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ELECTROPLATING METHOD AND PRODUCT

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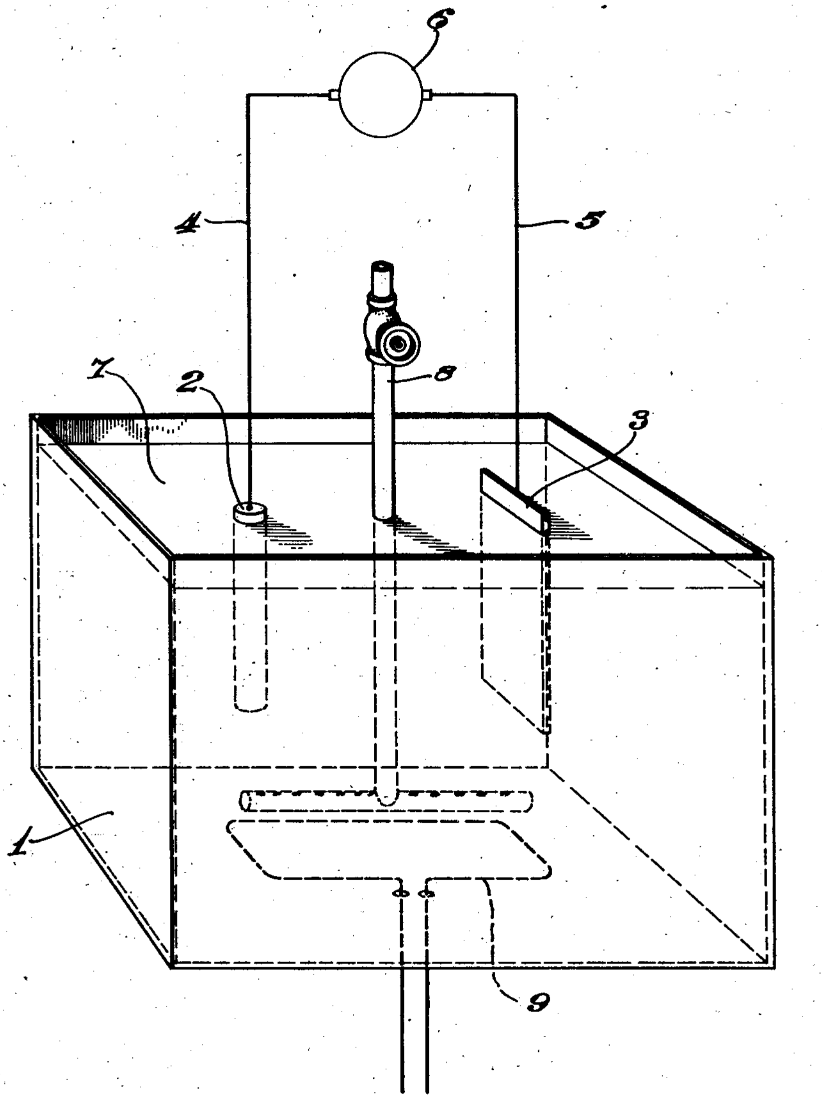

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ELECTROPLATING METHOD AND PRODUCT

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18 Claims. (Cl. 204—2)

Our invention relates to a process for electroplating tungsten alloys from aqueous solutions, and alloys of metals other than tungsten from the same type of electrolyte.

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

Up to the present time, tungsten or tungsten alloy plates, which have been produced by known any disclosed methods have been far from being resistant to strong acids, have been produced from decidedly alkaline electrolytes (pH 9 to 13), high current densities have been required (75 to 400 amperes per square foot of submerged cathode area) with excessive evolution of hydrogen at the cathode, and in most cases less than 1% current efficiency.

Our invention specifically relates to a practical and economical method of producing tungsten alloy plate, of variable tungsten content, which may be applied by means of standard equipment and common reagents, and which may be controlled and operated as continuously and readily as are the conventional nickel, chrome, cadmium, etc., processes.

As compared with the now known and disclosed methods of plating tungsten, our method embodies the following advantages:

1. The production of highly acid resistant plates;
2. The production of tungsten alloy plates of variable tungsten content (within reasonable limits), thus giving a wider field of application;
3. The production of a series of tungsten alloys, of variable tungsten content, and variable content of the metal or metals alloyed with the tungsten;
4. Satisfactory anode corrosion;
5. A pH range not too critical for easy control, and dense metal deposition;
6. High solution conductivity;
7. Moderately low current densities;
8. Much higher current efficiency;
9. Temperature of electrolyte not wastefully high.

