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ELECTRODEPOSITION OF TUNGSTEN ALLOYS

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This invention relates to a process of producing alloys of tungsten by electrodeposition from aqueous solutions.

The present invention is a continuation in part of our co-pending applications, Serial No. 744,566 and Serial No. 14,372.

We have found, as disclosed in our prior applications, that dense, coherent, resistant metal deposits may be produced by co-plating tungsten and other metals, such as nickel, from suitable aqueous solutions. Specifically, we have found that improved results are secured by dissolving tungsten containing compounds, such as tungstic acid, in a suitable acid fluoride such as ammonium acid fluoride and adding thereto predetermined proportions of an organic acid, such as boric and/or citric, and a nickel salt, such as the sulphate or chloride, which is soluble in such an acid electrolyte. As was disclosed in such prior applications, the tungsten and nickel may be co-plated as a dense, adherent, resistant plate by electrolyzing with inert, or preferably with tungsten containing, anodes, such as tungsten carbide anodes.

This type of proposed process represents a distinct advance in the art of tungsten plating.

It has been proposed in the past to electrodeposit pure tungsten by dissolving, say, sodium tungstate in a strongly alkaline bath (pH 9 to 13 or more). This prior type of process, however, presented many inherent disadvantages. In the first place, very high current densities were required, with the resultant excessive evolution of hydrogen at the cathode. Furthermore, in such prior processes, it was found that the electrodeposited plate could not be built up to any considerable depth due to passivity of the tungsten resulting from the particular characteristics of the bath employed.

Under our prior process, we have been able to produce tungsten alloy plates of a wide variation of the metal components and of considerable thickness coupled with improved uniformity of deposition.

In further research, we have found that by the use of certain adjuvants in a bath of the type described in our prior applications, greatly improved results are secured, such as a wider permissive operating range of temperature, current density and hydrogen ion concentration; improved cathode and anode efficiencies; higher concentration of tungsten metal coupled with low ion concentration; enhanced stability of the electrolyte; increased throwing power; and the production of a more resistant plate of greater uniformity in the thickness of the plated surface and with a higher permissive variation in the components of the electrodeposited alloy.

An object of the present invention, therefore, is to provide a novel type of electrolyte from which alloys of tungsten and analogous heavy, refractory metals may be electrodeposited.

Another object is to produce an improved coherent, fine grained, adherent electrodeposited tungsten containing plate characterized by a very high resistance to chemical corrosion and physical erosion.

Yet another object is to devise a process for producing a stable electrolytic bath from which tungsten alloys of variable percentage composition may be electrodeposited.

A further object is to produce novel electrodeposited tungsten alloys.

With these and other equally important and related objects in view, the invention comprehends the concept of producing an aqueous electrolyte which is characterized by marked stability and particularly by non-critical operating conditions.

The enumerated criteria or improvements are obtained by the utilization of phosphoric acid, or its equivalent, as a component of electrolytes containing soluble tungsten and co-platable metals. While no attempt is made to define the mechanism or rationale of the process or the several reactions involved, it would appear that the addition of the phosphoric acid, or equivalent compound containing an available phosphate, results in the formation of molecular phospho-tungsten complexes, which are readily reducible over a wide range of operating conditions. As a matter of fact, we have found that desirable plates can be secured by the direct addition, to a fluoride bath, of such compounds as phospho-tungstic acid. The plates thus produced, however, do not have the superior characteristics of those plated from a bath in which such complexes are formed in situ.

To enable a more ready comprehension of the invention, an example of an aqueous bath produced and operated according to the invention will be given didactically to exemplify the principles involved. It will be understood, however, that the invention is not limited to the precise quantities specified nor to the particular reagents employed for, as will be noted, the respective quantities of the components or ingredients may be widely varied and for the stated ingredients may be utilized other constituents.

As has been explained in our co-pending ap-

plications, the present invention is available for the production of binary alloys of tungsten with other coplatable metals such as nickel, cobalt, iron, manganese or polynary alloys of three or more of the enumerated or equivalent metals. Particularly useful articles, especially for employment in high temperature environment may be produced by plating a suitable ferruginous or non-ferruginous base metal, or over plating on a preliminarily plated metal, with alloys of tungsten and nickel; tungsten and tantalum; tungsten, tantalum and nickel; tungsten, tantalum and cobalt; etc.

