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PROCESS FOR ELECTROPLATING MOLYBDENUM AND MOLYBDENUM ALLOYS

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The invention relates to the electrodeposition of molybdenum.

We have discovered that molybdenum may be efficiently electrodeposited from aqueous electrolytes containing molybdic acid, its anhydride or its salts in the presence of the fluoride ion.

The work on which the electrodeposition of molybdenum is desired is placed in the electrolyte to form the cathode and the anode is a conducting material which will not be attacked by the reaction products at the anode such as carbon. A cathode of copper, iron or nickel has been found to be satisfactory.

The electrolyte bath consists of 100 grams of potassium fluoride dihydrate, $KF2H_2O$; 10 to 15 cc. of 48% aqueous hydrofluoric acid, HF; 50 to 130 cc. of water; and 5 grams of molybdic anhydride, MoO_3.

The current density used is from 0.25 to 0.35 ampere per square centimeter of outside surface. The temperature is preferably maintained between 30° C. and 50° C. Above 65° C. dark, nonadherent deposits are obtained.

With our process as above described, we have been able to obtain smooth, bright, adherent deposits of molybdenum in five minutes. The deposited metal is resistant to acid such as cold hydrochloric and sulfuric and is resistant to strong alkalies, but is soluble in nitric acid.

Alloys of mixtures of molybdenum with other metals may be prepared by codeposition. To prepare an iron alloy or mixture, 5 cc. of a solution of ferrous sulfate, $FeSO_4$, containing 0.02 gram of the element iron per cc., is added to the electrolyte. To prepare a nickel alloy, 3 cc. of a solution of nickel sulfate, $NiSO_4$, containing 0.02 gram of the element nickel per cc., is added to the electrolyte. To prepare a cobalt alloy, 3 cc. of a solution of cobalt sulfate, $CoSO_4$, containing 0.02 gram of the element cobalt per cc., is added to the electrolyte.

Our process is adapted for the electroplating of articles with molybdenum or with alloys of molybdenum with other metals to render them corrosion-resistant as well as to obtain a bright decorative effect. It is also useful for preparing molybdenum sheet by obtaining a thick deposit of the metal on a suitable cathode and subsequently dissolving off the cathode and leaving the molybdenum in sheet form.

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The fluoride ion which is present in high concentration increases the solubility of the hexavalent molybdenum compounds in the acid solution and also, with the hydrofluoric acid, increases the solubility of the reduction products of the hexavalent molybdenum compounds formed during the process of electrolysis, thereby preventing the precipitation of molybdenum hydroxide or basic salts.

One of the chief advantages of our process is that the molybdenum compounds used are the most readily available compounds of the element. Molybdic anhydride, MoO_3, and ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}4H_2O$, are both commercially available and are both operative in our process.

To illustrate our invention, the following examples are given:

Example I

An electrolyte is made up of the following composition:

5 g. molybdic anhydride
100 g. $KF.2H_2O$
13.5 cc. HF (48%)
50 cc. H_2O

The optimum conditions for obtaining deposition of molybdenum from this bath are cathode current density 0.3 ampere per square centimeter; temperature 30° to 50° C. Bright metallic deposits of molybdenum are obtained in five minutes. The weight of the average deposit is 0.7 mg. on an area of 12 square centimeters of cathode surface. The current density range for bright metal plating from this bath is from 0.2 to 0.4 ampere per square centimeter.

Example II

An electrolyte is made up of the following composition:

2.5 g. molybdic anhydride
50 g. $KF.2H_2O$
6.5 cc. HF (48%)
5 cc. $FeSO_4$ solution (0.02 g. Fe per cc.)

The optimum conditions for obtaining deposits containing molybdenum and iron from this bath are; cathode current density 0.2 ampere per square centimeter; temperature 30° to 50° C. Bright metallic plates are obtained in five minutes. The weight of an average deposit

is 0.9 mg. on an area of 12 square centimeters of cathode surface. The current density range for bright metal plating from this bath is from 0.2 to 0.35 ampere per square centimeters.

