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ELECTRODEPOSITION OF TUNGSTEN ALLOYS

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This invention relates to the electrodeposition of tungsten alloys of variable tungsten content and more particularly to the electrodeposition of tungsten together with difficultly platable metals, such as tantalum and the like, from aqueous baths.

The present invention is in part a continuation of prior application Serial No. 14,372, filed April 2, 1935.

The wide potential utility of the heavier refractory metals, such as those of the 5th and 6th groups, has long been recognized and considerable effort has been expended in attempting to electrodeposit such metals. Particularly valuable among such metals are tungsten and tantalum. These are each characterized by a very high resistance to chemical corrosion and are most refractory; furthermore they present decidedly pleasing chromatic characteristics. Such metals either alone or in the form of alloys present an excellent protective surface for the cheaper but less resistant metals and alloys and are especially useful when employed for apparatus utilized for high temperature operations.

Consonant with the recognition of the inherent value of these metals in the several technological fields many suggestions have been advanced as to methods of electrodepositing them. It has been proposed, for example, to produce pure tantalum by electrodeposition. This is, and has been, recognized as difficult of achievement because of the fact that compounds of tantalum hydrolyze relatively readily in water, giving rise to the formation of insoluble or very sparingly soluble salts. To evade this difficulty it has been proposed to plate tantalum from a non-aqueous or anhydrous bath. Thus it has been suggested to dissolve a suitable tantalum compound, such as tantalum chloride, in an organic solvent, such as toluene, to electrodeposit pure tantalum from the resulting solution. Similarly it has been suggested to dissolve tantalum compounds in anhydrous liquid ammonia and subsequently to electrodeposit tantalum from this solution.

All such methods involving the utilization of organic solvents are fraught with considerable difficulty and present inherent disadvantages. For example, such processes are obviously expensive due to the relatively high cost of the solvents employed. Likewise operative difficulties are presented, such as the high working temperature required, the very low inherent conductivity and the high solution resistivity of such organic baths. In some circumstances these difficulties are further accentuated by the physical or me-

chanical difficulties, such in the case of anhydrous ammonia, for example, as the problem of retaining the ammonia in the liquid phase.

Similarly, as pointed out in our prior application above referred to, comparable difficulties obtain in the electrodeposition of tungsten. This metal is difficult to electrodeposit because of the tendency of tungsten to oxidize and deposit in the oxide condition, thus giving rise to impure and loosely adherent plates. By reason of the difficulty of reducing oxides of tungsten in aqueous solution, due to active hydrolysis, it has been suggested to substitute an organic solvent for the water bath. Such methods however present the disadvantages enumerated above.

As fully disclosed in our copending application, we have found that it is not only possible but is eminently feasible and practical to electrodeposit tungsten containing alloys from aqueous baths.

We have now found that dense, lustrous, adherent alloy deposits containing tantalum may be obtained when employing aqueous baths. Improved results are secured, as will be seen, by codepositing other metals, such as tungsten and/or nickel, with the tantalum. When operating under the preferred conditions, smooth, even deposits of extremely small crystalline structure are procurable. Without advancing any definite statement as to the precise mechanism of the reactions involved, it would appear that ionic complexes are formed which present sufficient stability to resist the tendency of the tantalum, tungsten, and comparable metallic ions, to hydrolyze to form insoluble oxides or salts.

A major object of the present invention, therefore, is to electrodeposit tantalum from aqueous electrolytes.

Another object is to electrolytically produce alloys of tantalum.

Yet another object is to produce an aqueous electrolyte from which tantalum may be electrolytically deposited.

A further object is to produce, as a new article of manufacture, a metal base plate having an adherent electrodeposit plate containing tungsten and tantalum.

Yet another object of the invention is to electrolytically produce alloys of tungsten and tantalum of variable content ratios.

With these and other equally important and related objects in view, the invention comprehends the concept of producing electrodeposited plates of alloys containing tantalum, and prefer-

ably alloys containing tungsten and tantalum, from aqueous baths.