The plates produced under the present invention may be subjected to any desired type of after treatment for the purpose of modifying the physical characteristics of the plate. Thus the electrodeposited surfaces may be worked, heat treated, carbonized or nitrided to produce in situ compounds like tungsten carbide and/or tantalum carbide, to thus increase the hardness and wear resistance of the surface.

In a typical liter bath produced under our present invention may, for example, be comprised the following:

	Grams
Tungstic acid	50
Sodium hydroxide	20
Ammonium acid fluoride	50
Phosphoric acid (85%)	3.25
Citric acid	65
Nickel sulphate	16
Nickel chloride	8
Boric acid	20

This bath may be produced by reacting the tungstic acid with the sodium hydroxide in concentrated solution. The ammonium bifluoride may then be added in solid or dissolved form and the mass heated to elevated temperature of the order from 140° F. to 160° F. The solution is agitated to accelerate the dissolution. In these circumstances, a white precipitate usually forms. Thereafter the phosphoric acid in the noted or equivalent amounts, is added while the solution is maintained at the temperature stated. Upon the addition of the phosphoric acid, some additional precipitation will be noted. This solution may then be diluted to about 750 cc., by the addition of water and citric acid is added either in the solid form or dissolved in water. The solution is heated to maintain it at a temperature of approximately 140° F. and is agitated until the precipitate dissolves.

When the precipitate has dissolved, a solution of the nickel sulphate and nickel chloride is then added or if desired, solutions of these nickel salts may separately be added. The boric acid is then added, the solution is diluted to the ultimate dilution desired and filtered. When thus prepared, substantially from 95 to 98% of the original quantity of tungsten employed will remain in solution. In the event that there is an undissolved precipitate after the ultimate filtration is completed, such precipitate may be dissolved in the requisite quantity of citric acid and then added to the bath.

We have found that dense and particularly acid resistant plates are obtainable by electrolyzing a distinctly acid bath. In the preferred mode of operation, after the preparation of the electrolyte in the manner above described, the pH is adjusted to between approximately 5.6 and 6.2 utilizing any suitable base, such as sodium hydroxide.

Upon adjustment of the hydrogen ion concentration, the bath may be electrolyzed at temperatures ranging from 90° F. to 180° F. or above and the current density varying from 25 to 100 amps. or more per square foot of submerged cathode area.

While improved plates are secured by utilizing any suitable conductive inert anode, such as carbon, improved results are secured by utilizing conductive metal containing anodes, preferably of the metals to be plated, such as separate tungsten-nickel carbide anodes, tungsten carbide-nickel anodes and the like. We have found that a greater control of the operative conditions can be secured, and the metal concentration of the bath maintained by utilizing a plurality of anodes, i. e., separate inert carbon anodes and corrodible metal containing anodes, such as tungsten-carbide anodes and nickel anodes which are connected in the circuit so that the major portion of the current flows through the inert anodes. The circuit may be so hooked up, also, that differential corrosion of the separate metal containing anodes may be effected to thus not only maintain the total metal concentration of the bath but also to maintain the desired respective concentration of the metals utilized.

The electrodeposits herein defined may be plated out upon any suitable metallic cathode, such as brass, copper, irons and steels. As will be understood by those skilled in the art, the work should be suitably cleaned and where the characteristics of the base metals so indicate, should be suitably etched to insure the desired adherence of the tungsten containing plate to the work. It will also be appreciated that it is within the scope of the invention to deposit an initial plate of some metal such as copper, nickel and the like upon the work and to overplate the tungsten alloy upon such intermediate plate. In this circumstance, prior to the ultimate plating with the tungsten alloy, the intermediate or preliminary plate may be buffed, etched or otherwise treated to improve the adherence and/or appearance of the final tungsten containing plate. It will be appreciated also that conversely, a tungsten containing alloy may be directly plated upon the work and other metals may be electrodeposited upon the tungsten containing intermediate plate. Furthermore, it will be understood that the plating operation may be carried out in two phases. Thus a cathode may be plated with tungsten-nickel having a relatively high nickel content and a relatively low tungsten content (or vice versa) and a final plate of a relatively high tungsten and relatively low nickel content may be overplated upon the intermediate plate. Also, the invention is available for the production of built up or aggregated plates of this character in which the intermediate plate may be a tungsten alloy of, say, tungsten-cobalt, tungsten-manganese, or other electrodeposited tungsten alloy and the final plate may be a tungsten alloy of a specific composition, such as tungsten-nickel, tungsten-tantalum, or the like.

