

UNITED STATES PATENT OFFICE

2,145,241

ELECTROPLATING METHOD AND PRODUCT

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No Drawing. Application April 2, 1935,
Serial No. 14,372

11 Claims. (Cl. 204-2)

Our invention relates to a process for electro-
plating tungsten alloys of variable tungsten con-
tent from aqueous solutions, as well as depositing
other single metal deposits, and alloys of metals
other than tungsten from the same type of elec-
trolyte, and is a continuation in part of our co-
pending application Serial No. 744,566.

In our above mentioned application we have
disclosed a method for the electrodeposition of
tungsten alloy plate from an acid fluoride bath
containing WO_3 ions produced either by dissolv-
ing the low oxide directly in the bath or by elec-
trolyzing the said bath with a tungsten or tung-
sten bearing anode. While a substantially pure
and uniform alloy plate of excellent quality may
be produced by this method, further research
has shown that tungsten alloys and other metals
can be electrolytically deposited directly from a
fluoride solution of the oxides, tungstates, meta-
tungstates, para-tungstates, tungstic acid, etc.

Heretofore, various methods and processes for
electroplating tungsten have been proposed;
however, none of the prior art processes, of which
we are aware, produce a satisfactory plate and
the methods per se are not commercially feasible.
It has been suggested to provide a strongly alkali-
ne bath containing a tungsten complex radical
but this has been found to be impractical because
of the characteristic tendency of tungsten and
similar metals to oxidize and deposit as sub-ox-
ides, the resulting deposits being metallically im-
pure and not firmly adhering to the cathode base.
Because of the difficulty of reducing the oxides
of tungsten in an aqueous solution, due to the
tendency of those tungsten ions which are pro-
duced by electrolysis to hydrolytically react with
water, considerable study has been given to the
possibility of utilizing non-aqueous and therefore
non-oxidizing baths of tungsten salts or baths
containing organic solvents, such as carbon bi-
sulfide or acetone. These processes are not com-
mercially practical because of the high working
temperature required for a fused bath and be-
cause of the low cathode and high solution res-
istivity when organic solvents are used.

Our present invention overcomes the inherent
difficulties existing in the known prior art meth-
ods and in accordance with the improved process
described herein, we not only produce a satis-
factory tungsten alloy plate, but also provide a
method which is economical of operation and
commercially feasible.

We have found that a dense metallic alloy de-
posit containing tungsten can be obtained from
an acid bath containing WO_3 dissolved in a bi-

fluoride. The complexes therein formed provide
a low metal ion concentration producing a
smooth, even deposit of extremely small crystal-
line structure. These complexes also have suf-
ficient chemical stability to resist the tendency
of tungsten and similar metallic ions to hydro-
lyze and form an oxidic deposit. The high solu-
bility of the oxide in the bath yields a reasonably
high metal concentration, eliminating the neces-
sity of replenishing the bath by electrolyzing from
a tungsten or tungsten-bearing anode.

An object of our invention is the production of
tungsten alloy plates, of dense, closely adherent
quality which are highly resistant to the corro-
sive action of acids and salts, and withstand high
temperature.

Another object of our invention is to provide
an electroplating process capable of producing a
satisfactory plate under varying operating con-
ditions.

Yet another object of our invention is the for-
mation of a solution bath from which substan-
tially pure metallic tungsten may be produced
by plating tungsten with a soluble or volatile
metal.

Still another object of our invention is the for-
mation of tungsten complex ions of low valence
which are chemically stable over a wide pH range.

A further object of our invention is the pro-
duction of an electroplating bath solution con-
taining a high metal concentration and low ion
concentration.

A still further object of our invention is to pro-
duce alloy plates of variable content ratios.

