The workpiece with the coating of Example 16 was further processed and heat-treated by heating in an oven to a temperature of 600° for 1 hour thereby providing a coating having a corrosion rate of 45 mdd. when calculated from a 10% solution of sulfuric acid as contrasted with 91 mdd. for a nickel coating lacking any metallic particles dispersed therein after a similar heat treatment.

As shown in FIG. 2, the hardness of the electroless nickel coating including "Haynes Stellite No. 6" is similarly improved after heat-treatment thereof, having a peak hardness of about 775 V.P.N. at 500° C. as contrasted with a hardness of only 570 V.P.N. at 100° C.

Alkaline nickel plating baths may similarly be utilized advantageously to produce the articles of manufacture of the present invention, and particularly when coating such metals as aluminum, magnesium and others. The following example illustrates the use of an alkaline nickel bath in producing the articles of manufacture of this invention.

EXAMPLE 18

To one liter of deionized water was added the following:

	Grams
Nickel sulfate	33
Sodium hypophosphite	10
Ammonium citrate	100
Chromium powder (400 mesh)	10

The pH was adjusted to 8.5–9 with ammonia, and the solution was heated with agitation to 90° C. A clean aluminum workpiece was immersed in the bath and there resulted a coating consisting of electroless nickel having chromium particles dispersed therethrough having a thickness of 8.33 microns after 1 hour of plating time. The coating was dull in appearance and had excellent adhesion to the substrate and further, possessed the advantageous properties as described with respect to the coating of Example 1.

EXAMPLE 19

An acetate nickel bath is utilized incorporating the following components:

To 600 milliliters of deionized water was added the following:

	Grams
Nickel chloride	21.0
Sodium hypophosphite	25.0
Sodium acetate	10.0

The volume was brought to one liter with deionized water and 10 grams of chromium powder was added and the bath heated with stirring to 95° C. A clean aluminum workpiece was immersed in the bath and there resulted after 1 hour of plating, a coating thereon having the thickness of about 20 microns. This coating possessed similar desirable properties and characteristics as described above with respect to the coating produced by the process of Example 1.

The foregoing Examples 1 through 19 illustrate various embodiments for producing the articles of manufacture in the processes of this invention wherein the electroless metal plating salt employed in the electroless metallizing bath is a nickel salt. However, similarly good results are obtained in producing coatings with the desirable properties and characteristics described with respect to the nickel coatings when other electroless metal plating salts are utilized. The following example illustrates the use of cobalt as the electroless plating metal and the coating obtained thereby.

EXAMPLE 20

To 2,000 milliliters of deionized water is added the following:

	Grams
Cobalt chloride	105
Sodium citrate	185
Ammonium sulfate	210
Sodium hypophosphite	75

The pH was adjusted to 8:7±0.5 with ammonia and the volume brought to 3,000 milliliters with deionized water. To this bath was added 1% by weight of the solids in the bath of "Haynes Stellite No. 6" powder and the plating bath was then heated with stirring to 90° C. A clean aluminum workpiece was immersed in the bath and there resulted a coating having a thickness of 3.65 microns after 1 hour of plating time. The coated aluminum workpiece was dull gray in appearance and the coating had excellent adhesion to the substrate, such that when the workpiece was bent through 180° on a ¼ inch mandrel, the coating did not separate from the substrate.

Example 20 illustrates the use of a cobalt salt for plating an aluminum workpiece. It is to be understood that any other suitable workpiece may be employed in an electroless cobalt bath. The following example describes the coating of a steel workpiece in such an electroless cobalt bath.

EXAMPLE 21

An electroless bath was formulated having the following ingredients:

	Grams per liter
Cobalt chloride	50
Rochelle salt	375
Ammonium chloride	100
Sodium hypophosphite	35

The pH of the bath was adjusted to 9.0 with ammonia and the temperature of the bath maintained at about 98° C. There was then added 10 grams of chromium powder which was maintained in suspension by stirring the bath with a mechanical stirrer. A clean steel workpiece was immersed in the bath and after 1 hour of plating there was produced a coating having a thickness of 7.25 microns, being slightly rough and dull in appearance. The workpiece with the coating thereon possessed similarly desirable properties and characteristics as described for the coating produced by the process of Example 20.

