Electroless nickel-boron plating.

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Description

This invention generally relates to forming electroless nickel-boron deposits having a high boron content.

It has long been known that an electroless codeposit of nickel and boron is achieved by immersion of a substrate into an electroless bath including a source of nickel ions and a borane reducing agent. Often, it is desirable to lay down a deposit that has a relatively high boron content in order to enhance the hardness of the deposit when compared with a substantially pure nickel deposit of up to 99.9% nickel. Traditionally, however, borane-reduced baths form a codeposit that has severe limitations from the point of view of the ability to control the percentage of boron that could be laid down in the codeposit, borane-reduced baths being especially unsuitable for forming codeposits having a relatively high boron content on the order of 2 weight % and above. These borane-reduced deposits are limited generally by the pH of the bath and the stability of the borane reducing agent of the bath.

More particularly, as the pH of a borane-reduced bath is decreased, the percentage of boron codeposited with the nickel is increased; however, because boranes undergo hydrolysis at low pH values, borane reducing agents begin to lose their stability and thus are rapidly consumed as the bath pH is reduced below 4. A borane-reduced electroless nickel bath that will lay down a deposit having a high boron content would have to be at a low pH, but a low pH bath consumes the borane reducing agent at an excessive rate that is unacceptable commercially. Therefore, while the boron content of borane-reduced codeposits could be increased by decreasing the pH, this capability is limited by the fact that the boranes are consumed at rates that are unacceptable commercially when the pH is lowered to a level that produces a high-boron codeposit. Generally, a borane-reduced bath that is commercially viable from the point of view of acceptable levels of boron consumption should have a pH well in excess of 5.

It is known that the boron content of nickel born electroless deposits can be increased by the use of a borohydride ion as the reducing agent in the bath rather than a borane reducing agent, but borohydride-reduced baths lay down high-boron deposits only when such baths are operated at a pH of over 13 and at a temperature in excess of 90°C. These are relatively harsh conditions that are undesirable to maintain in a commercial electroless plating operation. But, if a borohydride-reduced bath is allowed to drop to a pH of below about 12, the bath undergoes spontaneous solution decomposition.

By the present invention, there has been discovered a manner of achieving the high boron percentage of above about 2% boron in the deposit from a borane-reduced electroless deposition bath, which avoids the use of the borohydride ion and avoids the high pH and high temperature conditions associated therewith. Baths according to this invention are borane reduced and can be operated under a relatively moderate temperature and a moderate pH.

It is accordingly a general object of the present invention to provide improved electroless nickel boron plating, characterized by a nickel-boron codeposit having a relatively high boron content, while using a borane reducing agent.

According to the present invention, electroless nickel-boron plating is deposited from baths including zirconyl ions, vanadyl ions, or combinations or mixtures thereof, together with a borane reducing agent and a source of nickel, the said baths being free of borohydride ions. Other typical electroless nickel bath ingredients may be included, such as complexing agents, stabilizers, buffers, and the like.

It is believed that the boron deposition enhancers impart added stability to the borane reducing agent in the bath while also enhancing its boron depositing capabilities at moderate pH values. Zirconyl ion boron deposition enhancers can be added to the bath by any compound that will liberate zirconyl ions (ZrO**), such as zirconyl chloride (ZrOCl₂·8H₂O). Vanadyl ion (VO**) boron deposition enhancers can be provided by compounds such as vanadyl sulfate or vanadium oxysulfate (VOSO₄·2H₂O) or other vanadyl salts, as well as by vanadates such as sodium metavanadate (NaVO₄·4H₂O), which vanadates oxidize organic compounds within the bath and in turn themselves undergo reduction to provide vanadyl ions within the bath.

The compounds which yield to zirconyl and/or vanadyl ions are included within baths at a concentration having a lower limit at which the particular enhancer increases the boron deposit percentage and an upper limit guided by economic and bath solubility considerations. A typical concentration of the boron deposition enhancer within the bath is at least about 0.0005 mol per liter, based on the total bath volume preferably at least about 0.0007 mol per liter, and most preferably at least about 0.001 mol per liter. Usually, there is no need to include these boron deposition enhancers at bath concentrations in excess of 0.5 mol per liter, preferably not greater than 0.1 mol per liter.

