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3,485,597
ELECTROLESS DEPOSITION OF NICKEL-
PHOSPHORUS BASED ALLOYS

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No Drawing. Original application Oct. 30, 1964, Ser. No. 407,941. Divided and this application May 1, 1968, Ser. No. 736,892
Int. Cl. B23p 3/00; C23c 17/00
U.S. Cl. 29—194

10 Claims

ABSTRACT OF THE DISCLOSURE

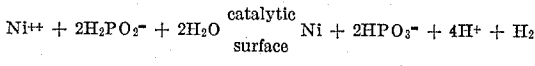
Articles of manufacture made from a basis metal having an electrolessly deposited nickel-phosphorus based alloy coating thereon, the alloy containing from more than 1% to about 45% of an element which is codeposited with the alloy, the element being tungsten, rhenium, beryllium, rhodium, palladium, platinum, tin, zinc, molybdenum or gold. The nickel predominates the phosphorus in quantity.

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment to one of any royalty thereon.

This invention is a divisional application of my co-pending application Ser. No. 407,941, filed Oct. 30, 1964, for "Electroless Deposition of Nickel-Phosphorus Based Alloys," now abandoned and relates to electroless deposition and more particularly concerns the electroless deposition of nickel-phosphorus alloys containing tungsten, zinc, tin, rhenium and molybdenum.

Nickel coatings have long been used for improving the appearance of steel products and yet protecting the basis metal from harmful or corrosive attacks. Until recently, nickel plating was accomplished by an electrodeposition process which suffered essentially in the poor throwing power of the electrodeposited nickel making it difficult to achieve uniformly of coating on irregularly shaped objects.

In the prior art, a chemical nickel plating process was developed based on the reduction of nickel salts by hypophosphite, and is represented approximately by the following reaction:



The electroless deposition of nickel, or more correctly, nickel-phosphorus alloys, occurs wherever the basis metal is in contact with the electroless plating solution and provides excellent deposition uniformity. I have plated numerous small, intricately shaped steel components, such, for example, as timing mechanisms, very successfully, with the electroless process, whereas the electrodeposition process was ineffective in plating such mechanisms. Similarly, the interiors of long, narrow tubes can readily be plated with the electroless nickel process whereas it is virtually an impossible task to be accomplished by standard electrodeposition methods. Further, the hardness of electroless deposited nickel is greater than that of electrodeposited nickel and can be further increased by additional heat treatment. A further interesting feature of electroless deposited nickel resides in the fact that it can be readily applied directly over properly activated non-conductors. However, the prior art electroless technique is restrictive in that very few metals can be deposited thereby. In addition, there are many applications wherein improved tarnish resistance,

to acid attack, ductility, corrosion protection of a basis metal, high temperature oxidation resistance and wear resistance would be desirable.

It is therefore a principal object of this invention to provide new and useful electroless nickel-phosphorus based alloys containing other metals.

Another object of the invention is to provide bath solutions for the electroless deposition of nickel-phosphorus alloys containing other metals.

Other and further objects of the invention will be apparent to those skilled in the art upon study of this disclosure.

Briefly, and in accordance with my invention, I have discovered that tarnish-resistant and/or corrosion resistant alloys can be successfully electroless plated onto the basis metals normally employed in electroless nickel deposition.

More specifically, I have found that when sodium tungsten is added to the prior art acid-citrate electroless nickel solution bath and the pH of the bath is raised above about 7, substantial tungsten content is detected in deposits. In order to prevent the precipitation of nickel salts at higher pH values, the concentration of the nickel salts is decreased to about 20% of the usual concentration (35 g./l. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) and the remaining 80% replaced by an atomic equivalent of tungsten obtained from sodium tungstate.

In Table I it will be seen that I have successfully electroless plated nickel-phosphorus alloys containing tungsten from an unammoniated alkaline citrate bath solution.

TABLE I.—NICKEL-PHOSPHORUS ALLOY OF TUNGSTEN FROM UNAMMONIATED ALKALINE CITRATE BATH

Compound	Preferred Quantity, g./l.	Quantity, Effective Range g./l.
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	7	3-21
Sodium Citrate $\cdot 2\text{H}_2\text{O}$	20	10-40
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	10	5-20
$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	35	8-80

The effective range of pH is between 7 and 10 although a pH of 8.2 is preferred. The bath temperature range is between about 90 to 100° C. with 98° C. being most desirable. The amount of tungsten in the electroless deposit is about 13% with the balance being about 94% nickel and 6% phosphorus when using the preferred bath of Table I above.

Similarly, I have found that tin, zinc, rhenium, beryllium and rhodium may be electroless deposited with the nickel-phosphorus when the appropriate metal salt is used in place of sodium tungstate in the example of Table I above. See Table II.

TABLE II

Compound Dissolved in Bath	Preferred Quantity in Bath (g./l.)	Metal Deposited	Approximate Content of Metal in Deposit, percent
$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	1.4	Sn	<1
$\text{InSO}_4 \cdot 7\text{H}_2\text{O}$	1.5	Zn	7
K_2BeO_4	1.5	Re	17
BeF_2	0.3	Be	<1
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	0.2	Rh	12

NOTE.—All bath solutions were operated at 98° C. and pH=8.2.