Two electroless plating metals may be co-deposited from an electroless plating bath as is known in the art and such plating solutions are useful in carrying out the process of the instant invention, the following being an example thereof:

EXAMPLE 22

An electroless plating bath was formulated having the following ingredients—

To 1 liter of deionized water was added:

	Grams
Cobalt chloride	20
Nickel chloride	40
Ammonium chloride	50
Sodium citrate	100
Sodium hypophosphite	30

The pH of the solution was adjusted to 9 with ammonia and the bath was heated with stirring to 95° C. To the bath was added 1% by weight of the solids in the bath of chromium powder and a steel workpiece was then immersed in the bath and plated for a period of 1 hour. After 1 hour there resulted a coating having a thickness of 34.75 microns, the coating being uniformly gray and exhibiting good adhesion to the substrate such that the coating did not peal or separate from the substrate when subjected to the bend test; the coating further had the several desirable properties and characteristics described above with respect to the coating produced by the process of Example 1.

In each of Examples 1 through 22, above, the reducing agent utilized has been a hypophosphite. It will be understood that other suitable reducing agents may be used in the place thereof, preferred alternative reducing agents being alkyl-borazanes and borohydrides. Specific examples of suitable alkyl-borazanes are N-diethyl-borazane and dimethyl-borazane. An example of a suitable borohydride is sodium borohydride.

The following example illustrates yet another electroless plating metal and an electroless plating bath useful in the articles of manufacture of the present invention:

EXAMPLE 23

An electroless plating bath was formulated having the following ingredients:

Copper sulfate	grams per liter	15
Sodium hydroxide	do	7.5
Rochelle salt	do	7.5
Formaldehyde solution (37%)	milliliters per liter	44
pH		12.5
Temperature	° C.	25

There was added to the electroless plating bath 1% by weight of the solids in the bath of chromium powder, maintained in suspension by mechanical agitation of the bath solution. A steel workpiece was immersed in the plating solution and plating was carried out for a period of 1 hour. After the 1 hour period, the workpiece carried an appreciable coating of copper thereon having dispersed uniformly therethrough chromium particles, the coating having the hardness and corrosion resistance as well as other desirable properties and characteristics discussed with respect to the coating produced by the process of Example 1.

The articles of manufacture of this invention are also fundamentally independent of the physical shape of the metallic particles. Hence these particles may be in the form of fibers, powders, flakes, chips, turnings or any other such shapes. The following example illustrates the use of metallic particles in the form of flakes.

EXAMPLE 24

Ten grams of Type 304 stainless steel flakes containing about 18% chromium and 8% nickel, the balance being essentially iron with small amounts of manganese, silicon and carbon, were treated with 100 ml. of concentrated nitric acid for one hour to clean and passivate the surface. The plating bath and process of Example 1 were again duplicated except that the flakes were substituted for the chromium powder. After one hour of plating time, there resulted on the surface of the steel workpiece a smooth, dull coating having a thickness of 15 microns. The physical and chemical properties of the coating produced compared favorably with coatings produced in the foregoing examples.

The following are yet other examples of workpieces which may be successfully coated, the chemical composition being other than the steel and aluminum given in the above specific examples.

EXAMPLE 25

The process of Example 19 was repeated using a workpiece consisting of magnesium with essentially the same results in regard to the hardness and corrosion resistance of the coating obtained therein.

EXAMPLE 26

The process of Example 1 was repeated using a workpiece consisting of copper with essentially the same results in regard to the hardness and corrosion resistance of the coating obtained therein.

EXAMPLE 27

The process of Example 1 was repeated using a workpiece consisting of nickel alloy with essentially the same results in regard to the hardness and corrosion resistance of the coating obtained therein.

EXAMPLE 28

The process of Example 1 was repeated using a workpiece consisting of beryllium alloy with essentially the same results in regard to the hardness and corrosion resistance of the coating obtained therein.

EXAMPLE 29

The process of Example 1 was repeated using a workpiece consisting of titanium alloy with essentially the same results in regard to the hardness and corrosion resistance of the coating obtained therein.

The various other methods for maintaining the metallic particles in suspension described previously herein may be substituted in the practice of the process described in Example 1 yielding similarly good results with respect to maintaning a good suspension of said metallic particles in the plating bath. For example, the steel workpiece in Example 1 may be slowly rotated while the bath solution is rapidly circulated throughout by means of a circulating pump resulting in a good suspension of the chromium particles in the bath solution.

From the above it will be seen that there have been provided workpieces having thereon electroless plating metal coatings incorporating therein metallic particles, which workpieces fulfill all of the objects and advantages set forth above.

While there have been described what are at present considered to be certain preferred embodiments of the invention it will be understood that various modifications may be made therein, and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. An article of manufacture comprising a workpiece, a metal coating carried by said workpiece and formed of electroless plating metal having dispersed therethrough metallic particles, said particles being essentially insoluble in the electroless plating bath and inert and non-catalytic and non-poisonous with respect thereto and non-displacing with respect to the electroless plating metal ions in the electroless plating bath, said particles having dimensions on the order of from about 0.1 micron to about 50 microns and constituting by volume from about 5% to about 65% of said coating.