Other objects of the invention will appear in the body of the specification.

In the drawing:

The figure is a diagrammatic view of a cell which may be utilized in practicing the invention.

Referring to the drawing, **1** is the cell box within which are placed an anode or anodes or cathode or cathodes **2** and **3**, respectively. Wires **4** and **5** lead from the anode and cathode respectively, to a source of current supply **6**. As is customary, the cell box is adapted to hold an electrolyte **7**. It may be desirable to agitate the electrolyte, and this may be done through the medium of air inlet means **8** constituting a pipe having a T-head, provided with perforations, to the end that air may be passed through said pipe and out the perforations to agitate the fluid. This T-head is preferably adjacent the base of the cell box. If desired, a heater may be placed in the base of the cell box, as indicated at **9**, the said heater being connected with a suitable source of current supply (not shown).

As descriptive of our process, approximately 4% by weight of $NAHF_2$ or KHF_2 or the equivalent amount of HF is dissolved in 100 parts of water and approximately 5% by weight of NaCl and 1% by weight of concentrated HCl is added to the solution. This solution is then heated to between 40° and 75° C. or higher, and electrolyzed for two hours or longer at 1½ to 6 volts or higher, using a tungsten carbide, a tungsten alloy carbide, such as tungsten-nickel carbide or a tungsten anode, and any good conducting cathode, such as Cu, brass, etc. During this treatment, the electrolyte turns a rich brown color, due to the corrosion of the anode and the going into the solution of a soluble tungsten salt, and we believe this to be in the form of tungsten dioxide (WO_2). If a tungsten alloy carbide anode, such as tungsten-nickel, tungsten-cobalt, etc., has not been used, we then add approximately two-tenths of one per cent. (.2 of 1%) by weight or more of a metal in the form of an acid soluble salt, the metal of which is to be alloyed with the tungsten in the plate, such as

$$NiCl_2,2NiCo_3 \cdot 3Ni(OH)_2 \cdot 4H_2O \text{ or } Ni(OH)_3,$$

etc. When this is dissolved, the pH of the solution is usually below 4. The pH is then adjusted to between 4.5 and 6.8 by the addition of

$$Na(OH),\ K_2(OH)$$

or some other alkaline reagent. The temperature of the solution is kept between 35° and 85° C. or even higher. The cathode to be plated is then placed in the solution, and electrolyzed at approximately 14 amperes per square foot of submerged cathode area. Small additions of the acid soluble salts of the metal or metals to be alloyed with the tungsten are required from time to time as the solution becomes depleted of these salts. Where a tungsten-nickel carbide anode is used, the addition of the acid soluble nickel salt is rarely necessary, as the corrosion of the anode is sufficient to give the necessary amounts of the two metals for satisfactory plating conditions.

We have found that it is possible to dilute the above solution 50% or more and still obtain satisfactory plates, slightly varying the voltage and current density.

Preferably Na(OH) and HCl are used as reagents for the control of the pH of the electrolyte.

However, various other acids and bases can be used without detrimental effects. For dense acid resistant plate, we have secured the best results at a pH between 5 and 6. It is possible to obtain bright metallic deposits below 5 and up to approximately 10. From a pH of the 6.8 and above, it is advisable to have present in the solution sufficient sugars, or weak organic acids, in order to prevent the precipitation of such metals as Ni, Co, etc., when these metals are to be alloyed with the tungsten.

While we have obtained bright metallic deposits throughout a current density range of from 6 to 35 and even higher amperes per square foot of submerged cathode area, we have obtained the plates giving the best acid resistant qualities at approximately 14 amperes per square foot of submerged cathode area.

By adjusting the ratio of the submerged anode and cathode area and the distances between same, bright metallic deposits have been obtained as high as 6 volts. However, we prefer a voltage range of from 1 to 3 volts.

Satisfactory plating conditions are obtained when using equal submerged areas of anode and cathodes. When high ratios of cathodes as compared to anodes are used, the electrolyte will in time become depleted in tungsten. It then becomes necessary to build up the tungsten content by electrolyzing at a more acid pH than it will plate, or by the addition of tungsten dioxide (WO_2), as described later.

