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CHEMICAL PLATING OF METAL-BORON ALLOYS

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This invention relates to a method of chemical plating and more particularly to a method of plating objects with metal-boron alloys.

Nickel-boron, cobalt-boron, and ferroboron alloys are known for their superior flowing properties, wear resistance, and hardness. Metal boron alloys, or metal borides are particularly useful as coatings for steel and other metals that do not possess these desirable properties. The metal-boron alloys are also useful as catalysts for a number of chemical reactions, e.g., hydrogenation reactions. Coatings of metal-boron alloys on metallic or non-metallic base materials are particularly desirable as catalysts since a maximum amount of catalytic surface is provided by a minimum amount of the metal-boron alloy.

It has long been known that alkali metal borohydrides, MBH_4, react spontaneously with aqueous solutions of nickel, cobalt, or iron salts to form precipitates of the corresponding metal borides. Metal-boron coatings on steel objects have previously been made by coating the object with a specially precipitated metal boride and firing the object to form an adherent coating.

This invention is based on my discovery that certain ammoniacal solutions of a borohydride and soluble nickel, cobalt or iron salts are stable and do not spontaneously react. When a material with a catalytically active surface is contacted with this stable solution, a reaction occurs at the surface forming an adherent continuous plate of metal-boron alloy on the surface. The alloy plate itself is catalytically active so that the surface reaction can be continued to form a plate of any desired thickness. I have found that any clean metal surface, free of oxide film, is catalytically active. Glass and ceramic material also exhibit catalytic activity, but they are much less active than metals. Waxes, e.g. paraffinic waxes, natural fibers, and synthetic organic polymers, e.g. polyethylene and nylon, exhibit essentially no catalytic activity.

The solution or plating bath of this invention comprises an aqueous solution containing from about: (1) 0.02 to 5 parts by weight metal ion of the metal boron alloy to be plated, (2) 0.01 to 0.2 part by weight of borohydride ion, and (3) 1.5 to 25 parts by weight of ammonia.

The metal ion, i.e., iron, cobalt, or nickel ion, is provided by use of any soluble metal salt such as nickel sulfate, nickel chloride, nickel acetate, cobaltous sulfate, cobaltous chloride or ferrous sulfate or other suitable soluble salts. It is preferred to use the metal ion of a lower oxidation so that the borohydride is not consumed in reducing a higher oxidation state ion. For example, although ferric chloride may be used, ferrous chloride is preferred as there is higher yield of plate produced per unit weight of borohydride used.

The borohydride ion is provided by use of any ionic borohydride, e.g., alkali metal borohydride, alkaline earth borohydride or quaternary ammonium borohydrides. Sodium and potassium borohydride are now preferred as they are widely available at moderate cost.

The ammonia serves a dual function in the plating bath. It acts as a sequestering agent of the metal ions and also acts to control the pH of the solution. There must be sufficient ammonia to provide a pH in excess

of about 10; if the pH of the solution is below about 10, the solution spontaneously reacts. It is preferable to maintain the pH below about 12 since at higher pH values, the plating reaction is very slow. If the pH of a plating bath is too high for plating at a satisfactory rate, it may be adjusted by the addition of an ammonium salt of a strong acid, e.g. ammonium chloride. In preparing the plating baths, the borohydride and metal salt should not both be added to the solution before ammonia is added. If the reactive borohydride and metal salt are mixed in aqueous solution a spontaneous reaction occurs. It is generally preferred to add the borohydride to an ammoniacal solution of the metal salt.

The plating baths of this invention have varying degrees of activity. The more active baths plate more rapidly and are particularly desirable for plating glass and ceramic surfaces. The activity of the bath increases with increasing metal ion concentration and increasing borohydride ion concentration. The ammonia concentration, or pH, is particularly important in determining bath activity; the activity increases with decreasing pH.

The plating bath may be used at any temperature between about room temperature and the boiling point of the solution. The activity of the bath increases with increasing temperature. A temperature of about 25 to 40° C. is preferred as the bath is sufficiently active to plate at a good rate, and the temperature is not sufficiently high to require closed vessels to keep ammonia in solution.

The object to be plated is immersed in the plating bath and the plating commences. The object may conveniently be suspended by a string or rope made of natural or synthetic fiber, or it may be suspended in a cloth or supported by a wooden or synthetic polymer rack. If a metal piece is used to support the object to be plated, some of the bath will be consumed in plating the support. After the object has been plated, it is removed from the bath and washed with water to remove the bath solution and permitted to dry.