When operating with this type of bath, we have found that cathode current efficiencies range from 26 to 42%, producing tungsten-nickel alloy deposits of the composition 30 to 38% tungsten and 70 to 62% nickel, with an anode efficiency, using combination anodes (of approximately 35% tungsten-carbide and 65% nickel) of 88%.

As has been explained in our co-pending applications, replenishment of the bath may be insured either by the direct addition of a soluble tungsten compound, such as tungstic acid

anhydride dissolved in ammonium bifluoride, or by the corrosion of tungsten containing anodes or by a combination of these two. Experience has shown that when retention of the metal concentration of the bath is achieved by anodic corrosion of tungsten and/or nickel, it is desirable to insure against too large an excess of the phosphate radical. Thus we have found that a satisfactory ratio of tungstic acid to phosphoric acid (85% con.) is of the order of 50 to 3.5. If, however, only tungsten-carbide anodes are employed, (i. e. where no nickel corrosion is involved) a relatively large excess of the phosphate radical may be maintained with no deleterious effects upon the ultimate alloyed plate.

While in the preferred example, a definite addition sequence of the respective ingredients has been indicated, it is clearly to be understood that this is by no means necessary. As a matter of fact, we have found improved results are secured by starting with a bath as described in the two co-pending applications and adding directly thereto a phosphate containing substance, such as phosphoric acid, sodium phosphate, and the like.

As indicated, the invention is susceptible to the employment of different ingredients. Thus while for the adjustment of the hydrogen ion concentration of the solution, we prefer to use sodium hydroxide or ammonium hydroxide for raising the pH and citric acid for lowering the pH, it will be understood that other similarly functioning bases and acids may be employed. Thus, we may utilize other hydroxides or if desired, other substances of alkaline reaction such as the alkali carbonates. Similarly, in lieu of citric acid, we may employ other organic acids or, if desired, inorganic acids, such as hydrochloric and sulphuric.

In the event that the bath becomes unduly depleted, that is to say, that the anodic corrosion of the tungsten containing compound is insufficient to maintain the desired tungsten ion concentration, this may be built up to the desired value by addition of tungsten to the bath. This may be done, for example, by making up a replenishing solution and adding this in the required amounts to the bath. Such replenishing solution may be made up, for example, by dissolving tungstic acid in approximately one-third its amount of sodium hydroxide and subsequently adding an equal part of sodium acid fluoride and substantially one-fifteenth as much phosphoric acid. The precipitate formed is dissolved in citric acid, the solution filtered and added to the bath to bring up the tungsten concentration to the normal value. In the same way, a solution depleted in nickel may be replenished in respect of this metal by dissolving nickel sulphate or nickel chloride, and preferably nickel sulphate and nickel chloride in the ratio of two parts of the sulphate to one of the chloride and adding this to the bath. Such replenishment, however, is not necessary if the current flowing through the corrodible anodes is adjusted in the manner described above.

As previously indicated, a bath of the general type described is effectively operative under rather widely variant conditions. Thus we have found that eminently satisfactory and highly acid resistant tungsten-nickel alloys may be produced by varying the ratio of the tungsten to nickel concentration from approximately 1 to 1, on the one hand, to 36 to 1 or higher, on the other. Likewise, we have found that the concentration of tungsten in the bath may be greatly modified. Thus, the bath is operative with the production of improved electrodeposited plates varying the tungsten concentration from approximately one and one-half ounces per gallon to ten ounces or more per gallon. For most purposes, however, we prefer to use a tungsten concentration of about five ounces per gallon with a tungsten to nickel ratio of approximately six to one. This condition of metal concentration will, under non-critical operating conditions, produce a tungsten-nickel alloy plate containing approximately 35% of tungsten and 65% of nickel. This plate is adherent, dense, fine grained and is characterized by a striking resistance to acids.

It is particularly to be understood that while the bath may be operated to produce tungsten alloys of an established percentage composition, the invention is by no means limited to the production of such a precise compound. Thus, by varying the composition of the bath, as by using higher or lower tungsten concentration and/or varying the tungsten-nickel ratio or by elevating or lowering the temperature, increasing or decreasing the current densities, the relative percentages of the tungsten and nickel in the plate may be varied. Thus by proper control of the stated conditions, electrodeposited plates varying in composition from 10% tungsten and 90% nickel on the one hand, to 70% tungsten to 30% nickel on the other, may be produced. It will be likewise appreciated that what has been said with respect to the variation of the tungsten and nickel plates applies equally to other binary or ternary alloys of tungsten.

