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ELECTRODEPOSITION OF NICKEL-TUNGSTEN ALLOYS

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This invention relates to the electrodeposition of nickel-tungsten alloys.

An object of the invention is to improve the electrodeposition of nickel-tungsten alloys, and the methods and compositions used therefor.

Other objects of the invention will be apparent from the description and claims.

A great deal of interest in the electrodeposition of tungsten and tungsten alloys has been in evidence in recent years but apparently none of the methods tried have been found suitable for commercial practice. Most of the efforts have been directed to the production of alloys having high tungsten content and many special baths have been proposed for this purpose.

It was applicants' belief that a nickel electrodeposit containing small percentages of tungsten would show advantages over pure nickel for many commercial applications and would also have utility in many cases where pure tungsten or high tungsten alloys have heretofore been thought necessary.

It would not ordinarily be supposed that nickel plating baths could be modified by the addition of soluble tungstates without deleterious effect. In fact such tungstates have a marked effect on such baths in lowering the cathode current efficiency and usually prevent electrodeposition of metal or result in a deposit which is non-metallic in character. This is perhaps due to the formation of a tungstate film on the cathode, preventing the deposition of metal, or permitting only a deposit which is non-metallic in appearance.

We have found, however, that under certain conditions a nickel plating bath, such as a Watts type bath, can be modified by the addition of tungstates, such as sodium tungstate, and the solution electrolyzed to obtain smooth, adherent metallic deposits of nickel-tungsten alloys on the cathode.

One suitable nickel-tungsten plating bath contained:

	Grams per liter
Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	250
Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	21
Boric acid (H_3BO_3)	30
Sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$)	4

The sodium tungstate was added to the nickel plating bath from a stock solution containing 71.7 grams per liter of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ which is equivalent to 2 grams of tungsten per 50 ml. When this tungstate solution was added directly to the nickel plating bath, a precipitate formed. This precipitate, perhaps a basic nickel tungstate, dis-

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solved on addition of a small amount of sulfuric acid and thorough stirring. Instead of permitting the precipitate to form, it seemed best to have a predetermined excess of the acid present before adding the sodium tungstate solution. The volume of H_2SO_4 required was indicated by an experimentally determined buffer curve plotted in terms of pH of the nickel plating bath and volume of added acid. Then an excess of 2 ml. of 6N H_2SO_4 was added for each 2 grams of tungsten equivalent to be added to the bath. The sodium tungstate solution was then added and as long as the pH was below 5.4, no precipitate remained in the bath. The bath was finally made up to a volume of one liter and the pH more carefully adjusted to the desired value. This completed bath was stable at temperatures as high as 70° C.

The pH of the bath was adjusted to about 3 and plating was carried out at a temperature between 40° and 50° C. and a cathode current density between 0.5 and 1.0 ampere per square decimeter.

The anode was of nickel. The cathode basis metal was copper although brass, iron, steel, nickel, or any of the other common basis metals either plain or with a preliminary flash or plated coating of copper may be used.

The resulting electrodeposit was a nickel-tungsten alloy containing about 4% tungsten. It formed a smooth, adherent, metallic deposit which took a high polish when buffed. The deposit had a higher corrosion resistance than pure nickel deposits.

The conditions and compositions of the baths may be varied to obtain different proportions of tungsten in the alloy deposit. Deposits containing from a trace up to 20% or more of tungsten can be obtained.

The amount of tungsten in the bath will generally be between 0.2 and 16 grams per liter and is added as sodium tungstate or other soluble tungstates, such as potassium tungstate, or ammonium tungstate. Usually 1 to 2 grams of tungsten per liter is preferred.

The pH of the bath should be maintained between 2 and 5.4, the preferred acidity being pH 3, although where higher percentages of tungsten are desired in the electrodeposited metal the upper part of the pH range given is more effective. The higher pH values also aid in increasing the current efficiency.