Above we have described one method of producing tungsten alloy deposits. Another way to produce an electrolyte, from which tungsten alloys can be deposited, is by dissolving tungsten dioxide (WO_2) in the same type of electrolytes as described above, then following the same procedure as above as regards pH, current density, temperature, addition of acid soluble metal salts, which are to be alloyed with the tungsten, and using tungsten or tungsten carbide alloy anodes, or even inert conductive anodes, such as platinum or carbon.

For restoring the tungsten content of depleted solution, we prefer either to acidify with acid fluorides or hydrofluoric acid to a pH of approximately 4, then electrolyze or to add WO_2 dissolved in acid fluorides or hydrofluoric acid. After either of the above steps, it may be necessary to adjust to the proper pH for plating conditions. Undoubtedly many of the acid soluble salts containing the WO_2 radical, such as $2NaF \cdot WO_2F_2$; $KF \cdot WO_2F_2 \cdot 2H_2O$; $NH_4F \cdot WO_2F_2 \cdot H_2O$, etc., could be used for reviving depleted solutions. These salts, however, are difficult to prepare, costly, and usually unstable. In describing the above, it is to be understood that our invention is not intended to be limited to the production of tungsten alloy deposits, as the following single metals (Ni, Co, Sb, Zn, Cd, Aq, Hg, and Sn) have been plated through substantially the same acid fluoride bath as above described, by either straight anode corrosions or adding acid soluble salts of the metals. Also, a chrome-nickel alloy has been produced under approximately the same conditions, and our results indicate that many other alloys, such as nickel-chrome-iron, chrome-iron, manganese-iron, etc., can be produced.

Nor is it intended that our invention be limited to the use of the specific reagents mentioned. For sample, sodium or potassium hydroxide, plus hydrofluoric, to produce the approximate equivalent of the acid fluorides can be used. Also various strengths of hydrofluoric acid can be electrolyzed with tungsten, tungsten carbide, or tungsten-alloy carbide anodes then brought to the proper WO_2 ion concentration by dilution or concentration as required. It is to be understood that the sodium chloride and hydrochloric acids are not essential to the operation of the process, being added primarily to increase the conductivity of the bath, and increase anode corrosion. Also, various reagents, ammonium hydroxide, beryllium hydroxide, lithium hydroxide, lithium carbonate, boric acid, etc., may be used as pH regulators with satisfactory results. We have noted that small amounts of ammonium hydroxide in the bath produces especially bright plate.

In addition, we do not limit ourselves to the production of tungsten alloy deposits, in which the metals alloyed with the tungsten are nickel, cobalt, chrome, or antimony, as our results have indicated that any of the metals which form acid fluorides, such as $NiF_2 \cdot 5HF \cdot 6H_2O$, $CoF_2 \cdot 5HF \cdot 6H_2O$, etc., or those metals which form two fluorides, such as SbF_3 and SbF_5, $CuF_2 \cdot 2H_2O$ and Cu_2F_2, CrF_3 and CrF_2, etc., will, under substantially the same conditions as described above, alloy with the tungsten as a metallic and adherent plate.

So far as we are aware, tungsten carbide or tungsten carbide alloy anodes have not been employed or suggested by past disclosures or used by operators. Nor do we find any suggestion or disclosures of the use of tungsten dioxide (WO_2) dissolved in any acid electrolyte. Nor do we find any mention or suggestion of any direct attempt to produce tungsten alloys, where the soluble metal salt, the metal of which to be alloyed with tungsten, is added to the electrolyte for the direct purpose of producing tungsten alloy plates of variable tungsten content, suitable for various specific purposes.

We find with tungsten-nickel deposits that when very small amounts of the soluble nickel salt are present in the electrolyte usually higher than ordinary current density is required, and that the plates so produced are not as dense and therefore less acid resistant than plates produced from the same solution after the addition of more soluble nickel salt. As the amount of soluble nickel salt is increased higher and higher, the plate becomes less and less acid resistant. An appreciable amount of acid soluble nickel salt must be present in the electrolyte and an appreciable amount of metallic nickel must actually plate out alloyed with the tungsten before the best acid resistant deposit is obtained. This may be due possibly to the fact that in a certain range of proportions of the two metals, the alloy is more acid resistant, or that certain amounts of nickel must be present in order to produce a dense, closely adherent deposit.