We have found as a result of considerable ex-
perimentation that improved results in respect
of the electrodeposition of tungsten and analo-
gous metals may be secured by directly dissolving
a suitable tungsten compound, such as tungstic
acid anhydride, in an acid fluoride. Particular-
ly we have found that ammonium acid fluoride
serves effectively as a solvent for the acid anhy-
dride. We have found additionally that the
physical characteristics of the plate may be con-
siderably improved by the use of certain ad-
juvants in the bath for the purpose of controlling
the acidity or hydrogen ion concentration, the
establishment and maintenance of complex ions
and the like. Considered more specifically, we
have determined that an improved tungsten al-
loy plate of widely variant content may be elec-
trodeposited by immediately utilizing tungstic
acid anhydride, tungstates, meta-tungstates,
para-tungstates, tungstic acid, etc., that is to say

without the necessity of producing tungsten ions in the bath by means of anodic corrosion.

In preparing the improved bath, tungstic acid anhydride and ammonium bifluoride are dissolved in water at a temperature of substantially 106° F. to 210° F. and the solution filtered. Boric acid (H_3BO_3), sodium fluoride (NaF) and tartaric acid are then added and the resulting solution brought to a temperature of between 120° F. and 140° F. or higher. At this stage in the preparation of the bath a soluble salt of the metal to be alloyed with tungsten is added. If nickel is desired as an alloy constituent, basic nickel carbonate ($2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) may be added. The resulting solution is then subjected to a current density of from 6 to 100 amperes per square foot of submerged cathode area. We have found that good results are obtained by controlling the pH value of the solution within the range of from substantially 1 to 10 or even higher during the plating operation.

Our process is flexible and susceptible of modification with reference to the constituents used and the procedure which may be followed in the preparation of the bath. As an illustration of one modification of our invention, tungstic acid anhydride, ammonium bifluoride, sodium chloride and a soluble salt of the metal to be alloyed are added simultaneously to water. The solution is maintained at a temperature of 140° F. to 210° F. for approximately 30 minutes, and clarified by filtration. The pH value is adjusted to substantially 5.3. The resulting solution is maintained at a temperature of substantially 140° F., and a current of about 30 amperes passed through it from a tungsten carbide (W_2C) anode to the cathode base to be plated, having an immersed surface of 1 square foot including its two faces.

In another modification of our process, which has been found particularly adapted for the production of a tungsten alloy plate, fused ammonium bifluoride and tungstic acid anhydride are dissolved in water at approximately 160° F. and the resulting solution clarified by filtration. To this solution is added sodium fluoride, sodium chloride, and the soluble salt of the metal to be alloyed. The solution is maintained at a temperature of substantially 160° F. and electrolyzed at a current density of approximately 35 amperes per square foot of submerged cathode area. A platinum or tungsten carbide (W_2C) anode may be used. In addition an anode of the metal desired to be alloyed with the tungsten plate may be used either alone or in combination with the platinum or tungsten carbide anode.

The following examples of our process are presented as specific illustrations of the reaction quantities and operation conditions which have been found to give a plate of desirable quality.

Example I

200 grams of WO_3 and 240 grams of NH_4HF_2 are added to one gallon of water and the solution raised to a temperature of between 160° F. to 210° F. and clarified by filtration. 120 grams of boric acid, 60 grams of NaF and 60 grams of tartaric acid are added to the filtrate, the solution transferred to the plating vessel and heated to a temperature of between 120° F. and 140° F. If an alloy plate, as for instance a nickel-tungsten plate, is desired, a soluble nickel salt is added; an excellent alloy plate is obtained by adding 10 grams of basic nickel carbonate to the bath. The pH value of the solution is then adjusted to be between 5.3 and 6.3. During electrolysis a current

density of between 6 and 100 amperes per square foot of submerged cathode areas is employed, using either a tungsten or nickel anode and any suitable metallic plating base as a cathode. Good results, however, may be obtained with a combination tungsten carbide and nickel anode or with a platinum anode.

Example II

To one gallon of water raised to a temperature of between 140° F. and 210° F. the following admixed dry salts are added:

	Grams
WO_3 -----	120
$\text{NiCO}_3 \cdot \text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ -----	60
NH_4HF_2 -----	240
NaF -----	240
NaCl -----	240

The above temperature is maintained for about 30 minutes and the solution clarified by filtration. Adjusting the pH value as in Example I the bath is placed in the plating tank and maintained at a temperature of substantially 140° F. during plating operations. Excellent results are obtained by electrolyzing with a tungsten carbide or nickel anode, or both, at a current density of about 30 amperes per square foot of submerged cathodic area.