Borane reducing agents utilized in baths according to this invention include any bath-soluble borane source such as ammine boranes, amine boranes, lower alkyl substituted amine boranes, and cyclic amine boranes such as the nitrogen-inclusive heterocyclic boranes including pyridine borane and morpholine borane. Generally, the alkyl amine boranes are preferred, especially dimethyamine borane. Reducing agent concentrations within these baths are those that are sufficient to effect adequate reduction and are also cost-efficient for reducing the nickel cations within the bath. Typical minimum concentrations are at least about 0.001 mol per liter of bath, more usually at least about 0.005 mol per liter, while as much as 1 mol per liter could be
Thereof such as a solution of the pentasodium salt thereof such as the trisodium salt of 1-hydroxy-oxyacid with one mole of the polyhydric alcohol compound which contains at least two complex formed by reacting two or more mols of such as tartaric acid, gluconic acid or gluco-oxyacids used in forming the ester are generally compound.

Specific hydroxy substituted carboxylic acid complexing agents include citric acid, glycolic acid, lactic acid and malic acid, while exemplary amino-substituted carboxylic acids, aminodiacetic acid, and the amino acids such as α-alanine, aspartic acid, glutamic acid, glycine, lucine, serrine, triosine, and valine. Complexing agents falling within the category of ester complexes of polyhydric compounds formed by reacting an oxyacid with a polyhydric acid or alcohol such as those described in Mallory United States Letters Patent No. 4019910. Other complexing agents include phyrophosphoric acid and its derivatives as well as organo-phosphoric complexing agents including phosphonates.

These baths may optionally include stabilizers such as those of the carboxylic acid type, sources of antimony or of lead for controlling the sulfide ion content, or a sulfur containing compound such as thiourea or a combination thereof such as thioglycolic acid. Whenever a sulfur-containing compound is added, the sulfur content must be carefully controlled, since excessive sulfur will reduce the boron content of the deposit. Any such sulfur addition should be monitored so that the maximum sulfur concentration is about 20 ppm as divalent sulfur. Otherwise, when stabilizers are added to the bath, they are at a concentration typical for the particular compound.

In proceeding with the method according to this invention, a nickel-boron codeposit having a high boron content is laid down by deposition from a borane-reduced electroless nickel bath having a moderate pH and a moderate temperature, which bath includes a source of zirconyl and/or vanadyl ions. The operational pH is less than 13, typically between 4 and 10, and, in order to take the greatest advantage of the capabilities of this method to proceed under moderate conditions while still forming a high boron deposit, preferably the bath pH is maintained between about 5 and 7 while the temperature is maintained below 90°C, typically between about 60 and about 70°C. By such a method, nickel from the nickel source in the bath codeposit with boron from the reducing agent, this codeposit including in excess of 2 weight % boron, based on the total weight of the deposit.

The method includes preparing an electroless deposition bath including a bath-soluble source
of nickel, a bath-soluble borane reducing agent, a boron deposition enhancer that liberates vanadyl ions and/or zirconyl ions when added to the bath, preferably in combination with an electroless bath complexing agent. Preparing the bath may optionally include adding one or more stabilizers, sulfide-content controllers, buffers, buffering systems, polyalloy deposition sources, codeposition enhancers, and the like. Typically, it will be necessary to adjust the pH of the bath to within the desired moderate pH range, which is usually a strong base such as hydroxide to the bath, or when the pH becomes too high by adding a strong acid, such as sulfuric acid or other mineral acids.

Substrates to be deposited are immersed in the bath thus prepared. The weight or thickness of the nickel-boron complexed codeposit laid down by the bath will vary, of course, with the plating rate and the length of time that the substrate is immersed within the bath. Plating rates according to this method are about 0.2 and about 0.5 mil (about 0.5 to about 1.25 cm x 10^-3) per hour, and typical tank loadings are about 0.25 and 1.0 square foot per gallon (about 0.006 and 0.025 m²/l) of bath.

Products produced according to this invention include substrates, both metal and non-metal, that are plated with a protective coating of an electroless nickel-boron codeposit having a boron content of at least about 2 weight %, which codeposit is laid down by a bath according to this invention. These products can have boron contents as high as or in excess of 5 weight %, based on the weight of the deposit. Usually, the balance of the deposit will be nickel. Such plated codeposits exhibit an enhanced hardness, on the order of from 800 to 1000 VHN⁰.

