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[73] Assignee **The United States of America as**
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[54] **NONAQUEOUS ELECTROPLATING SOLUTIONS**
AND PROCESSING
6 Claims, 2 Drawing Figs.

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B01k 1/00
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59

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ABSTRACT: Nonaqueous electroplating solutions containing dimethyl sulfoxide and a plating metal salt, a process for electroplating using these solutions wherein the solution is heated to a temperature between about 160° and 200° F. and a modified process for selectively electroplating as a composite coating more than one material at separate plating rates.

FIG. 1

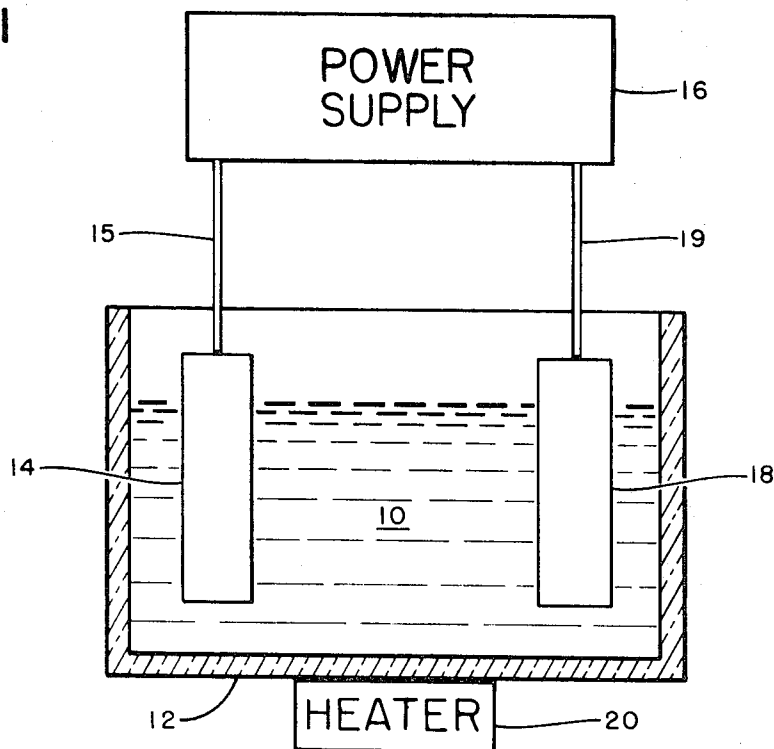
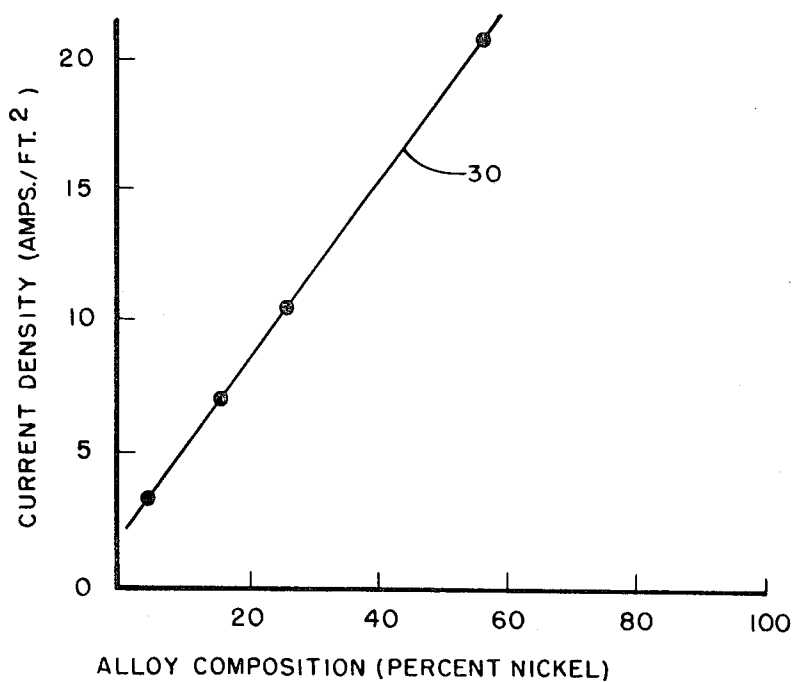


FIG. 2



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NONAQUEOUS ELECTROPLATING SOLUTIONS AND PROCESSING

BACKGROUND OF THE INVENTION

New and improved electrolytic solutions and electroplating techniques are continually being sought to improve plated products. Electroplating is used in such areas as corrosion protection, preparation of materials for later joining operations by soldering or welding or the like, reduction of coefficients of friction, production of electrical contacts or contacting surfaces as well as for other similar applications.