Example III

170 grams of NH_4HF_2 and 80 grams of WO_3 are fused at a temperature just above the melting point of the NH_4HF_2 and the resulting fused cake dissolved in one gallon of water raised to a temperature of substantially 160° F. To this solution is added 160 grams of NaF , 80 grams of NaCl , and if desired, 20 grams of



or a similarly suitable soluble salt of a metal desired to be alloyed with the tungsten plate. The pH value of the bath is adjusted as in Examples I and II. Excellent results are obtained by electrolyzing at a bath temperature of substantially 160° F. A platinum, tungsten carbide, or nickel anode has been found to give satisfactory results with a bath prepared in this manner when a current density of substantially 35 amperes or higher per square foot of submerged cathode area is used.

It will be appreciated that the above examples should not be construed as limiting our process as to the constituents used, the quantities employed or the operating conditions set forth. We have found that satisfactory tungsten deposits can be obtained with a pH range of from 1 to 10 or higher. The current density also may be varied with good results from substantially 6 to 500 or more amperes per square foot of submerged cathode area. A variation of temperature ranges from 80° F. to 180° F. or higher have been found to give satisfactory results.

The commercial value of our process, however, does not alone depend upon the flexibility or non-critical nature of the operating conditions. With our improved process it is possible to obtain wide variations of solution concentrations which are satisfactory for commercial plating operations. For example, a tungsten concentration up to 6 oz. per gallon of bath solution can be obtained by dissolving WO_3 in a bifluoride solution; a mixture of WO_3 and tungsten metal gives a relatively high tungsten content and fused WO_3 - NH_4HF_2 also forms an exceptionally soluble compound producing high tungsten concentrations in an

acid solution. These solutions, even though high in tungsten content, are substantially clear and free from undissolved materials, such as the oxides usually present in tungsten plating baths. We have further discovered that the fixed alkali fluorides will fuse with tungsten oxides and tungsten salts to produce a satisfactory cake soluble in a dilute HF solution.

Quantitative tests show that solutions prepared by these methods have a much higher tungsten concentration than solutions to which the tungsten content is provided by means of anodic corrosion. The highest tungsten concentration which can be obtained by anodic corrosion is about 2 oz. of W per gallon. We have found, however, that when 40 grams of $\text{WO}_3 \cdot \text{NH}_4\text{F}$ are added to 200 cc. of water in equal quantities by weight, substantially 90% or more of the reaction compound will go in complete solution. We have found that depleted solutions caused by continuous plating operation, may be restored merely by adding WO_3 and a bifluoride in proper quantities to a heated portion of the electrolyte or by the more simple method of adding an aqueous solution of WO_3 and the bifluoride to the bath.

We have further discovered that the solubility of the WO_3 -bifluoride mixture is not affected by the presence of other desirable salts such as, for instance, the alkali halides, citric, tartaric and boric acids, sugars or soluble nickel salts. Two factors, therefore, (1) the high tungsten content of the bath solution and (2) the unaffected solubility of water soluble salts of metals such as Ni which may be desired to be alloyed with the tungsten, operate to provide great flexibility in the ratio range of tungsten and, for instance, nickel, in the solution. We have produced satisfactory alloy plates from a solution varying from substantially 15 parts tungsten to 1 part nickel to substantially 1 part tungsten to 1 part nickel. Alloy plates of this character can be produced by merely adding a soluble salt of the metal to be alloyed, to the WO_3 -bifluoride bath and electrolyzing with a suitable anode.

It is well known in the electroplating art that in order to obtain a fine grain deposit the metal ion concentration of the bath solution must be low. It is also desirable in most cases to have a large amount of the metal bearing compounds dissolved in the solution so that a constant supply of metal ions will be supplied at substantially the same rate that they are removed. We have obtained a bath solution of this character in that we have discovered a method of producing a water soluble double salt of tungsten capable of supplying stable complex ions.