The following examples are offered to illustrate the present invention.

Example I
An electroless bath was prepared to include 0.3 mol per liter of lactic acid, 0.08 mol per liter of citric acid, 0.04 mol per liter of dimethylamine borane, 0.01 mol per liter of zirconyl chloride octahydrate, 0.01 mol per liter of nickel, and enough ammonium hydroxide to maintain the pH at 6.0. The bath was raised to a temperature of 65°C, and a substrate was immersed therein, upon which there was formed a deposit of 4.1 weight % boron and 95.9 weight % nickel.

Example II
Another electroless nickel deposition bath was prepared by adding the following to an aqueous bath: 0.3 mol per liter of lactic acid, 0.08 mol per liter of citric acid, 0.04 mol per liter of dimethylamine borane, 0.001 mol per liter of vanadyl sulfate, 0.1 mol per liter of nickel, and a concentration of ammonium hydroxide to raise the bath to a pH of 6.0 at a temperature of 70°C. A deposit composition was formed containing 3.6 weight % boron and 96.4 weight % nickel.

Claims
1. An electroless nickel bath for laying down a nickel-boron deposit, said bath comprising:
   - a bath-soluble source of nickel and a bath-soluble borane reducing agent; and
   - being characterized in that it includes zirconyl ions, vanadyl ions, or a combination or mixture thereof, is free of borohydride ions, and does not substantially deposit zirconium or vanadium with the nickel-boron deposit.

2. An electroless bath according to claim 1, wherein the said reducing agent is an amine borane or a cyclic amine borane, present within the bath at a concentration of at least about 0.001 mol per liter, based on the total bath volume.

3. An electroless bath according to claim 2, wherein said compound is included within the bath at a concentration of at least about 0.0005 mol per liter, based on the total bath volume.

4. An electroless bath according to claim 3, wherein said reducing agent is an amine borane or a cyclic amine borane, present within the bath at a concentration of at least 0.001 mol per liter, based on the total bath volume.

5. An electroless bath according to any one of the preceding claims, wherein said bath further includes a complexing agent at a concentration of at least about 0.0005 mol per liter, based on the total bath volume.

6. An electroless bath according to claim 5, wherein said complexing agent is a carboxylic acid or hydroxy substituted carboxylic acid or a bath soluble derivative of either, or an organo-phosphoric compound.

7. An electroless bath according to claim 5, wherein said complexing agent is an ester complex of an oxyacid and a polyhydric acid or alcohol.

8. An electroless bath according to any one of the preceding claims which further includes at least one of a stabilizer, a buffer and a codeposition enhancer.

9. An electroless bath according to any one of the preceding claims which is at a pH of less than 13.

10. An electroless bath according to claim 9 which is at a pH of between about 4 and about 7.

11. An electroless bath according to claim 10 which is at a pH of between about 5 and about 7.

12. A method for electrolessly plating with a nickel-boron deposit, comprising immersing a substrate into an electroless nickel bath and depositing a high-boron-content nickel-boron deposit thereon, said bath being according to any one of the preceding claims.

13. A method according to claim 12, wherein said bath is at a temperature of not greater than 90°C.

Patentansprüche
1. Ein strömloses Nickelbad zum Abscheiden einer Nickel-Bor-Auflage, das genannte Bad umfassend:
   - eine badlösliche Nickelquelle und
eine badlösliche Boran-Reduktionsmittel; und dadurch gekennzeichnet, daß es Zirkonylionen, Vanadylionen oder eine Kombination oder eine Mischung derselben enthält, frei von Borhydridionen ist und nicht wesentlich Zirkon oder Vanadium mit der Nickel-Bor-Auflage abscheidet.

2. Ein stromloses Bad nach Anspruch 1, worin sich die genannten Ionen aus der Verbindung Zirkonylchlorid, Vanadylsulfat, Natriummeta-

Vanadylionen oder ein Gemisch derselben ableiten.

3. Ein stromloses Bad nach Anspruch 2, worin die genannte Verbindung im Bad in einer Konzen-

tration von wenigstens 0,0005 Mol pro Liter, bezogen auf das Gesamtvolumen des Bades, enthalten ist.

