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ELECTROLESS DEPOSITION OF VANADIUM ALLOYS

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Our invention relates both to a process in which vanadium together with at least one metal selected from the group composed of iron, nickel, cobalt and chromium can be electrolessly codeposited on a suitable metallic substrate and to electroless plating solutions used in said process.

The term "electroless deposition" as known in the art described a process wherein a metallic substrate is inserted in a bath containing, in aqueous solution, a salt (such as a chloride or sulphate) of a metal selected from the group composed of nickel, cobalt and chromium; a hypophosphite salt (such as sodium hypophosphite); and a suitable buffering (pH controlling) agent (such as sodium acetate). In the ensuing reaction the nickel, cobalt or chromium is deposited as a pure metal on the surface of the substrate. While the mechanism of this process is not fully understood, it is believed that the hypophosphite ion continuously reduces the dissolved metal salt to the metallic state on the surface of the substrate by means of a catalytic action involving the surface.

It has been found that this reaction, which proceeds in the absence of an externally applied electric field, can take place when the pH of the bath is maintained within the acidic range, as for example a pH of 4–6, or alternatively within the basic range, as for example a pH of 8–10.

This process is defined as electroless plating or deposition to differentiate it from the conventional electroplating or electrolytic deposition technique.

In the copending application of Philip H. Eisenberg, Serial No. 561,670, filed January 26, 1956, there is disclosed a process for electrolessly depositing iron. Thus, any metal of the group composed of iron, nickel, cobalt and chromium can be electrolessly deposited through use of known techniques or through the use of the technique disclosed in the above mentioned copending application.

From theoretical considerations, we believed that vanadium could be electrolessly deposited in a similar manner. Accordingly we attempted to deposit vanadium in this way. Our attempts were unsuccessful; apparently the activity of vanadium is so high that it will oxidize before deposition occurs. In any event, the vanadium could only be electrolessly deposited in the form of an oxide. However, we discovered that vanadium could be electrolessly codeposited with at least one metal from the group composed of iron, nickel, cobalt and chromium in the form of a vanadium alloy.

Accordingly, it is an object of the present invention to provide a process for electrolessly codepositing vanadium together with at least one metal from the group composed of iron, nickel, cobalt and chromium.

Another object is to provide new and improved plating solutions out of which vanadium together with at least one metal from the group composed of iron, nickel, cobalt and chromium can be codeposited.

Still another object is to provide a new and improved electroless deposition process for depositing alloys containing vanadium and at least one metal from the group composed of iron, nickel, cobalt and chromium upon the surface of a metal substrate.

These and other objects will either be explained or will become apparent hereinafter.

In our invention there is provided an electroless plating solution containing a vanadium salt soluble in the solution together wtih a soluble salt of at least one metal from the group composed of iron, nickel, cobalt and chromium. To this is added a buffering agent and at least one reducing and complexing agent which maintains the positive ions of these salts in states of lowest ionic valence and at the same time forms at least one complex with these ions which is readily reducible to an alloy composed of vanadium, and at least one metal from the group composed of iron, nickel, cobalt and chromium. A hypophosphite salt is then added together with a suitable buffering agent; the pH of the solution is adjusted to a selected range (either acidic or basic), and the metal substrate is inserted into the solution. The complex is then rapidly reduced to the alloy on the substrate surface through action of the hypophosphite ion.

When vanadium is to be codeposited with at least one metal in the group composed of nickel, cobalt and chromium, either acidic or basic solutions can be used. However, when vanadium is to be codeposited with iron, a basic bath must be used, as outlined in more detail in the above identified copending application.

Any organic or inorganic compound which acts as a combined reducing and complexing agent can be used in the manner indicated providing that this compound is soluble in the plating solution and that the resultant complex can be readily reduced to the alloy. Typical compounds of this type for example include oxalic acid and its salts.

All metal substrates which can be electrolessly plated with chromium can be plated in the manner set forth in this application. In this connection it will be understood that as in conventional chromium plating, the passive metals must be flash coated (i. e. an electrolytic strike) with an extremely thin layer of an active metal, such as nickel, iron, and the like, before a subsequent electroless deposition can ensue.

Our invention will now be explained with reference to the detailed examples which follow.

Example I

A steel substrate was immersed in an aqueous electroless plating solution having the following composition:

	G./l.
$CrF_3.9H_2O$	32
$CrCl_3.6H_2O$	1
Sodium acetate	10
Sodium hypophosphite	10
$K_2C_2O_4.H_2O$	50
$NaVO_3$	5

The bath was maintained at a temperature within the range 75°–90° C. and at a pH falling within the range 4–6. It was found that a dense, adherent, non-porous chromium-vanadium alloy layer was formed on the substrate surface and that the deposition rate was approximately 0.3 mil per hour. This alloy contained approximately 80% by weight of chromium and 20% by weight of vanadium.

A brass disc was flash coated (i. e. a "strike" coating) with nickel and then immersed in the same solution. The same operating conditions were established and the results were substantially identical.

Example II

A brass disc was flash coated with nickel and then immersed in an aqueous electroless plating solution having the following composition:

	G./l.
$CrBr_3.9H_2O$	32
$CrI_3.9H_2O$	1
Sodium citrate	100
Sodium hypophosphite	10
$Na_2C_2O_4.H_2O$	9.0
$Na_3VO_4.16H_2O$	20

The bath was maintained at a temperature within the range 75°–90° C. and at a pH falling within the range 8–10. The results were substantially identical with Example I.

A steel substrate was immersed in the same solution. The same operating conditions were established and the results were substantially the same.