We have found that, similarly to tungsten, readily available compounds of tantalum, such as the oxides, may be dissolved in suitable aqueous solutions. We have further found that when, to an electrolyte containing soluble tungsten and tantalum, there is added another metal, such for example as nickel, the alloy plates of these metals, of widely variant ratios, may efficiently be produced. We have found in particular that such a common tantalum compound as tantalum pentoxide (Ta_2O_5) may directly be dissolved in a suitable aqueous solution, such as a solution of ammonium acid fluoride (NH_4HF_2). As has been disclosed in our prior application, common tungsten compounds, such as the oxides and tungstic acid anhydride, are likewise directly soluble in ammonium acid fluoride. We have also further found that such compounds are soluble within a relatively wide range and thus, by reason of the common solubility of compounds of the two metals in a single cheap aqueous solvent, a most economic method of electrolytically producing alloys of the metals is presented. The advantages of the employment of simple, cheap and readily controllable aqueous baths over the organic solvents heretofore suggested will immediately recommend themselves to those skilled in the art.

As will appear more fully hereinafter, the bath of the present invention may be considerably modified with respect to such factors as the specific amounts of the respective metals dissolved in the bath, the acid concentration, temperature and current density ranges, the character of the buffers and addition agents and the like. Similarly the anodes employed may be of the inert type or may comprise one or more of the metals which are to be deposited, it being particularly understood that the invention comprehends the establishment of the desired metal ions in the bath by direct dissolution or anodic corrosion.

The invention will be more readily understood from a consideration of the compounding and composition of typical electrolytes and the operative procedure. As a typical example an improved bath from which an alloy plate may be deposited may be made up by simultaneously or sequentially dissolving tungstic acid, tantalum pentoxide and ammonium biffuoride in water while maintaining the water at a temperature of between approximately 106°F . and 210°F . Thus, to, say one liter of water maintained at the temperature stated, there is added approximately 85 grams of ammonium biffuoride, 40 grams of tungstic acid and 35 grams of tantalum pentoxide. After complete dissolution the solution is filtered and then there is added 60 grams of tartaric acid, 30 grams of citric acid, 60 grams of sodium fluoride and 15 grams of a soluble nickel salt, such as nickel chloride. The solution is then adjusted to a pH of approximately 5.3 using sodium hydroxide or other suitable alkali hydroxide. This solution may then be electrolyzed using a platinum cathode and two tungsten carbide anodes at 4 amps. per 8 sq. in. and 3.5 volts. During the plating the bath temperature was maintained at approximately 160°F . After 15 minutes electrolyzing a dense, fine grained plate was deposited which, upon analysis, showed appreciable percentages of tungsten tantalum and nickel.

The present process is quite flexible and, as noted, may be considerably modified with respect to the constituents and the method of preparing

the bath. For example, an improved bath may be made up by dissolving 40 grams of tungstic acid, 45 grams of ammonium biffuoride and 30 grams of tartaric acid in 500 cc. of water maintained at elevated temperature for a period of time sufficiently prolonged to insure complete dissolution. There is then separately prepared a solution of 35 grams of tantalum pentoxide, 40 grams of ammonium acid fluoride, 30 grams of tartaric acid and 20 grams of nickel chloride dissolved in 500 cc. of water. This second batch was similarly heated to a temperature of the order of 160°F . until complete dissolution was effected. The two solutions were then mixed and 75 cc. of sodium hydroxide added. Upon electrolyzing, using brass, copper, steel or other suitable cathode and tungsten carbide and/or nickel anodes, dense acid resistant plates were produced.

This type of bath may be considerably modified with respect to the acid concentration. Thus to the above described bath there was added an additional quantity in the amount of 50 cc. of sodium hydroxide and the bath electrolyzed, using a steel cathode and four tungsten carbide anodes. The bath temperature was maintained at 160°F . and an 8 sq. in. test plate was plated for fifteen minutes at 4 amps. and 3 volts. Upon analysis this plate was found to contain 25.8% tantalum, 39.8% tungsten and 34.4% nickel.