Metal objects to be plated must have clean surfaces free of oxide film. The objects are cleaned by any of the conventional cleaning procedures. The clean metal surface catalyzes the chemical reduction reaction which results in a metal-boron alloy plate on the clean surface. Objects of steel, iron, nickel, cobalt, copper and copper base alloys, aluminum and aluminum base alloys, palladium, and other metals may be plated according to this invention.

Glass and ceramic objects to be plated must have clean surfaces free of oil or grease films. They may be cleaned by any of the conventional procedures.

It is preferred to contain the plating solution in a vessel that exposes only non-active surfaces to the bath. Synthetic polymer vessels, such as polyethylene, may be used, and vessels lined with non-active material are particularly convenient, e.g. paraffin wax lined, polyethylene lined, or polyvinylidene chloride lined vessels. The plating process is then selective; the plating occurs on the metal, glass or ceramic object immersed in the solution and does not occur on the vessel walls. Glass containers may be used when metals are being plated with plating solutions of moderate activity; although the plating is not entirely selective undesired plating on the glass container is slight.

When plating has proceeded for several hours, a small amount of metal-boron alloy is precipitated from the solution and collects at the bottom of the vessel. This precipitate is itself catalytically active so that if it is not removed some of the plating solution will be consumed by reaction induced by the precipitate. The precipitate may be removed by filtration.

The chemical plating consumes borohydride and metal

ion; and desired concentration or concentration range may be maintained by adding additional borohydrides or metal salts to the plating solution. As the plating proceeds there is a build up of by-product salt concentration in the bath; e.g., when the reactive ingredients of the plating solution are sodium borohydride and nickel chloride, the by-product salt is sodium chloride. The by-product salts are not detrimental to the process unless they reach a concentration such that the reactive bath components do not have sufficient solubility. It is more economical to discard the bath rather than remove the by-product salt.

The following examples are illustrative of the plating solutions of this invention. The compositions of the solutions are expressed in weight percent of anhydrous reactants. The actual metal salts used were hydrates and the ammonia was added as ammonium hydroxide.

EXAMPLE I

A plating solution containing 1.9 wt. percent $NiSO_4$, 0.2 wt. percent $NaBH_4$, 2.7 wt. percent NH_3 and 95.2 wt. percent water was made up by adding the borohydride to an ammoniacal solution of nickel sulfate contained in a wax coated beaker. Clean metal strips of copper, Phosphor bronze, brass, antimonial Admiralty, Olympic bronze, cartridge brass, nickel, Inconel, Monel, cupro nickel, aluminum, and carbon steel were plated with nickel-boron alloy by immersing the individual metal strips in aliquots of the plating solution for two hours, at about 18° C.

EXAMPLE II

A clean carbon steel panel was immersed in a plating solution containing 0.13 weight percent $NiSO_4$, 0.04 wt. percent sodium borohydride, 1.42 wt. percent ammonia and 98.41 wt. percent water. The plating solution was contained in a glass vessel. The metal panel was plated with nickel-boron alloy and only a negligible amount of alloy was plated on the container.

EXAMPLE III

Ferroboron alloy was plated on aluminum and carbon steel panels by immersing the panels for several hours at 18° C. in a plating solution containing 1.78 wt. percent $Fe(NH_4)_2(SO_4)_2$, 0.03 wt. percent sodium borohydride, 12.90 wt. percent ammonia, and 85.29 wt. percent water. Some black precipitate formed in the plating solution.

EXAMPLE IV

A clean, mild steel test panel was immersed in a plating solution of the composition 4.0 wt. percent $CoCl_2$, 0.6 wt. percent $NaBH_4$, 4.5 wt. percent NH_3, 6.1 wt. percent NH_4Cl, and 84.8 wt. percent water. After about 2 hours a cobalt-boron alloy plate of 1×10^{-3} inches thickness was plated on the test panel. An adherent plate was also formed on the surface of the glass container where it was in contact with the solution.

EXAMPLE V

A series of plating reactions were performed in which nickel-boron alloy was plated on carbon steel. The conditions and results are set forth in Table I.