The theory of our invention is believed to be as follows:

We quote Mellor for the existence of the following dioxyfluoride salts of tungsten:

$$NH_4F \cdot WO_2F_2 \cdot H_2O;\ 2NaF \cdot WO_2F_2;$$
$$KF \cdot WO_2F_2 \cdot 2H_2O;\ CuF_2 \cdot WO_2F_2 \cdot 4H_2O;$$
$$NH_4F \cdot 2CuF_2 \cdot WO_2F_2 \cdot 4H_2O;\ ZnF_2 \cdot WO_2F_2 \cdot 10H_2O,$$

and also there are mentioned the double dioxyfluoride salts of Cd, Th, Co, and Ni. Also quoting from Mellor, "Mariguac states that when normal or metatungstates are dissolved in hydrofluoric acid, compounds of the metal fluorides with tungsten dioxyfluorides are formed. These salts are usually soluble in water."

It seems reasonable to believe in our invention that electrolyzing tungsten, tungsten carbide, or tungsten alloy carbide anodes in an acid bath containing fluorine or dissolving WO_2 in an acid fluoride solution, the radical (WO_2F_2) is formed. The solutions in both cases, under normal plating conditions, are a rich brown color.

Assuming that the dioxyfluoride radical (WO_2F_2) is formed, it would ionize as

$$(WO_2)^{++}(F_2)^{--}.$$

The two valence of the (WO_2) is as low a valence as any oxide of tungsten, plus being the lowest oxide of tungsten that we are sure exists as an individual compound. In any case, we believe we are dealing with a tungsten ion in our electrolyte in a low state of oxidation, and more easily reducible than any form of tungsten so far attempted from aqueous solutions.

A tungsten carbide anode can be corroded in a hydrochloric acid solution by electrolysis, producing the same rich brown color. The corrosion seems to be faster than in a fluoride solution. We, however, have so far been unable to produce a deposit in any acid solution except when fluorine was present. The fact leads us to believe that the tungsten will only plate from the radical $(WO_2)^{++}(F_2)^{--}$ and further to the possibility (taking into account the fact that there must be present an acid soluble salt of some metal, which will plate out of the solution, alloyed with the tungsten) that in order to plate tungsten from aqueous solutions, there must be present in the electrolyte some certain amount of a metal fluoride with tungsten dioxyfluoride, or, in other words, the equivalent of a double salt.

Knowing that Ni and Co, both formed dioxyfluorides with tungsten, and both formed acid fluorides, we reason that any metal (that could be plated from an acid fluoride electrolyte) which formed an acid fluoride, or which formed two fluorides will form the equivalent of double salts, when dissolved in solutions containing $(WO_2)^{++}$, and such metals will plate out alloyed with the tungsten, our theory being that the metals, which formed two fluorides, such as SbF_3 and SbF_5, CrF_3 and CrF_2, etc., when the higher fluoride was dissolved, that the equivalent of an acid fluoride was produced, as SbF_5 when dissolved would ionize as $Sb^{+++}(F_3)^{---}$ and $(H_2)^{++}(F_2)^{--}$. On this theory, we proved that both Cr and Sb would plate out of the electrolyte alloyed with the tungsten, and we believe that all metals falling under the above classifications such as Cu, Fe, Ni, Cr, Co, Mn, Hg, As, Sn, etc., will act the same.

Our opinion of the value of the Cl^- in the electrolyte is that it increases anode corrosion, and possibly there is formed $(WO_2)^{++}Cl^{--}$, thus increasing the concentration of the tungsten metal ion, which would tend to produce better and more uniform plating conditions.

According to Mariguac's result that when normal and metatungstates are dissolved in hydrofluoric acid, compounds of the metal fluorides with tungsten dioxyfluorides are formed, it should be possible to produce from these compounds an electrolyte from which tungsten alloys could be plated. Our experience has been from the attempted use of WO_3, various tungstates, metatungstates and paratungstates in various acid fluoride baths, that the solutions are in all cases difficult to control. In most cases, the solutions when heated and electrolyzed, turn blue due to the formation probably of some W_2O_5 compound and also precipitate out large amounts of hydrated WO_3. As stated above, we prefer to use anode corrosion or WO_2.

It has been suggested by Holt and Kahlenberg that tungsten will not plate on tungsten. This fact, if true, would satisfactorily explain why past investigators have failed in their efforts to develop a commercial method of plating tungsten. Our experiments and results prove that various tungsten alloys will plate in a dense, adherent deposit on many metals and alloys, as well as on themselves.