It is important in many of these applications that the base metal part or member not be adversely affected or deteriorated by the electroplating operation. This is a particular problem in the electroplating of high-strength steel in conventional aqueous baths due to hydrogen embrittlement which may occur from the hydrogen byproduct which may normally be produced at the cathode.

Static loads of substantially less than normal strength may produce fracture of high-strength steel parts if the parts have been embrittled by hydrogen. Failure by embrittlement is thought to be the result of atomic hydrogen absorbed by steel during processing in which hydrogen is evolved at the surface of the steel part, accompanied by diffusion of hydrogen through the surface and accumulation of the hydrogen at points of stress. When stressing occurs, embrittlement may be produced at the points of stress with resultant failure of the part. A plated part may be treated such as by heat treating to reduce embrittlement but there is no guarantee of results. Also, no technique is presently known, without destructive testing, of accurately predicting or determining the degree or extent of hydrogen embrittlement of a steel member. Any electrolytic solution which may be used to electroplate steel with tightly adherent coatings without generating or evolving hydrogen would have obvious advantages.

There are applications, such as with corrosion-inhibiting coatings and with joining operations, where it may be desirable to plate a single-phase alloy onto a part or member from a single electrolytic solution over a range of constituent proportions. In some of these applications it may be desirable to vary the constituent proportions as plating proceeds to produce a gradient in composition percentages. Such an application may be where the initial plating layer is an alloy having high adherence qualities and subsequent alloy layers have high joining capabilities. Another application may be where varying electrical resistances with plating depth may be desirable. The obtaining of these characteristics without hydrogen embrittlement may be desirable.

SUMMARY OF INVENTION

It is the object of this invention to provide new nonaqueous plating solutions and electroplating processes for these solutions.

It is a further object of this invention to provide a process for selective electrodeposition of mixtures of plating metal salts in nonaqueous electrolytic solutions.

Various other objects and advantages will appear from the following description of the invention, and the most novel features will be particularly pointed out hereinafter in connection with the appended claims.

The invention comprises nonaqueous electrolytic solutions including dimethyl sulfoxide and a plating metal salt and processes for electroplating using these solutions.

DESCRIPTION OF DRAWING

Aspects of the invention are shown in the drawings wherein: FIG. 1 is a diagrammatic view, partially in cross section, of an electroplating apparatus which may be used with this invention; and

FIG. 2 is a graph showing composite deposition rates for changing plating current.

DETAILED DESCRIPTION

Metals may be plated onto any desired conductive part or member from essentially nonaqueous, electrolytic solutions including the solvent dimethyl sulfoxide (hereinafter referred to as DMSO) and a salt of the plating metal. The solution may also include, where appropriate, one or more other solvents such as dimethyl formamide (DMF) and ethylene glycol mixed in solution with DMSO. Various combinations of solvent mixtures including DMSO may be used depending on the particular plating metal salt being used and its solubility in one or the other of the solvents.

Various salts, such as nitrates, chlorides and sulfates as well as others of the plating metals may be used, as determined by the solubility and plating characteristics of the salt. Complexing agents may also be used to increase solubility in desired instances including such ammonia-complexing agents as ammonium chloride, ammonium nitrate and ammonium cyanide and other cyanide-complexing agents like sodium cyanide.

Metals which may be conveniently plated from these solutions include nickel and copper. Other metals may include cobalt, lead, zinc, silver and cadmium. These metals may be plated on such conductive materials or parts as brass, bronze, copper, steel, iron, zinc and cadmium. In the case of iron and steel, electroplating may be conducted with these solutions without hydrogen embrittlement even though some water may be introduced into the solution from hydrated salts or the atmosphere to as high as about 5 percent or more. In order to limit the amount of moisture absorbed from the atmosphere, it may be desirable to protect or shield the solution from this moisture as much as possible, especially when the solution is cool.

These solutions may be used in any conventional electroplating apparatus such as that shown in the drawing wherein an electrolytic solution 10 made in accordance with this invention is disposed within suitably shaped vessel 12. Vessel 12 may be made of any nonconducting material which is not reactive with solution 10 such as glass, polytetrafluoroethylene or polychlorotrifluoroethylene or a structural material coated with one of these nonconducting materials. The member or part 14 to be plated may be immersed in solution 10 and connected to a direct current power supply 16 through conductor 15 as the cathode. A suitable electrode 18, preferably made of the metal being plated, so as to provide a continuous supply of metal ions to the solution, may also be immersed in solution 10 and connected to power supply 16 through conductor 19 as the anode. Solution 10 may be heated to the desired plating temperature by a conventional heater 20 such as an immersion heater, burner or the like.