As suggested in our copending application Serial No. 744,566, the double salts



$2\text{NaF} \cdot \text{WO}_2\text{F}_2$ and $\text{KF} \cdot \text{WO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$ are known. If these are the correct formulae of the soluble salts which we produce, it follows that the complex radical supplying the tungsten ions is a WO_2F_2 complex with a negative valence of two. The even, small grained plate which is produced leads us to believe, however, that we plate from a reduced complex such as WOF_2 for, as is well known, the lower the valence of the metal, the more even the deposit.

The formation of stable complexes prevents precipitation of the metal ions. Small amounts of such organic compounds as tartrates, citrates

and acetates or their corresponding acids, have been found useful in forming the desirable complex tungsten radical. The presence of dextrose, probably because of its tendency to act as a reducing agent, has also been found to be a desirable addition agent in that it aids in the formation of a fine grained and acid resisting plate.

The addition of boric acid has been found advantageous as a pH regulator or buffer, for the reason that the resulting borates, being weak acid salts, prevent an appreciable variation of the hydrogen ion concentration caused by changes in anode and cathode efficiency. In lieu of boric acid we may employ a number of other materials as pH regulators, as for example ammonium hydroxide, beryllium hydroxide, lithium hydroxide and lithium carbonate and the like.

While the presence of NaF and NaCl increase the conductivity of the bath, the increase of halide ion concentration aids anodic corrosion where a tungsten, tungsten carbide or nickel is used. This conclusion has been verified by solution tests showing an increased metal content when NaCl and NaF were present. HF has also been found to aid anode corrosion.

In lieu of employing nickel carbonate for supplying the nickel content, we may of course employ any other compound which will supply an available nickel ion, such for example as nickel chloride or nickel sulfate.

As indicated hereinbefore, the composition of a bath according to the present invention may be adjusted within a relatively wide range so as to secure tungsten alloy plates of specifically different compositions. It will be appreciated also that the fundamental principles of the present invention may be utilized to prepare ternary alloys of tungsten, as for example by preparing a bath, as described, and adding thereto a soluble salt of nickel and a soluble salt of the third metal component which is desired to be incorporated in the plate. Similarly, as intimated hereinbefore, the invention is not limited to the utilization of nickel as the second component. As pointed out in the copending application referred to, any metals which form an acid fluoride, such as iron, nickel and cobalt, or those which form two fluorides, such as antimony, copper, etc., may be incorporated in the bath, as by way of a soluble salt, so as subsequently to be plated out with the tungsten.

It will be appreciated that within the inventive principles defined herein wide permissive variations in the composition of a specific bath, in the type and character of the ultimate plate and in the character of the anodes and cathodes (base plates) are permissible. Thus, as indicated in Example II, if desirable a so-to-speak bath concentrate may be made up by admixing predetermined portions of the salts so as to produce a standard dry mix which, upon addition to water, under regulated temperature conditions and after adjustment of the hydrogen ion concentration, may be employed for plating.

It will also be understood that in accordance with the present invention double dioxyfluoride salts of the two metals to be plated may separately be prepared, which, upon dissolution in water and adjustment of the acidity, may be employed as the electrolytic bath. Thus, for example, the present method comprehends the direct utilization of such compounds as $\text{NiF}_2 \cdot \text{WO}_2\text{F}_2$; $\text{CoF}_2 \cdot \text{WO}_2\text{F}_2$; $\text{CuF}_2 \cdot \text{WO}_2\text{F}_2$ as well as $\text{NH}_4\text{F} \cdot \text{WO}_2\text{F}_2$; $\text{NaF} \cdot \text{WO}_2\text{F}_2$; $2\text{KF} \cdot \text{WO}_2\text{F}_2$ and the like.