Table I

PLATING NICKEL-BORON ALLOYS ON MILD STEEL

Run No.	1	2	3	4
Plating Composition (wt. percent):				
$NiCl_2$	2.62	2.62	2.62	1.80
$NaBH_4$	0.45	0.45	0.45	0.22
NH_3	17.20	17.20	13.90	3.32
H_2O	79.73	79.73	83.03	94.46
Temperature (deg.)	22.50	40	40	40
Plating Time (min.)	213	213	52	108
Average Plating Rate (in $\times10^{-3}$/hr.)	0.0027	0.006	0.016	0.029

The increase in plating rate with increasing temperature is illustrated by runs 1 and 2. The decrease in plating rate with increasing ammonia concentration, or pH, is illustrated in runs 2, 3, and 4.

EXAMPLE VI

A mild steel test panel was immersed in a plating solution containing 1.9 wt. percent $NiSO_4$, 0.2 wt. percent $NaBH_4$, 2.7 wt. percent NH_3 and 95.2 wt. percent water maintained at 18° C. After about 2 hours the plating on the panel had essentially stopped. Additional sodium borohydride in an amount equal to 0.1 percent of the weight of the solution was added, and plating immediately recommenced.

EXAMPLE VII

A plating solution containing 1.9 wt. percent $NiSO_4$, 2.9 percent NH_3, 0.2 percent $NaBH_4$, and 96 percent water was made in a glass beaker. After several hours standing at room temperature, a continuous adherent coating of nickel-boron plate formed on the portion of the beaker in contact with the solution.

The metal-boron coatings formed by the process of this invention generally appear dark to semi-bright. The plated alloy contains from about 4 to 10 percent boron.

According to the provisions of the patent statutes, I have explained the principle and mode of practicing my invention, have described what I now consider to be its best embodiments. However, I desire to have it understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

I claim:

1. An aqueous chemical plating solution containing as essential components (1) an ionic borohydride, (2) a compound selected from the group consisting of soluble salts of iron, cobalt and nickel, and (3) ammonia, the proportions of each component being such that the concentration of borohydride ion is between about 0.01 and 0.2 wt. percent, the concentration of metal ion is between about 0.02 to 5 wt. percent, and the concentration of ammonia is between about 1.5 to 25 wt. percent.

2. A method of plating metal-boron alloys on an object selected from the class consisting of metal, glass and ceramic objects which comprises the step of contacting the object to be plated with an aqueous plating solution containing as essential components (1) an ionic borohydride, (2) a compound selected from the group consisting of soluble salts of iron, cobalt and nickel, and (3) ammonia, the proportions of each component being such that the concentration of borohydride ion is between about 0.01 to 0.2 wt. percent, the concentration of metal ion is between about 0.02 to 25 wt. percent, and the concentration of ammonia is between about 1.5 to 25 wt. percent.

3. A method according to claim 2 in which the borohydride is sodium borohydride.

4. A method according to claim 2 in which the plating solution is maintained at a temperature between about 25° C. and 40° C.

5. A method according to claim 2 in which the pH of the plating solution is maintained between about 10 and 12.

6. A method according to claim 5 in which an ammonium salt of a strong acid is added to the solution to maintain the pH of the solution.

7. A method according to claim 2 in which the concentration of borohydride ion is maintained by the periodic addition of an ionic borohydride.

8. A method according to claim 2 in which the concentration of metal ion is maintained by the periodic addition of a soluble metal salt.

9. A method according to claim 2 in which the object to be plated is a metal selected from the group consisting of iron and iron base alloys.

10. A method of plating metal-boron alloys on an object selected from the class consisting of metal, glass and ceramic objects which comprise the step of contacting the

object to be plated with an aqueous plating solution containing as essential components (1) an ionic borohydride, (2) a compound selected from the group consisting of soluble salts of a heavy metal, and (3) ammonia, the concentration of borohydride ion being about 0.03 weight percent, the concentration of metal ion being about 0.1 weight percent and the concentration of ammonia being about 3.0 weight percent.

11. A method of plating metal-boron alloys on metal objects which comprises the step of contacting the metal object to be plated with an aqueous plating solution containing as essential components (1) an ionic borohydride, (2) a compound selected from the group consisting of soluble salts of a heavy metal, and (3) ammonia, the

concentration of borohydride ion being about 0.03 weight percent, the concentration of heavy metal ion being about 0.1 weight percent and the concentration of ammonia being about 3 weight percent.

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