Example III

An electrolyte is made up of the following composition:

2.5 g. molybdic anhydride
50 g. $KF.2H_2O$
6.5 cc. HF (48%)
65 cc. H_2O
3 cc. $CoSO_4$ solution (0.02 g. per cc.)

The optimum conditions for obtaining deposits containing molybdenum and cobalt are; cathode current density 0.2 ampere per square centimeter; temperature 30° to 50° C. Bright metallic plates are obtained in five minutes. The weight of an average deposit is 2.4 mg. on on area of 12 square centimeters of cathode surface. The current density range for bright metal plating from this bath is from 0.2 to 0.3 ampere per square centimeter.

Example IV

An electrolyte is made up of the following composition:

5 g. molybdic anhydride
50 g. $KF.2H_2O$
6.5 cc. HF (48%)
65 cc. H_2O
3 cc. $NiSO_4$ solution (0.02 g. Ni per cc.)

The optimum conditions for obtaining deposits containing molybdenum and nickel are; cathode current density 0.2 ampere per square centimeter; temperature 30° C. to 50° C. Bright metallic plates are obtained in five minutes. The weight of the average deposit is 1.5 mg. on an area of 12 square centimeters of cathode surface. The current density range for bright metal plating from this bath is from 0.2 to 0.3 ampere per square centimeter.

The above examples are given by way of illustration only.

What we claim as our invention is:

1. An electrolyte for the electrodeposition of molybdenum comprising an aqueous solution of a molybdate compound and a concentration of fluoride ion at least several times greater than said molybdate compound.

2. An electrolyte for the electrodeposition of molybdenum comprising an aqueous solution of a molybdate compound, a concentration of fluoride ion at least several times greater than said molybdate compound and a soluble salt of a metal of the class consisting of iron, nickel and cobalt.

3. The process of electroplating metallic molybdenum which comprises passing a current between an anode and the work to be plated as a cathode in an electrolyte comprising an aqueous solution of a molybdate compound of the class consisting of molybdic acid, its anhydride, and its salts, hydrofluoric acid and an alkali fluoride, the concentration of the fluoride ion in said electrolyte being at least several times the concentration of said molybdate compound, at a temperature from room temperature to 65° C. and maintaining the current density between 0.2 and 0.4 ampere per square centimeter.

4. The process according to claim 3 in which the temperature is maintained between 30° and 50° C.

5. The process of electroplating metallic molybdenum which comprises passing a current between an anode and the work to be plated as a cathode in an electrolyte comprising an aqueous solution of a molybdate compound of the class consisting of molybdic acid, its anhydride, and its salts, and a concentration of fluoride ion at least several times the concentration of said molybdate compound, at a temperature between room temperature and 65° C. and maintaining the current density between 0.2 and 0.4 ampere per square centimeter.

6. The process of electrodepositing molybdenum alloys which comprises passing a current between an anode and the work to be plated as a cathode in an electrolyte comprising an aqueous solution of a molybdate compound of the class consisting of molybdic acid, its anhydride, and its salts, a concentration of fluoride ion at least several times the concentration of said molybdate compound and a soluble salt of a metal to be codeposited with molybdenum of the class consisting of iron, nickel, and cobalt, at a temperature between room temperature and 65° C. and maintaining the current density between 0.2 and 0.4 ampere per square centimeter.

7. An aqueous electrolyte containing the following ingredients in proportions on the order of 5 grams molybdic anhydride, 100 grams potassium fluoride, and 13 cubic centimeters of 48% hydrofluoric acid.

8. The process of electroplating metallic molybdenum which comprises passing a current between an anode and the work to be plated as a cathode in an aqueous electrolyte containing the following ingredients in proportions on the order of 5 grams molybdic anhydride, 100 grams potassium fluoride, and 13 cubic centimeters of 48% hydrofluoric acid at a temperature between 30° and 50° C. and maintaining the current density between 0.2 and 0.4 ampere per square centimeter.

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