These alloys however require that the bath solution be stabilized against decomposition such as by the addition of about 0.2 ml./l. of a solution of 10 g./l. of mercaptobenzothiazole in 2 N NaOH.

In addition, I have found that a number of metals, including rhenium, zinc, molybdenum and tin, can be co-deposited with nickel-phosphorus using an ammoniated alkaline citrate bath. See the examples of Table III.

TABLE III

	Bath Composition		Content of Deposit* from Preferred Bath Composition
	Effective	Preferred	
Sodium Citrate-2H ₂ O	50-100 g./l.	85 g./l.	
NH ₄ Cl	5-60 g./l.	50 g./l.	
NaH ₂ PO ₄ ·H ₂ O	5-20 g./l.	10 g./l.	
Nickel salt+X	0.04-0.2 mol./l.	0.133 mol./l.	
pH	8 to 10 with NH ₄ OH	9 with NH ₄ OH	
Tungsten as Na ₂ WO ₄ ·2H ₂ O	20-80 mol percent	60 mol percent	12% Tungsten.
Rhenium as KReO ₄	1-20 mol percent	4 mol percent	45% Rhenium.
Zinc as ZnSO ₄ ·7H ₂ O	10-40 mol percent	20 mol percent	8% Zinc.
Tin as Na ₂ SnO ₃ ·3H ₂ O	5-20 mol percent	10 mol percent	2% Tin.
Molybdenum as Na ₂ MoO ₄ ·2H ₂ O	0.1-0.4 mol percent	0.2 mol percent	6% Molybdenum.
Palladium as PdCl ₂	0.1-1.0 mol percent	0.7 mol percent	5% Palladium.
Platinum as H ₂ PtCl ₆ ·3H ₂ O	0.1-1.0 mol percent	0.4 mol percent	<1% Platinum.
Gold as HAuCl ₄ ·3H ₂ O	0.1-1.0 mol percent	0.4 mol percent	<1% Gold.

* Balance being Ni+P.

NOTE.—X—metal salt which is the source of metal codepositing with Ni.

The preferred pH for the electroless plating from the ammoniated alkaline citrate bath is 9.0 at a bath temperature of 98° C. The effective pH and temperature ranges will be about 8 to 10 and 90 to 100° C. respectively. The pH is maintained by periodic additions of NH₄OH. Further, any combination of tungsten, tin, rhenium, zinc and molybdenum may be codeposited electrolessly with nickel-phosphorus. For example, nickel-phosphorus-rhenium-tungsten may be electroless deposited from both an unammoniated and an ammoniated alkaline citrate bath.

Salt Spray Corrosion tests were performed on steel panels coated with 0.3 mil of some of the deposits shown in Tables I and III. My nickel-phosphorus-tin and nickel-phosphorus-rhenium deposits exhibited superior corrosion protection of the steel substrate as compared to the standard electroless nickel deposit. My nickel-phosphorus-tin and particularly my nickel-phosphorus-tungsten deposits provided superior tarnish resistance qualities.

Acid resistance tests performed on the aforementioned panels revealed that my nickel-phosphorus-tungsten deposit has superior resistance to 50% nitric acid attack over conventional electroless-nickel coated panels.

The nickel-phosphorus-zinc coating was found to be 100 millivolts more active in potential than conventional electroless nickel deposits. This property is useful for sacrificial protection of certain metals.

It is apparent that in the foregoing description of my invention, new bath compositions are described for yielding electroless deposited alloys which are useful for providing superior corrosion protective properties to a basis metal and for imparting excellent tarnish resistant properties thereto.

I claim:

1. An article of manufacture comprising a basis metal structure having an electroless deposited coating thereon, said coating consisting essentially of an alloy of nickel, phosphorus and at least one element selected from the group consisting of tungsten, molybdenum, rhenium, beryllium, rhodium, palladium, and platinum, said alloy being

characterized as a nickel-phosphorus based alloy wherein nickel is present in major proportions and phosphorus is present in minor proportions, and wherein said element is present in an amount ranging between greater than 1% to about 45%.

2. An article according to claim 1 wherein said element comprises tungsten.

3. An article according to claim 1 wherein said element comprises molybdenum.

4. An article according to claim 1 wherein said element comprises rhenium.

5. An article according to claim 1 wherein said element comprises beryllium.

6. An article according to claim 1 wherein said element comprises rhodium.

7. An article according to claim 1 wherein said element comprises palladium.

8. An article according to claim 1 wherein said element comprises platinum.

9. An article according to claim 2 wherein said tungsten comprises at least 13% by weight of said coating.

10. An article according to claim 4 wherein said rhenium comprises at least 45% by weight of said coating.

References Cited

UNITED STATES PATENTS

2,828,227	3/1958	Eisenberg	117—130
2,995,473	8/1961	Levi	117—130 X
3,077,285	2/1963	Budininkas	29—196.6 X
3,178,311	4/1965	Cann	117—130 X
3,202,538	8/1965	Beynon	117—130 X
3,234,031	2/1966	Zirngiebl et al.	106—1
3,370,979	2/1968	Schmeckenbecher	117—130 X

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U.S. Cl. X.R.

29—198, 199; 106—1; 117—130