The bath temperature was maintained at a temperature between 75°–90° C. and at a pH between 8–10. An iron-vanadium alloy was deposited in the same manner as indicated in the preceding examples. This alloy contained approximately 84% by weight of iron and 16% by weight of vanadium.

Example III

The process outlined in Example I was repeated using an electroless plating solution having the following composition:

	G./l.
$NiSO_4.7H_2O$	30
Sodium acetate	10
Sodium hypophosphite	10
$K_2C_2O_4.H_2O$	50
$NaVO_3$	5

A vanadium-nickel alloy was deposited in the same manner as indicated in Example I. This alloy contained approximately 85% by weight of nickel and about 15% by weight of vanadium.

Example IV

The process outlined in Example II was repeated using an electroless plating solution having the following composition:

	G./l.
$CoCl_2.2H_2O$	45
NaH_2PO_2	20
Sodium citrate	50
$NaVO_3$	5
$Na_2C_2O_4.H_2O$	20

A cobalt-vanadium alloy was deposited in the same manner as indicated in Example II. This alloy contained approximately 90% by weight of cobalt and about 10% by weight of vanadium.

While we have shown and pointed out our invention as applied above, it will be apparent to those skilled in the art that many modifications can be made within the scope and sphere of our invention as defined in the claims which follow.

What is claimed is:

1. An electroless plating bath containing in aqueous alkaline solution, a vanadium salt; a salt of at least one metal selected from the group consisting of iron, nickel, cobalt and chromium, the positive ions of the vanadium and metal salts being in their lowest ionic valence state, the combined concentration of said vanadium salt and said one metal salt falling within the approximate range 50–53 grams per liter; a hypophosphite salt having a concentration falling within the approximate range 10–20 grams per liter; a buffering agent; and at least one reducing and complexing agent which maintains said positive ions in their lowest valence states and also forms at least one complex with said ions which is readily reducible to an alloy composed of vanadium and said selected metal when an electroless deposition operation is intended, said agent being selected from the group consisting of oxalic acid and its salts, said agent having a concentration falling within the approximate range 9–20 grams per liter.

2. A method for electrolessly depositing an alloy composed of vanadium and at least one metal selected from the group consisting of iron, nickel, cobalt and chromium onto the surface of a metal substrate comprising the step of inserting said substrate into an electroless plating solution containing in aqueous alkaline solution hypophosphite ion and at least one oxalate complex containing ions of vanadium and said one metal in their lowest ionic valence states, said complex being readily reducible to said alloy at said surface under the action of said hypophosphite ion, whereby said alloy is electrolessly deposited on said surface, the source of hypophosphate ion having a concentration falling within the approximate range 10–20 grams per liter, the sources of said vanadium ion and said one metal ion having a combined concentration falling within the approximate range 50–53 grams per liter, the the source of said oxalate having a concentration falling within the aproximate range 9–20 grams per liter.

3. An electroless plating bath containing in aqueous alkaline solution, a source of vanadium ions; a source of metal ions, the metal from which said metal ions are produced being selected from the class consisting of iron, nickel, cobalt and chromium, said vanadium and positive ions being maintained in their lowest ionic valence states, the combined concentration of said vanadium salt and said one metal falling within the approximate range 50–53 grams per liter; a source of hypophosphite ion having a concentration falling within the approximate range 10–20 grams per liter; and at least one reducing and complexing agent which complexes said vanadium and metal ions in their lowest ionic valence states; said complex when reacted with hypophosphite ion at a metal surface being readily reduced to an alloy formed from vanadium and said metal, said agent being selected from the group consisting of oxalic acid and its salts, said agent having a concentration falling within the approximate range 9–20 grams per liter.

4. An electroless plating bath containing in aqueous solution, a source of vanadium ions; a source of metal ions, the metal from which said metal ions are produced being selected from the class consisting of nickel, cobalt, iron and chromium, said vanadium and positive ions being maintained in their lowest ionic valence states, the combined concentration of said vanadium salt and said one metal salt falling within the approximate range 50–53 grams per liter; a source of hypophosphite ion having a concentration falling within the approximate range 10–20 grams per liter; a buffering agent maintaining the pH of said bath in an alkaline range; and at least one reducing and complexing agent which complexes said vanadium and metal ions in their lowest ionic valence states, said complex when reacted with hypophosphite ion at a metal surface being readily reduced to an alloy formed from vanadium and said metal, said agent being selected from the group consisting of oxalic acid and its salts, said agent having a concentration falling within the approximate range 9–20 grams per liter.

5. A method for electrolessly depositing an alloy composed of vanadium and at least one metal selected from the group consisting of iron, nickel, cobalt and chromium onto the surface of a metal substrate comprising the steps of adding a buffering agent to a bath containing in aqueous solution hypophosphite ion and at least one complex containing ions of vanadium and said one metal in their lowest ionic valence states, said complex being readily reducible to said alloy at said surface under the action of said hypophosphite ion to establish a basic pH in said bath; inserting said substrate into said bath whereby the electroless deposition ensues, the source of said hypo-

phosphate ion having a concentration falling within the approximate range 10–20 grams per liter, the sources of said vanadium ion and said one metal ion having a combined concentration falling within the approximate range 50–53 grams per liter, the source of said oxalate having a concentration falling within the approximate range 9–20 grams per liter; and maintaining said pH within the basic range until said deposition is completed.

References Cited in the file of this patent

UNITED STATES PATENTS

2,532,283 Brenner et al. ---------- Dec. 5, 1950

OTHER REFERENCES

Brenner et al.: Part of the Journal of Research of the National Bureau of Standards, Research Paper RP 1835, vol. 39, November 1947, pp. 385–395.