As has been clearly explained in the co-pending applications, the preparation of the electrolytic bath is not limited to the specific reagents employed. Thus, in lieu of utilizing tungstic acid anhydrite, other tungsten containing materials may be availed of, such as sodium tungstate, tungstic acid and the like. Similarly, in lieu of ammonium acid fluoride, other operable bifluorides may be utilized or hydrofluoric acid may be employed.

Since, as has been noted, an acid soluble precipitate is formed by the interaction of the phosphoric acid and a bifluoride or fluoride (in concentrated condition) with a compound containing WO_3 and since this may be redissolved as for example, in citric acid and added to the bath, it is within the contemplation of the invention to utilize this type of procedure to produce either a replenishing compound or a compound which may be employed initially to make up the bath. This is to say that the invention comprehends the concept of producing a fluophospho-tungsten compound in dry form, which upon the addition of a suitable solvent such as citric acid, hydrochloric acid or an acid fluoride, may be dissolved and utilized either as a replenishing solution or as an initial solution from which a bath under the present invention may be produced.

As indicated hereinbefore, the invention is not only available for the electrodeposition of alloys of tungsten with such metals as nickel, iron, cobalt and manganese, but it also may be employed for the production of electrodeposited plates of tungsten with other refractory metals, such as tantalum. Tantalum containing baths have been prepared and electrodeposited plates containing tungsten and tantalum have been produced therefrom which are characterized by

a high thermal resistance and, due to the nature of the components, by very desirable electronic characteristics. We have found that the addition of phosphoric acid, or other compounds having an available phosphate radical, acts equally beneficially on electrolytic baths from which tungsten-tantalum or tungsten-tantalum and nickel are co-deposited.

An example of such a bath, of a gallon volume, is as follows:

Tungstic acid anhydride	ounces	10
Sodium hydroxide	do	3
Ammonium acid fluoride	do	4
Nickel chloride	do	5
Citric acid	do	6
Boric acid	do	4
Tantalum hydroxide	do	3
Phosphoric acid	cc	20

This solution may be made up in the same general manner as the tungsten-nickel solution previously described. To the WO_3 and NaOH, in the quantities specified, is added 1000 cc. of water and the materials are allowed to react at elevated temperature. The ammonium acid fluoride, dissolved in approximately 250 cc. of hot water is then added and the solution heated to temperatures of from 140° F. to 160° F. Thereafter, the phosphoric acid is added while an elevated temperature is maintained. This solution may then be diluted and a solution of 5 oz. of nickel chloride and 6 oz. of citric acid in 500 cc. of water then added. Preferably, during these additions, the solution is maintained at elevated temperature. The boric acid, dissolved in approximately 500 cc. of water, may then be added. The stated quantity of tantalum hydroxide is dissolved in a concentrated solution of ammonium acid fluoride and added to the solution. The solution may then be diluted with water to bring the total volume up to one gallon and the hydrogen ion concentration is preferably adjusted, as with sodium hydroxide solution to a value of pH 5.8. As in the manner described, the precipitate formed during the production of the solution may be filtered off, dissolved in a mixture of hydrochloric and hydrofluoric acid and added to the solution. This solution may be electrolyzed using tungsten anodes with or without inert anodes of carbon and if desired, with tantalum containing anodes. From this type of solution, excellent tungsten-nickel-tantalum plates are produced under the plating conditions defined above. This type of solution may be replenished by additions of nickel chloride and tantalum pentoxide in the manner described.

Operating on the same procedure, alloys such as tungsten-tantalum-cobalt, tungsten-tantalum-iron, tungsten-tantalum-manganese, and the like may be electrodeposited. It is particularly to be noted that the tantalum concentration of the bath may be maintained by utilizing tantalum containing anodes. For this purpose, we have found that cast corrodible tantalum-carbide-nickel anodes serve very effectively. Preferably, such anodes are used in association with tungsten-carbide or tungsten-carbide nickel anodes and may be connected in a circuit in the manner described, such that differential corrosion of the respective anodes may be insured. If desired, a combination anode comprising tungsten-carbide and nickel-carbide may be utilized.

While a number of metals which are co-depositable with tungsten have been mentioned, it is to be understood that the invention is not limited to the production of electrodeposited plates containing only such metals in association with tungsten and/or tantalum. It will be appreciated that any metal which can be put into solution in a bath of the character defined herein may be utilized and co-electrodeposited with tungsten and/or tantalum.