2. The article of manufacture set forth in claim **1**, wherein said coating has a thickness in the range from about 1 micron to about 250 microns.

3. The article of manufacture set forth in claim **1**, wherein said particles are formed of a metal selected from chromium and alloys thereof.

4. The article of manufacture set forth in claim **1**, wherein said particles are formed of a metal selected from molybdenum and alloys thereof.

5. The article of manufacture set forth in claim **1**, wherein said particles are formed of a metal selected from tungsten and alloys thereof.

6. The article of manufacture set forth in claim **1**, wherein said particles comprise a mixture of first particles formed of a metal selected from chromium and alloys thereof and second particles formed of a metal selected from molybdenum and alloys thereof.

7. The article of manufacture set forth in claim **1**, wherein the workpiece is essentially formed of a material selected from iron, aluminum, magnesium, copper, nickel, titanium, beryllium, and alloys thereof.

8. An article of manufacture comprising a workpiece, a metal coating carried by said workpiece and formed of electroless plating metal having dispersed therethrough metallic particles, said particles being selected from the group consisting of chromium, molybdenum, tungsten, boron, titanium, vanadium, zirconium, hafnium, niobium, tantalum, and alloys thereof, said particles having dimensions on the order of from about 0.1 micron to about 50 microns and constituting by volume from about 5% to about 65% of said coating.

9. An article of manufacture comprising a workpiece, a metal coating carried by said workpiece and formed of electroless nickel having dispersed therethrough metallic particles, said particles being essentially insoluble in electroless plating baths and being inert and non-catalytic and non-poisonous with respect thereto and non-displacing with respect to the nickel ions in the electroless plating bath, said particles having dimensions on the order of from about 0.1 micron to about 50 microns and constituting by volume from about 5% to about 65% of said coating.

10. The article of manufacture set forth in claim **9**, wherein said metallic particles are selected from the group consisting of chromium, molybdenum, tungsten, boron, titanium, vanadium, zirconium, hafnium, niobium, tantalum, and alloys thereof.

11. The article of manufacture set forth in claim **10**, wherein said particles are formed of a metal selected from chromium and alloys thereof.

12. The article of manufacture set forth in claim **9**, wherein said particles are formed of a metal selected from molybdenum and alloys thereof.

13. The article of manufacture set forth in claim **9**, wherein said particles are selected from tungsten and alloys thereof.

14. The article of manufacture set forth in claim **9**, wherein said particles comprise a mixture of first particles formed of a metal selected from chromium and alloys thereof and second particles formed of a metal selected from molybdenum and alloys thereof.

15. The article of manufacture set forth in claim **9**, wherein said workpieces is essentially formed of a material selected from iron, aluminum, magnesium, copper, nickel, titanium, beryllium, and alloys thereof.

16. An article of manufacture comprising a workpiece, a metal coating carried by said workpiece and formed of electroless cobalt having dispersed therethrough metallic particles, said particles being essentially insoluble in electroless plating baths and being inert and non-catalytic and non-poisonous with respect thereto and non-displacing with respect to the cobalt ions in the electroless plating bath, said particles having dimensions on the order of from about 0.1 micron to about 50 microns and constituting by volume from about 5% to about 65% of said coating.

17. An article of manufacture comprising a workpiece, a metal coating carried by said workpiece and formed of electroless copper having dispersed therethrough metallic particles, said particles being essentially insoluble in electroless plating baths and being inert and non-catalytic and non-poisonous with respect thereto and non-displacing with respect to the copper ions in the electroless plating bath, said particles having dimensions on the order of from about 0.1 micron to about 50 microns and constituting by volume from about 5% to about 65% of said coating.

18. An article of manufacture comprising a workpiece, a metal coating carried by said workpiece and formed of electroless plating metal having dispersed therethrough metallic particles, said particles being essentially insoluble in electroless plating baths and inert and non-catalytic and non-poisonous with respect thereto and non-displacing with respect to the electroless plating metal ions in the electroless plating bath, said particles having dimensions on the order of from about 0.1 micron to about 50 microns and constituting by volume from about 5% to about 65% of said coating, said electroless plating metal and said metallic particles being heat-treated and bonded at least at the interfaces thereof.

19. The article of manufacture set forth in claim **18**, wherein the heat-treatment is carried out at a temperature in the range from about 200° C. to about 1,300° C. for about at least one-quarter hour.