As will be appreciated and as indicated above, the nickel or tungsten content of the bath may be replenished either by using tungsten containing and/or nickel containing anodes and producing the tungsten and nickel ions respectively by anodic corrosion. Similarly, if desired, replenishment of the bath may be achieved by dissolving a tungsten oxide or tungstic acid separately in ammonium acid fluoride and adding this in required amounts. The tantalum content is most readily replenished by making a replenishing solution comprising tantalum pentoxide dissolved in a solution containing ammonium biffuoride and an organic acid, such as tartaric.

Similarly in other experiments conducted it was found that tartaric acid may be replaced in whole or in part by equivalent amounts of citric and/or boric acid. These acids appear to function to prevent precipitation of the tungsten and tantalum from the bath. Sodium tartrate likewise has been found to be a useful and effective adjuvant.

It is further found that additions of ammonium phosphate improve the efficiency of the bath and the character of the ultimate plate.

As a result of considerable experimentation we have found that the plate may be produced over a wide pH range extending from a very acid to a definitely alkaline solution. This should be adjusted to secure the desired results. Similarly the modification of the other factors, such as the current density, has a marked effect upon the character of the plate. Thus on plating an 8 sq. in. test plate at 2 amps. a bright plate is produced which may be buffed to a very brilliant finish. With the same bath and size test plate, plating at 4 amps. produces a less brilliant but more acid resistant plate. Again, when carrying out the plating at 8 amps. a plate is produced which is extremely hard to buff and which when buffed is not as brilliant as the plates described, but which is characterized by an extremely high resistance to acid. This variation in the brilliancy and acid resistance of the plate applies generally whatever the character of the work or base plate.

We have found that the respective quantities

of the alloying components of the plate may be widely varied, as for example by adjusting the initial respective concentrations of the several metals in the bath. Furthermore the proportions of the several metals in the plate may be varied during a given continuous plating operation by changing the current density and/or the temperature. It will be appreciated that the examples given above are presented as illustrative of the process and not as the exclusive methods of either making up the bath or effecting the plating operation. Thus plates of the character described may be produced operating at pH ranges from 1 to 8 or more. Likewise current density may be varied with good results from substantially 6 to 500 or more amps. per sq. ft. of submerged cathode area. Also, while an optimum temperature of 150° to 160° F. has been described, it is to be understood that this temperature may be varied over a range of from 80° F. or less to 180° F. or more.

A striking feature of the present invention is the non-critical nature or flexibility of the process, especially with respect to the solution concentrations. Thus, employing the method described, namely by utilizing an ammonium bifiuoride to solubilize the tungsten and tantalum a very high concentration of these metals may be obtained in the bath. For example a tungsten concentration of up to 6 oz. per gal. of bath solution can be obtained by dissolving tungstic acid or tungstic acid anhydride in a bifiuoride solution.

The invention is not limited to the employment of ammonium bifiuoride. In lieu of this other similarly acting bifiuorides, such as those described in the copending application referred to, may be employed. Again, if desired, sodium acid fluoride may be utilized to bring the tungsten into solution, as for example by dissolving sodium tungstate in hydrogen fluoride and thereafter adjusting the bath to the desired acid concentration. It will be appreciated that this process is amenable to the general operative technique of the plating art. Thus it is directly contemplated, when desired, to utilize addition agents, such as heavy molecular weight colloids of the character of glue, for enhancing the quality of the plate. Likewise for certain types of work the bath may be subjected to very fine clarification to remove undesired suspended matter, as for example by treating the bath with a precipitated colloid and then filtering out the precipitated material.

It is particularly to be understood that the process is not limited to the production of a ternary alloy or an alloy containing nickel. Thus in lieu of nickel chloride, other nickel salts may be utilized in the bath. Similarly in lieu of nickel any other metal which forms an acid fluoride may be employed, such for example as iron, nickel, cobalt and the like.