The invention also directly comprehends the production as a separate article of manufacture a dry composition or a liquid concentrate from which the electrolytic bath may readily be made up. Similarly it will be appreciated that many of the ultimate constituents of the bath may be incorporated in the form of an anode. Thus certain of the bath constituents, as for example the alkali acid fluoride and the tungstic acid anhydride, may be fused (with or without the other adjuvants, such as the nickel salts) in combination or association with conductive material such as carbon or tungsten carbide, or tungsten nickel alloy and the like. In making up such a composite anode a suitable binder may be employed to bond the metallic or other conductive constituent of the anode.

These and all other similar modifications or ramifications of the method and of the ingredients, or their equivalents, of the bath and the anode are considered to be comprehended within the present disclosure. The present invention is considered to reside broadly in the concept of plating a tungsten or similar metal alloy, either of binary or polynary type, in which the tungsten content can be varied over a wide range and in which the tungsten is made available for electrodeposition by the direct utilization of tungsten salts in the manner indicated.

We claim:

1. A process of coelectroplating with metals such as nickel and tungsten which comprises forming an aqueous bath by adding an oxyfluoride of tungsten and a soluble salt of nickel to water, adjusting the bath to a definite acidity and electrolyzing with a metal anode.

2. An electroplating bath for electrodepositing tungsten with other metals comprising a solution of a tungsten-containing compound in aqueous alkali bifuoride, together with a salt of a metal chosen from the group consisting of iron, nickel, cobalt, antimony and copper.

3. An electroplating bath for coelectrodepositing tungsten with other metals comprising a solution of tungstic acid anhydride in aqueous ammonium bifuoride, together with a salt of a metal chosen from the group consisting of iron, nickel, cobalt, antimony and copper.

4. An electroplating bath for coelectrodepositing tungsten with other metals comprising a solution of a tungsten-containing compound, in aqueous alkali bifuoride and an alkali halide, such solution also containing a salt of a metal chosen from the following group: iron, nickel, cobalt, antimony and copper.

5. An electroplating bath for coelectrodepositing tungsten with other metals comprising a so-

lution of tungstic acid anhydride, in aqueous alkali bifuoride, and an alkali halide such solution also containing a salt of a metal chosen from the following group: iron, nickel, cobalt, antimony and copper.

6. An electroplating bath for coelectrodepositing tungsten and other metals which comprises a solution of tungsten acid anhydride, in aqueous ammonium bifuoride, and an alkali halide such solution also containing a salt of a metal chosen from the group consisting of iron, nickel, cobalt, antimony and copper.

7. A method of producing an electroplating bath for electrodepositing tungsten alloys which comprises, fusing a tungsten-containing compound with an alkali bifuoride, dissolving the resulting product in water and adding thereto an aqueous solution containing an alkali halide, boric acid, and a salt of a metal of the group consisting of iron, nickel, cobalt, antimony and copper.

8. An electroplating bath for electrodepositing tungsten alloys comprising a solution of tungstic acid anhydride in aqueous alkali bifuoride, together with a salt of a metal chosen from the group consisting of iron, nickel, cobalt, antimony and copper.

9. An electroplating bath for electrodepositing tungsten alloys comprising a solution of a tungsten-containing compound, in aqueous ammonium bifuoride and a salt of a metal chosen from the group consisting of iron, nickel, cobalt, antimony and copper.

10. A method of producing tungsten alloys of variable tungsten content which comprises, reacting a tungsten-containing compound with an alkali bifuoride, at elevated temperatures, dissolving the resulting product in water, adding to the solution a soluble salt of a second metal to be alloyed with the tungsten, said metal being chosen from the group consisting of iron, nickel, cobalt, antimony and copper, and electrodepositing an alloy of tungsten and one of said metals upon a suitable metallic cathode by electrolyzing the bath with a plurality of anodes, at least one of which contains tungsten and another of which contains the said second metal to be coplated therewith.

11. A method of producing an electroplating bath for electrodepositing tungsten alloys comprising fusing a tungsten-containing compound with an alkali bifuoride, dissolving the resulting product in water and adding thereto a soluble salt of a metal chosen from the group consisting of iron, nickel, cobalt, antimony and copper.

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