We attribute the better acid resistant quality of our alloy plate, as compared with those produced from high alkaline solutions, to the fact that our alloy plates are deposited as a dense metallic plate from the instant the cathode is immersed. Whereas, using high alkaline solutions, the cathode first turns brown or blue due, we believe, to an oxide film, before it becomes metallic looking. In other words, the oxide is first formed and then reduced. This would not tend to produce a dense deposit. Also, with high alkaline electrolytes, it is necessary to use high current densities, with correspondingly high evolution of hydrogen at the cathode. This condition tends to produce pitting, and a plate, which is not dense, and therefore not as acid resistant.

We have noted in testing the acid resistant qualities of our tungsten alloy plates, that in some cases (for instance, the plating over copper, brass, or iron flashed with cadmium) the results indicate better acid resistant coatings (tungsten-nickel alloy over cadmium) than would be expected considering the distance apart in the electromotive series, of cadmium and a high percentage tungsten alloy. This leads to the possibility that tungsten and tungsten alloys in contact with certain metals may have a protective quality due to such contact, just as platinum in contact with certain metals is known to protect these metals from the corrosive action of acids.

We have found that 15 minute test plates (tungsten-nickel over brass, or brass copper flashed or copper electrodes) will stand immersion in cold concentrated hydrochloric or sulphuric acid 100 hours or more with apparently no effect on the plates or electrodes. The same type of plates have withstood cold concentrated nitric acid for eleven hours before definitely breaking down.

It is known that tungsten when heated to 1500° F. or perhaps much lower, in the presence of carbon or in a carbonizing atmosphere, will be converted to a carbide. At higher temperatures, this change is much more rapid than at lower temperatures.

We do not find used or disclosed in documents or industry any mention of the use of tungsten or tungsten alloy plates being converted to carbides, (with approximately 9.5 hardness, diamond 10) by subjecting such plates to heat in the presence of carbon, or in a hot carbonizing atmosphere.

We believe that our tungsten alloy plates have a direct application, when a hard, heat resisting surface is required, such as valves, valve seats, cylinder walls of internal combustion engines, pump lines, engine ports, gun barrels, etc. In case such plates are used, as valves, cylinder walls, gun barrels, etc., where heat and carbonizing atmospheres are a natural condition under operating conditions, we believe the tungsten alloy plate will gradually be converted to a carbide. For other uses, the plate would be converted to a carbide by a separate treatment.

We have noted that tungsten-nickel alloy plates, for instance, when deposited by our process on chrome plated cathodes, do not closely adhere to said cathodes, but deposit in scales and flakes, which are readily scraped or brushed free from the surface of the cathode. These flakes or scales show under the microscope a very fine, dense, crystalline structure. Treating these tungsten-nickel flakes or scales with dilute nitric acid removes all of the nickel, leaving a substantially pure fine-grain crystalline tungsten residue. When hot concentrated nitric acid is used instead of dilute acid, and the scales are in contact with the acid for several hours, the oxidizing action of the acid will gradually convert the tungsten crystals to tungsten oxide (WO_3).

It, therefore, is advisable in producing pure tungsten crystals to deposit the tungsten alloyed with a metal, which is either volatile and can be freed from the tungsten by heat, or one which is readily soluble in a single acid, preferably hydrochloric or sulphuric. In this way, it is possible to produce substantially pure fine-grained metallic tungsten crystals, free from metal or oxide impurities.

We claim:

1. The method of putting tungsten from a tungsten carbide anode into solution, which consists in causing electrolytic corrosion of the tungsten carbide anode in aqueous acid solution containing a fluoride ion.

2. The method of putting a metal to be alloyed with tungsten into solution, which consists in causing electrolytic corrosion of a tungstic alloy carbide anode in an aqueous acid solution containing a fluoride ion.

3. The process of electroplating with tungsten alloys, which comprises electrolyzing tungsten carbide anodes in an aqueous acid fluoride bath, to produce available tungsten ions in said bath; adding an acid soluble salt of a metal of group 8, series 4 of the periodic table to be alloyed with the tungsten to said bath, adjusting the pH of said bath to between 4.5 to 6.8; maintaining the solution at a temperature between 35° C. to 80° C., with a current density of about 14 amperes per square foot of submerged cathode area.

4. The process of electroplating with tungsten alloys, which comprises electrolyzing tungsten alloy carbide anodes in an aqueous acid fluoride bath, to produce available tungsten ions in said bath; adding an acid soluble salt of a metal of group 8, series 4 of the periodic table to be alloyed with the tungsten to said bath, adjusting the pH of said bath to between 4.5 to 6.8; maintaining the solution at a temperature between 35° C. to 80° C., with a current density of about 14 amperes per square foot of submerged cathode area.