For some purposes or uses a surface combining the decidedly refractory characteristics of tungsten and tantalum is desirable. In these circumstances the present method is available for the production of a tungsten tantalum alloy. Thus, for example, a plate of this character may be produced by heating 20 grams of tantalum pentoxide, 60 grams of tungstic acid and 85 grams of ammonium bifiuoride and 65 grams of tartaric acid in approximately 800 cc. of water. This may be adjusted to the desired pH value, say a pH of 2.73. It has been found that in producing a resistant tungsten tantalum alloy the higher acid concentrations are desirable, for at low acid concentrations, of the order of pH 6.2, it is difficult to

maintain the tantalum in solution. When electrolyzing the above solution, using a 4 sq. in. copper cathode and tungsten carbide anode, at 9 amps. and 6 volts and maintaining the bath at 175°, an adherent acid resistant plate is produced.

In commercial operations a bath concentrate may be made up in the dry or liquid condition. Thus a standardized liquid concentrate may be made up, as will be appreciated, by dissolving predetermined quantities of a tantalum and tungsten compound in ammonium bifiuoride and adding to this the required amounts of organic acids, such as tartaric or citric, to maintain the metals in solution. Thus for subsequent use this bath may be diluted with water and additional metal, such as nickel, by way of the soluble nickel salt, and the bath electrolyzed by an inert anode tungsten carbide and/or nickel or other metal containing anodes.

It will be appreciated that the invention is not limited to the use of the particular tantalum compounds mentioned or to the described method of bringing tantalum into solution, but comprehends any method by which the tantalum is made available in an aqueous system. Thus improved results are procured by dissolving freshly prepared tantalum hydroxide in tartaric acid and adding this solution to a solution of a tungsten compound in a bifiuoride, and utilizing the resulting solution after adjustment of the acid concentration as the plating bath.

While the invention has been described with respect to plating out the nickel alloys on common metals, such as steel, brass, copper and the like, it will be appreciated that it is equally applicable for purposes of overplating on more expensive metals, such as overplating on an electrodeposited nickel plate. Thus the invention is susceptible of wide modifications with respect to the ingredients employed and their method of compounding. The invention is considered to reside broadly in the concept of producing tantalum containing electrodeposited plates from aqueous baths and also in the production of a highly serviceable electrodeposited tungsten tantalum surface.

We claim:

1. A method of producing tantalum containing electrodeposited plates which comprises electrolyzing an aqueous acid solution of an alkali bifiuoride containing dissolved tantalum and tungsten.

2. A method of producing tantalum containing electrodeposited plates which comprises electrolyzing an aqueous acid solution of an alkali bifiuoride containing dissolved tantalum and nickel.

3. A method of producing protective electrodeposited plates which comprises electrolyzing an aqueous solution of an alkali bifiuoride containing dissolved tantalum, tungsten and nickel.

4. A method of producing surfaces containing tungsten, tantalum and nickel which comprises dissolving tungsten containing and tantalum containing compounds in a hot aqueous solution containing an alkali bifiuoride and citric acid; adjusting the hydrogen ion concentration of the solution to substantially pH 5.3 and electrolyzing the solution with a metal cathode and a tungsten containing anode.

5. A method of producing surfaces containing tungsten and tantalum which comprises dissolving a tantalum containing compound in an aqueous solution of an alkali bifiuoride, acidifying the solution, electrolyzing the solution with a tung-

sten containing anode and coplating tungsten and tantalum upon a conductive cathode.

6. A method of producing surfaces containing tungsten and tantalum which comprises dissolving tungsten and tantalum containing compounds in an aqueous solution of an alkali bifluoride, acidifying the solution and electrolyzing the solution with a conductive cathode and a tungsten carbide anode.