Good deposits are best obtained at elevated temperatures, the range between 40° C. and 70° C.

being most suitable. The higher temperatures increase the current efficiency.

Cathode current densities between 0.1 ampere and 5 amperes per square decimeter are preferred, although still higher densities may be used. Current density has little effect on current efficiency or on percentage of tungsten in the alloy deposit.

It is to be understood that in the present specification and claims the term "Watts nickel-plating bath" is used to denote a nickel-plating bath of the type described by Oliver P. Watts in Transactions of the American Electrochemical Society, 1916, vol. 29, page 395 and ff. and consisting of an aqueous solution of nickel sulfate, nickel chloride and boric acid in the above described concentrations.

The nickel-tungsten alloy plate can be used in places where straight nickel plating fails to give proper corrosion resistance. It may also be used as a substitute for chromium plating on hardware, automobile parts and accessories and other uses. This has the advantage of requiring less plating operations. In chromium plating it is necessary to plate iron or steel parts with copper, nickel and then chromium. With our process the parts may be plated with copper and then with the nickel-tungsten alloy.

What is claimed is:

1. A modified Watts bath for nickel-tungsten alloy plating consisting of an aqueous solution containing about 250 grams per liter of nickel sulfate, about 21 grams per liter of nickel chloride, about 30 grams per liter of boric acid, and about 4 grams per liter of sodium tungstate, said bath having a pH of about 3.

2. A modified Watts bath for nickel-tungsten alloy plating consisting of an aqueous solution containing nickel sulfate, nickel chloride, boric acid, and about 1 to 2 grams per liter of a soluble tungstate, said bath having a pH of about 3.

3. A modified Watts bath for nickel-tungsten alloy plating consisting of an aqueous solution containing nickel sulfate, nickel chloride, boric acid, and sufficient sodium tungstate to provide a concentration of about 1 to 2 grams per liter of tungsten, said bath having a pH of about 3.

4. In the art of electrodepositing a nickel-tungsten alloy, the step of passing a current between a cathode and a nickel anode through a modified Watts bath consisting of an aqueous solution containing nickel sulfate, nickel chloride, boric acid, and sufficient sodium tungstate to provide a concentration of about 1 to 2 grams per liter of tungsten, said bath having a pH of about 3.

5. In the art of electrodepositing a nickel-tungsten alloy, the step of passing a current be-

tween a cathode and a nickel anode through a modified Watts bath consisting of an aqueous solution containing nickel sulfate, nickel chloride, boric acid, and about 1 to 2 grams per liter of a soluble tungstate, said bath having a pH of about 3.

6. In the art of electrodepositing a nickel-tungsten alloy, the step of passing a current between a cathode and a nickel anode through a modified Watts bath consisting of an aqueous solution containing about 250 grams per liter of nickel sulfate, about 21 grams per liter of nickel chloride, about 30 grams per liter of boric acid, and about 4 grams per liter of sodium tungstate, said bath having a pH of about 3.

7. In the art of electrodepositing a nickel-tungsten alloy, the steps which consist in passing current between an anode and a cathode through a modified Watts bath containing nickel sulfate, nickel chloride, boric acid, and a soluble tungstate, maintaining the tungstate content of the bath at such a value as to provide a tungsten concentration within the range of 0.2 to 16.0 grams per liter, operating the bath at a pH within the range of 2.0 to 5.4, and controlling the tungsten concentration and pH so as to produce a metallic deposit.

8. In the art of electrodepositing a nickel tungsten alloy, the steps which consist in passing current between an anode and a cathode through a modified Watts bath containing nickel sulfate, nickel chloride, boric acid, and sodium tungstate, maintaining the sodium tungstate content of the bath at such a value as to provide a tungsten concentration within the range of 0.2 to 16.0 grams per liter, operating the bath at a pH within the range of 2.0 to 5.4, and controlling the tungsten concentration and pH so as to produce a metallic deposit.

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