20. The article of manufacture set forth in claim **19**, wherein said coating has a thickness in the range from about 1 micron to about 250 microns.

21. The articles of manufacture set forth in claim **19**, wherein said particles are formed of a metal selected from chromium and alloys thereof, and wherein said heat treatment is carried out at a temperature in the range from about 200° C. to about 1,300° C. for about at least one-quarter hour.

22. The article of manufacture set forth in claim **18**, wherein said particles are formed of a metal selected from molybdenum and alloys thereof.

23. The article of manufacture set forth in claim **18**, wherein said particles are formed of a metal selected from tungsten and alloys thereof.

24. An article of manufacture set forth in claim **18**, wherein said particles comprise a mixture of first particles formed of a metal selected from chromium and alloys thereof and second particles formed of a metal selected from molybdenum and alloys thereof.

25. The article of manufacture set forth in claim **18**, wherein said workpiece is formed of a material selected from iron, aluminum, magnesium, copper, nickel, titanium, beryllium, and alloys thereof.

26. The article of manufacture set forth in claim **18**, wherein said electroless plating metal and said metallic particles upon being heat-treated are alloyed at least at the interfaces thereof.

27. An article of manufacture comprising a workpiece, a metal coating carried by said workpiece and formed of electroless plating metal having disposed therethrough metallic particles; said metallic particles being selected from the group consisting of chromium, molybdenum, tungsten, boron, titanium, vanadium, zirconium, niobium, hafnium, tantalum and alloys thereof with other metals, said particles having dimensions on the order of from about 0.1 micron to about 50 microns and constituting by volume from about 5% to about 65% of said coating, said electroless metal and said metallic particles being heat-treated and alloyed at least at the interfaces thereof.

28. An article of manufacture comprising a workpiece, a metal coating carried by said workpiece and formed of nickel having dispersed therethrough metallic particles, said particles being essentially insoluble in electroless plating baths and inert and non-catalytic and non-poisonous with respect thereto and non-displacing with respect to the nickel ions in the electroless plating bath, said particles having dimensions on the order of from about 0.1 micron to about 50 microns and constituting by volume from about 5% to about 65% of said coating, said nickel and said metallic particles being heat-treated and bonded at least at the interfaces thereof.

29. The article of manufacture set forth in claim **28**, wherein said particles are selected from the group consisting of chromium, molybdenum, tungsten, boron, titanium, vanadium, zirconium, hafnium, niobium, tantalum, and alloys thereof.

30. The article of manufacture set forth in claim **29**, wherein said particles are formed of a metal selected from chromium and alloys thereof, and wherein said heat treatment is carried out at a temperature in the range from about 200° C. to about 1,300° C. for about at least one-quarter hour.

31. The article of manufacture set forth in claim **29**, wherein said particles are formed of a metal selected from molybdenum and alloys thereof.

32. The article of manufacture set forth in claim **29**, wherein said particles are formed of a metal selected from tungsten and alloys thereof.

33. The article of manufacture set forth in claim **29**, wherein said particles comprise a mixture of first particles formed of a metal selected from chromium and alloys thereof and second particles formed of a metal selected from molybdenum and alloys thereof.

34. An article of manufacture comprising a workpiece, a metal coating carried by said workpiece and formed of cobalt having dispersed therethrough metallic particles, said particles being essentially insoluble in electroless plating baths and inert and non-catalytic and non-poisonous with respect thereto and non-displacing with respect

to the cobalt ions in the electroless plating bath, said particles having dimensions on the order of from about 0.1 micron to about 50 microns and constituting by volume from about 5% to about 65% of said coating, said cobalt and said metallic particles being heat-treated and bonded at least at the interfaces thereof.

35. The article of manufacture set forth in claim **34**, wherein said particles are selected from the group consisting of chromium, molybdenum, tungsten, boron, titanium, vanadium, zirconium, hafnium, niobium, tantalum, and alloys thereof.

36. An article of manufacture comprising a workpiece, a metal coating carried by said workpiece and formed of copper having dispersed therethrough metallic particles, said particles being essentially insoluble in electroless plating baths and inert and non-catalytic and non-poisonous with respect thereto and non-displacing with respect to the copper ions in the electroless plating bath, said particles having dimensions on the order of from about 0.1 micron to about 50 microns and constituting by volume from about 5% to about 65% of said coating, said copper and said metallic particles being heat-treated and bonded at least at the interfaces thereof.

37. The article of manufacture set forth in claim **36**, wherein said particles are selected from the group consisting of chromium, molybdenum, tungsten, boron, titanium, vanadium, zirconium, hafnium, niobium, tantalum, and alloys thereof.

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