Typical solutions and representative constituent amounts which may be used for the electrodeposition of copper and nickel onto a desired member or article are as follows:

SOLUTION A

DMSO	1,250 cc.
DMF	75 cc.
Cuprous chloride	50 grams
Ammonium chloride	50 grams

SOLUTION B

DMSO	1,000 cc.
Cuprous chloride	12.5 grams
Ammonium chloride	25 grams

SOLUTION C

DMSO	840 cc./liter
DMF	133 cc./liter
Cuprous chloride	35 grams/liter
Ammonium chloride	40 grams/liter

SOLUTION D

DMSO	
750 cc.	
DMF	120 cc.
Cuprous chloride	32 grams
Ammonium chloride	32 grams

SOLUTION E

DMSO	
	800 cc.
Ethylene glycol	480 cc.
DMF	20 cc.
Nickel chloride	40-160 grams
Nickel sulfate	160-40 grams

SOLUTION F

DMSO	
	800 cc.
Ethylene glycol	400 cc.
Nickel sulfate	114 grams

SOLUTION G

DMSO	
	750 cc.
Ethylene glycol	450 cc.
Nickel chloride	180 grams

SOLUTION H

DMSO	
	562 cc./liter
Ethylene glycol	343 cc./liter
DMF	14.3 cc./liter
Nickel chloride	Nickel 114 grams/liter
Nickel sulfate	24.6 grams/liter

The members or parts to be plated, such as member 14 in FIG. 1, may be degreased in a solvent wash or by vapor degreasing or caustic cleaning. Some cleaning may occur from immersion in the electrolytic solution itself. After plating, the plated member may be cleaned and rinsed by any appropriate means. It has been found with copper plating that the member may be rinsed with DMSO or the like to remove any remaining plating solution to prevent discoloration of the copper.

Using solution A, copper may be plated having a bright, tightly adhering and dense coating on a wide range of materials. Deposition rates may be achieved with good coatings varying from about 0.05 mil/minute with plating current of 3.0 a./square foot of cathode area to about 0.5 mil/minute at 25 to 30 a./square foot with bath or solution temperatures between about 160° and 20° F. preferably at about 190° F. Higher deposition rates may be achieved with solution agitation and using the higher operating temperature.

With solution C, bright, adherent copper coatings may be produced at a temperature of about 180° F. over a current range of from about 3 to 25 a./square foot. Platings may be produced with solutions, such as with solution C, using the metal salt at concentrations as low as about 3 grams/liter to as high as about 300 grams/liter with commensurate amounts of a complexing agent. The other copper solutions may be used within the temperature range set forth above (namely 160° F. to 200° F.) to produce copper coatings at different deposition rates depending on temperature and current densities.

It has been found that cuprous ions provide more satisfactory coatings than cupric ions. Any oxidation of cuprous ions to cupric ions may be reversed by reduction of the cupric ions with hypophosphite ions from such materials as sodium hypophosphite, ammonium hypophosphite or hypophosphorous acid. If the pH of the copper electrolyte solutions increases from the best plating range, which may be between about 2.3 and 4.5 the solution may be buffered with the same agent.

A tightly adhering, good quality nickel plating with a dense matte finish may be produced with solution E. Deposition rates may be achieved with good coatings varying from about 0.01 mil/minute with plating current of 1.1 a./square foot

(cathode area) to about 0.10 mil/minute at 12 a./square foot or more with a bath temperature of about 170° to 200° F. with a preferred temperature of from about 180° F. to 190° F. With solution H, a good quality plating may be achieved at a temperature of about 180° F. and a plating current of about 10 a./square foot while maintaining a good long term stability solution. Good quality nickel coatings may also be achieved with the other solutions within the above plating current and temperature ranges.

It has been found that in order to provide a plating having good adherence, texture and appearance, the minimum plating solution temperature for all solutions is about 160° F. If the plating solutions are heated to above about 200° F. the plating solution begins to decompose.

The quantity of water in the solutions may be determined by infrared spectroscopic techniques or by calculations. Solution H may have about 8 percent by volume water while solution C may have about 3 percent by volume water from stock reagents and metal salts. Other solutions may have more or less water concentrations depending on the purity of the reagents, the amounts of metal salts used and the techniques used to exclude moisture from the solutions.

Test bars made of steel having a 45° notch 0.02 inch deep and plated by solutions B and E with coatings of about 0.0002 inch were subjected to a constant static stress of 90 percent ultimate strength. These bars failed after periods of about 560 hours to greater than 850 hours. Control test bars plated by conventional aqueous electroplating techniques and subjected to the same static stress failed on the average in less than about 2 hours with the majority of test bars failing in less than 1 hour.