While preferred bath compositions have been described, it is to be understood that they are given for the purpose of explaining the underlying principles of the invention and particularly the efficacy of the use of phosphoric acid or other compounds containing an ultimately available phosphate ion in such solutions. Similarly, as has been pointed out, the invention comprehends the concept of producing dry or liquid concentrates of phospho-tungsten or fluo-phospho-tungsten compounds for replenishing additions to existing baths or for the purpose of initially compounding such baths. The invention, therefore, is not to be considered limited to the specific examples of baths or alloys herein set forth except as such limitations are clearly imposed by the appended claims.

We claim:

1. A method producing an electrolyte from which alloys of tungsten may be electrodeposited, which comprises adding to an aqueous solution of an alkali bifluoride a tungsten compound which is soluble therein, adding a predetermined quantity of phosphoric acid to the aqueous bath; dissolving in the bath a compound of the metal to be co-plated with the tungsten and chosen from the group consisting of tantalum, nickel, cobalt and manganese, adding an organic acid in an amount sufficient to substantially completely dissolve any formed precipitate, and adjusting the pH of the bath to a definitely acid value.

2. A process of producing electrodeposited plates of tungsten alloys which comprise dissolving a compound of tungsten and a compound of the metal to be co-plated therewith and chosen from the group consisting of tantalum, nickel, cobalt and manganese, in an aqueous solution of an alkali bifluoride, adding a predetermined quantity of a compound having an available phosphate ion, adding an organic acid, adjusting the solution to a definite acidity and electrolyzing the acid bath to co-deposit tungsten and said co-platable metal.

3. An electrolyte bath for co-electrodepositing tungsten with other metals which comprises an aqueous alkali bifluoride solution of acid pH containing available tungsten ions and ions of the metal to be plated therewith and chosen from the group consisting of tantalum, nickel, cobalt and manganese and also containing a predetermined quantity of an available phosphate, and an organic acid.

4. A method of producing an electrolyte from which tungsten and nickel may be co-plated which comprises dissolving an alkali tungstate in an aqueous solution of an alkali bifluoride maintained at elevated temperature; adding thereto a minor quantity of phosphoric acid; dissolving a quantity of citric acid in the solution which is sufficient to substantially completely dissolve any formed precipitate, and then adding to the solution a soluble nickel containing compound.

5. A method of producing resistant metallic surfaces which comprises dissolving a compound of tungsten and a compound of tantalum in an aqueous solution of an alkali bifluoride, adding a predetermined quantity of a compound having an available phosphate ion, adding a quan-

tity of an organic acid which is sufficient to substantially completely dissolve any formed precipitate, adjusting the solution to a definite acidity and electrolyzing the acid bath to co-deposit tungsten and tantalum.

6. An electrolyte bath for co-depositing tungsten and tantalum which comprises an aqueous alkali bifluoride solution of definitely acid pH and containing available tungsten and tantalum ions and also containing available phosphate ions.

7. A process of producing electrodeposited plates of tungsten alloys which comprises dissolving compounds of tungsten, tantalum and nickel in an aqueous solution of an alkali bifluoride, which solution contains an available phosphate ion and an organic acid; adjusting the solution to a definite acid value and electrolyzing the solution.

8. In the process of co-electrodeposition of tungsten and tantalum by electrolysis of aqueous alkali bifluoride baths of definite acidity containing tungsten and tantalum ions, that improvement which comprises adding phosphoric acid to the bath.

9. In the process of electrodeposition of tantalum-containing surfaces, that improvement which comprises electrolyzing an acid electrolyte containing available tantalum and available material chosen from the group consisting of tungsten, nickel, cobalt and manganese, and also containing an alkali bifluoride and a phosphate, and utilizing an anode containing tantalum carbide for the electrolysis.

10. In the process of electrodepositing alloys of tungsten and tantalum, that improvement which comprises electrolyzing an acid electrolyte containing available tungsten and tantalum ions and including phosphate and an alkali bifluoride, and utilizing tungsten carbide and tantalum carbide anodes for the electrolysis.

11. The process of producing electrodeposited plates containing tungsten metal which comprises dissolving a tungsten containing compound and a compound of a metal co-platable with tungsten, chosen from the group consisting of tantalum, nickel, cobalt and manganese in an aqueous bath comprised of the reaction products of an alkali bifluoride and phosphoric acid, adding an organic acid and electrolyzing the bath at a pH of between 5 and 6.2.

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