7. A method of producing surfaces comprising tungsten tantalum and nickel which comprises dissolving tungsten, tantalum and nickel containing compounds in an aqueous solution of an alkali bifluoride, acidifying the solution, and electrolyzing the solution with a conductive cathode and tungsten containing and nickel containing anodes.

8. A method of producing tantalum containing surfaces which comprises dissolving tungsten tantalum compounds in an aqueous solution of an alkali bifluoride, adjusting the hydrogen ion concentration of the solution to between pH 1 and pH 8 and electrolyzing the solution with a metal cathode and a tungsten containing anode.

9. A method of producing adherent, acid resistant tantalum containing electrodeposited plates which comprises dissolving tungsten and tantalum in an aqueous solution of an alkali bifluoride, acidifying the solution, and electrolyzing the solution with a conductive cathode and a tungsten containing anode, and increasing the amperage in proportion to the desired degree in acid resistance of the electrodeposited plate.

10. A method of producing tantalum containing surfaces which comprises dissolving tungsten and tantalum containing compounds in an aqueous solution of an alkali bifluoride, adding thereto an organic acid which acts to prevent the precipitation of the dissolved metals from the solution; adjusting the hydrogen ion concentration of the solution to between pH 1 and pH 8; adjusting the temperature of the solution to between substantially 80° F. and substantially 180° F., electrolyzing the solution with a conductive cathode and a metal anode, and varying the current density to between substantially 6 and substantially 500 amps. per sq. ft. or submerged cathode area.

11. An electroplating bath for electrodepositing tantalum comprising an aqueous solution formed by dissolving a tantalum-containing compound and a compound of a metal of a group consisting of tungsten, iron, nickel and cobalt in an aqueous acid solution of an alkali bifluoride.

12. An electroplating bath for electrodepositing tantalum comprising an aqueous solution formed by reacting a tantalum-containing compound with an alkali bifluoride and dissolving in the

solution a compound of a metal of a group consisting of tungsten, iron, nickel and cobalt.

13. A method of producing tantalum-containing electrodeposited plates which comprises electrolyzing an aqueous acid solution of an alkali bifluoride containing dissolved tantalum and a metal of the group consisting of tungsten, iron, nickel and cobalt and an organic acid of the group consisting of citric acid and tartaric acid, said acids being adapted to prevent precipitation of the metals from the solution.

14. An electroplating bath for electrodepositing tantalum comprising an aqueous solution formed by dissolving a tantalum containing compound and a compound of a metal coplating with tantalum, said metal being chosen from the group consisting of tungsten, iron, nickel and cobalt, in an aqueous acid solution of a bifluoride.

15. An electroplating bath for electrodepositing tantalum which comprises tantalum pentoxide and a tungsten containing compound dissolved in an aqueous solution of an alkali bifluoride, the bath containing a predetermined amount of an organic acid of the group consisting of tartaric and citric acids, adapted to prevent precipitation of the metals from the bath.

16. A method of producing tantalum containing electrodeposited plates which comprises electrolyzing a definitely acid aqueous alkali bifluoride solution containing tantalum and tungsten ions.

17. A method of producing tantalum containing electrodeposited plates which comprises electrolyzing an acid aqueous solution of a fluoride containing dissolved tantalum, a metal coplating with tantalum chosen from the group consisting of tungsten, iron, nickel and cobalt, and an organic acid of the group consisting of tartaric and citric acid, adapted to prevent precipitation of the metals from the solution.

18. A method of producing tantalum containing alloys which comprises dissolving an oxide of tantalum in an alkali bifluoride, adding an organic acid of the group consisting of tartaric and citric acids, adjusting the hydrogen ion concentration to between pH 1 and pH 8, electrolyzing the solution and depositing tantalum on an electrode.

19. A method of protecting metals which comprises immersing the metal in an aqueous alkali bifluoride electrolyte containing dissolved tantalum and tungsten, adjusting the acidity to between pH 2.7 and pH 6.2, electrolyzing the solution and plating out tungsten and tantalum on the said metal.

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