Composite depositions constituting alloys of two or more metals may be plated from a mixture of two or more nonaqueous electrolytic solutions with all the advantages commensurate therewith and described above. The percentage of the constituents of the plated alloy may be determined by selecting the proper plating current for the desired alloy percentages. A gradient of different alloys and constituent percentages may be achieved by varying the plating current during deposition.

Such composite electrodepositions may be achieved using an apparatus similar to FIG. 1 with an anode 18 made of one of the plating metals or a plurality of separate or composite anodes connected in electrical parallel and made of each plating metal. The respective electrolytic plating solutions may be separately prepared and then mixed together in a single composite solution 10.

For example, solutions D and G may be prepared independently by heating and stirring the salts in the respective solvents and, after the solutions are completed in both systems, mixing the solutions together in a single composite solution. The composite solution may then form complexes of copper and nickel. With the composite solution disposed in a suitable electroplating container such as vessel 12, the solution may be heated by heater 20 to a suitable plating temperature as noted above. Electroplating may then be started by adjusting power supply 16 to some desired plating current by any conventional means (not shown), such as a rheostat, and the current appropriately metered (not shown).

Using a composite or mixture of solutions D and G and a composite solution temperature of about 180° F., good platings may be achieved with plating current densities from about 2.0 to about 22 a./square foot cathode area. As the plating current is increased over this range, the percentage of nickel in the plated coating of a copper-nickel alloy may vary linearly from slightly above 0 (generally about 5 percent) to about 55 percent as shown by the curve 30 in FIG. 2. Thus, copper-nickel alloys from about Cu 95 percent-Ni 5 percent to about Cu 45 percent-Ni 55 percent may be reliably achieved by this process by selecting the desired plating current level. A varying gradient of alloy percentages may be achieved by changing the plating current continuously by some automatic or manual means, if desired. Distinct layers of

alloys, possibly with intermediate gradients, may be achieved by changing the plating current in steps shown by the dots along curve 30 depending on the desired properties of the plating or platings. With conventional X-ray diffraction techniques, it may be determined that these platings are single-phase materials, e.g. a true alloy.

Such an alloy gradient may be particularly useful in the fabrication or manufacturing of printed circuitry, fluid amplifiers and similar devices where a plating is etched and it is desirable that the boundary between unetched and etched portions be near perpendicular or vertical. Using a plating having a higher percentage copper along the plated member with a gradient of increasing nickel as plating progressed, perpendicular etching may be achieved by selecting an etchant which reacts at a faster rate for copper than for nickel. As the plating is dissolved away, the remaining portion may be richer in copper causing a continued acceleration of etching in the desired direction.

The present invention provides new nonaqueous electrolytic plating solutions which may be used in a wide range of applications particularly where possible hydrogen embrittlement may be a factor. These solutions in turn may be mixed to provide composite alloy platings of more than one metal.

It will be understood that various changes in the details, materials and arrangements of plating apparatus, which have herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art within the principles and scope of the invention as expressed in the appended claims.

What is claimed:

1. A nonaqueous electroplating solution comprising a mixture of a first anhydrous solution including dimethyl sulfoxide and a copper salt of a plating metal; and a second anhydrous

solution including dimethyl sulfoxide, an organic solvent selected from the group consisting of ethylene glycol and dimethyl formamide, and a nickel salt of a plating metal, each of said salts being simultaneously plateable from said solution at any desired rate by adjusting plating current.

2. The solution of claim 1 wherein said solution includes a complexing agent selected from the group consisting of ammonium chloride, ammonium nitrate, ammonium cyanide and sodium cyanide and said copper salt is a copper chloride and said nickel salt is selected from the group consisting of nickel chloride and nickel sulfate.

3. A process of electroplating a metal coating on a metallic member comprising, dissolving a copper salt of said coating metal in dimethyl sulfoxide to form a first anhydrous electrolytic solution, dissolving a nickel salt in dimethyl sulfoxide to form a second anhydrous electrolytic solution, mixing said first and second solutions, immersing said metallic member in said mixed electrolytic solution, immersing an anode electrode in said mixed solution, heating said mixed solution to a temperature of from about 160° to 200° F., passing predetermined plating current through said mixed solution from said anode electrode to said metallic member for controlling plating rates from said salts.

4. The process of claim 3 wherein said heating is to a temperature between about 170° to 190° F.

5. The process of claim 3 including the additional step of adjusting said plating current by prescribed amounts during said process for plating alloys thereof with selectable constituent percentages.

6. The process of claim 5 wherein said plating current is adjusted between about 2 and 22 a./square foot of said metallic member.

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