5. The process of electroplating with tungsten alloys, which comprises dissolving tungsten dioxide WO_2 in an aqueous acid fluoride bath to produce available tungsten ions in said bath; adding an acid soluble salt of a metal of group 8, series 4 of the periodic table to be alloyed with the tungsten to said bath, adjusting the pH of said bath to between 4.5 to 6.8; maintaining the solution at a temperature between 35° C. to 80° C., with a current density of about 14 amperes per square foot of submerged cathode area.

6. A process for producing tungsten nickel alloy plates consisting of electrolyzing tungsten containing alloy anodes in an acid fluoride bath a sufficient length of time to build up the ion concentration of the metals in the alloy anodes, for good plating conditions, adding to the solution a quantity of an acid soluble nickel salt, then adjusting the pH to between 4.5 and 6.8 and electrolyzing at temperatures of from 35° C. to 80° C. at current densities of from 6 to 35 amperes per square foot of submerged cathode area.

7. A process of electroplating tungsten nickel alloys which comprises electrolyzing an acid bath containing a fluoride and available tungsten and nickel ions.

8. That method of preparing an electroplating bath which comprises anodically corroding a tungsten containing electrode in contact with an aqueous acid solution containing a fluoride, adding a compound containing available nickel, adjusting the pH of the solution to between 4 and 6.8 and plating out a tungsten nickel alloy upon a suitable metallic cathode.

9. An electroplating bath for electrodepositing tungsten alloys comprising an aqueous solution formed by dissolving tungsten dioxide in an aqueous solution of an alkali bifluoride and adding thereto a solution containing a soluble salt of a metal of group 8, series 4 of the periodic table.

10. A method of producing tungsten alloys of variable tungsten content which comprises dissolving a tungsten containing compound in a hot aqueous solution of an alkali acid fluoride, adding thereto a salt of a metal of group 8, series 4 of the periodic table, and electrolyzing the solution while it is maintained definitely acid to codeposit tungsten and said second metal from the solution.

11. The process of electroplating with tungsten alloys which comprises electrolyzing a tungsten containing anode in an aqueous acid fluoride bath to produce in said bath available tungsten ions, adding to the bath a soluble salt of a metal of group 8, series 4 of the periodic table, while maintaining the bath at a pH of between approximately 4 and 6.8 and at elevated temperatures, and then plating out a tungsten alloy from the bath upon a metal cathode.

12. An electrolyte bath for producing alloys by codeposition of tungsten with other metals, comprising an aqueous acid solution containing a fluoride together with available tungsten ions and ions of a metal of group 8, series 4 of the periodic table, and an organic acid.

13. A process for arresting and preventing corrosion of metals, which consists in first electroplating said metal with a metal close to it in the electromotive series, then immersing the preliminarily plated metal as a cathode in an aqueous fluoride bath having an acid reaction, which bath contains ions of tungsten and ions of a metal of group 8, series 4 of the periodic table.

14. An electrolyte bath for producing alloys by codeposition of tungsten with other metals comprising an aqueous acid solution containing available fluoride ions together with available tungsten ions and ions of a metal of group 8, series 4 of the periodic table.

15. A method of producing tungsten alloys of variable tungsten content by electrodeposition from an aqueous solution comprising, establishing an aqueous solution of definite acidity containing fluoride ions, ions of tungsten and ions of a metal of group 8, series 4 of the periodic table, and controlling the amount of tungsten in the alloy deposit by varying the metal ion concentration in the bath of the metal to be alloyed with the tungsten.

16. A method of producing electrodeposited

plates of tungsten which comprises electrolyzing a tungsten-containing anode in an aqueous, strongly acid bath which contains fluoride ions and ions of a metal of group 8, series 4 of the periodic table, and then plating out tungsten from the bath at a lower acid concentration.

17. A method of preparing an aqueous electrolyte for the electrodepositing of tungsten which comprises electrolyzing a tungsten containing anode in an aqueous solution of an acid fluoride at a pH of substantially 4, adding to the bath a salt of a metal of group 8, series 4 of the periodic table, then adjusting the acid concentration to approximately a pH of 4.5 to 6.8.

18. A method of preparing an electrolyte from which tungsten may be electrodeposited which comprises, electrolytically corroding a tungsten-containing anode in contact with aqueous hydrochloric acid, adding to the bath a fluoride and a soluble salt of a metal of group 8, series 4 of the periodic table.

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