4. Ein stromloses Bad nach Anspruch 1, Anspruch 2 oder Anspruch 3, worin das genannte Reduktionsmittel ein Aminoboran oder ein zylisches Aminoboran ist, das im Bad in einer Konzentration von wenigstens etwa 0,001 Mol pro Liter, bezogen auf das Gesamtvolumen des Bades, enthalten ist.

5. Ein stromloses Bad nach einem der vorherge-

henden Ansprüche, worin das genannte Bad weiters einen Komplexbildner in einer Konzen-

tration von wenigstens etwa 0,0005 Mol pro Liter, bezogen auf das Gesamtvolumen des Bades, enthält.

6. Ein stromloses Bad nach Anspruch 5, worin der genannte Komplexbildner eine Carbonsäure oder eine hydroxy-substituierte Carbonsäure oder ein badlösliches Derivat einer der beiden oder eine Organophosphorverbindung ist.

7. Ein stromloses Bad nach Anspruch 5, worin der genannte Komplexbildner ein Esterkomplex einer Oxysäure und einer mehrwertigen Säure oder eines mehrwertigen Alkohols ist.

8. Ein stromloses Bad nach einem der vorherge-

henden Ansprüche, das weiters wenigstens einen Stabilisator, Puffer oder Ko-Abscheidungs-

Verstärker enthält.

9. Ein stromloses Bad nach einem der vorherge-

henden Ansprüche, das einen pH-Wert von weniger als 13 aufweist.

10. Ein stromloses Bad nach Anspruch 9, das einen pH-Wert zwischen etwa 4 und etwa 10 aufweist.

11. Ein stromloses Bad nach Anspruch 10, das einen pH-Wert zwischen etwa 5 und etwa 7 aufweist.


13. Ein Verfahren nach Anspruch 12, worin das genannte Bad eine Temperatur von nicht mehr als 90°C aufweist.

Revendications

1. Bain de nickel à immersion pour former un dépôt de nickel-bore, ledit bain comprenant:

une source de nickel soluble dans la bain et un agent réducteur de borane soluble dans le bain; et

caractérisé en ce qu’il contient des ions de zirconyl, des ions de vanadyle ou une combinaison ou un mélange de ceux-ci, est exempt d’ions de borohydure et ne dépose sensiblement pas de zirconium ou de vanadium avec le dépôt de nickel-bore.

2. Bain avec immersion selon la revendication 1, où ledits ions dérivant du composé chlorure de zirconyl, sulfate de vanadyl, métavanadate de sodium ou un mélange.

3. Bain avec immersion selon la revendication 2, où ledit composé est incorporé dans le bain à une concentration d’au moins environ 0,0005 mole par litre, en se basant sur le volume total du bain.

4. Bain avec immersion selon la revendication 1, la revendication 2 ou la revendication 3, où ledit agent réducteur est une amine borane ou une amine borane cyclique, présente dans le bain à une concentration d’au moins environ 0,001 mole par litre, en se basant sur le volume total du bain.

5. Bain avec immersion selon l’une quelconque des revendications précédentes, où ledit bain contient de plus un agent complexant à une concentration d’au moins environ 0,0005 mole par litre, en se basant sur le volume total du bain.

6. Bain avec immersion selon la revendication 5, où ledit agent complexant est un acide carboxylique ou un acide carboxylique hydroxy substitué ou un dérivé soluble dans le bain de l’un d’entre eux ou un composé organophosphorique.

7. Bain avec immersion selon la revendication 5, où ledit agent complexant est un ester complexe d’un oxyacide et un acide polyhydrique ou un alcool.

8. Bain avec immersion selon l’une quelconque des revendications précédentes qui contient de plus au moins un stabilisant, un tampon et un agent améliorant le codépôt.


10. Bain avec immersion selon la revendication 9 qui est à un pH entre environ 4 et environ 10.

11. Bain avec immersion selon la revendication 10 qui est à un pH entre environ 5 et environ 7.

12. Procédé pour le placage avec immersion au moyen d’un dépôt de nickel-bore, consistant àimmerger un substrat dans un bain de nickel sans courant et à y déposer un dépôt de nickel-bore à forte teneur en bore, ledit bain étant selon l’une quelconque des revendications précédentes.

13. Procédé selon la revendication 12, où ledit bain est à une température ne dépassant pas 90°C.