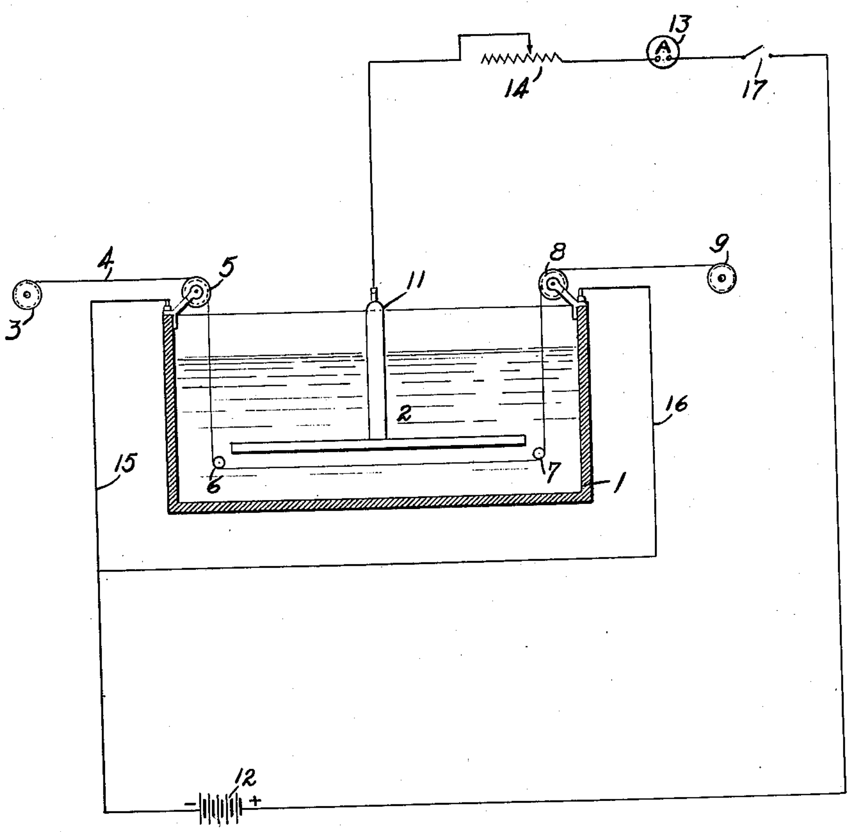
March 18, 1924. J. W. MARDEN ET AL 1,487,174

ELECTROLYTIC DEPOSITION OF THORIUM

Filed July 31, 1922



INVENTOR
JOHN W. MARDEN.
JOHN E. CONLEY.
THOMAS P. THOMAS.
BY J. H. Lebert
ATTORNEY

Patented Mar. 18, 1924. 1,487,174

UNITED STATES PATENT OFFICE.

JOHN WESLEY MARDEN, OF EAST ORANGE, AND JOHN EDWARD CONLEY AND THOMAS PHILIP THOMAS, OF BLOOMFIELD, NEW JERSEY, ASSIGNORS TO WESTINGHOUSE LAMP COMPANY, A CORPORATION OF PENNSYLVANIA.

ELECTROLYTIC DEPOSITION OF THORIUM.

Application filed July 31, 1922. Serial No. 578,813.

To all whom it may concern:

Be it known that we, JOHN WESLEY MARDEN, JOHN EDWARD CONLEY, and THOMAS PHILIP THOMAS, citizens of the United States, and residents of East Orange, Bloomfield, and Bloomfield, respectively, in the county of Essex and State of New Jersey, have invented a new and useful Improvement in Electrolytic Deposition of Thorium, of which the following is a specification.

This invention relates to the electrolytic deposition of thorium and more particularly to the electroplating of filamentary material, electrodes and the like with metallic thorium for the purpose of increasing the electronemissivity thereof.

An object of our invention is the formation of a plating of thorium deposited from aqueous solution.

Another object of our invention is the production of thorium directly in metallic form from aqueous solution thereof.

A further object of our invention is the preparation of metallic material and other articles with a coating of thorium metal deposited thereon directly from aqueous solution.

A still further object of our invention is the cold preparation of electron-emitting material by a continuous process in a convenient manner.

An additional object is the electrolytic deposition of a thorium alloy or mixture with other metals suitable for electron-emitting material.

Other objects and advantages of the invention will be apparent upon reading the following detailed description.

The chemical and metallurgical literature fails to disclose a method for depositing thorium or thorium alloys, electrolytically from aqueous solutions. Moissan and Honigschmidt, Monatshaft für Chemie 27,685 (1906) and later Von Wartenburgh, Zeit. Elektrochem. 15,866 (1909) claimed to have prepared impure thorium by the electrolysis of the fused double salt, sodium thorium chloride, (Na_2ThCl_6).

The metal thus obtained contains at least 15% of thorium oxide and the method was shown to be difficult of manipulation. Heating is necessary for the fusion of the salt and the electrolysis should be conducted in dry, oxygen-free, nitrogen, hydrogen or inert gas so that the metal may be as pure as possible. Such a method is obviously not very suitable for coating or plating articles such as X-ray targets or filamentary material for electron-emitting purposes.

According to our invention, we have devised a process whereby articles may be plated or coated electrolytically with thorium directly from aqueous solutions thereof. The exact composition of the solution is not essential, the essence of the invention being the preparation of a solution of thorium which upon electrolysis thereof will deposit a coherent and adherent coating of thorium or an alloy thereof so that the article or material coated therewith may be used for electron emission, X-ray or other purposes in the same way in which solid metallic thorium could be used.

One embodiment of our invention comprises dissolving thorium hydroxide in fluoboric acid. Although thorium hydroxide is only slightly soluble in fluoboric acid we have found that when some other compound, such as lead hydroxide or carbonate, is added, we are able to deposit a mixture or alloy of the two metals from such a solution.

Another embodiment of our invention comprises dissolving thorium hydroxide in fluosilicic acid in the presence of a compound of lead such as heretofore mentioned. Thorium and lead may be deposited electrolytically from such a solution in the same manner in which they are deposited from a fluoborate solution.

A further embodiment of our invention comprises preparing a solution by mixing neutral potassium lactate with thorium chloride in the presence of ferrous chloride. In such a solution the iron acts in much the same manner as the lead in a fluoborate or fluosilicate solution and deposits electrolytically along with the thorium with the formation of a coherent and adherent coating on a suitable cathode immersed therein. This embodiment of our invention may be slightly modified by substituting lead for iron, thereby avoiding a slight confusion that might arise if coated articles were used for electron-emitting purposes because of the slight electron-emission of iron.

Although it has heretofore been considered impossible to deposit thorium electrolytically, it should be noted that lead alone has been deposited or plated from fluosilicate and fluoborate solutions and reference is made to the paper of W. Blum et al., Lead Plating from Fluoborate Solutions, published in vol. 36, pages 243 to 268 inclusive, of the Transactions of the American Electrochemical Society, 1919.

Our invention will better be understood by referring to the accompanying drawing which illustrates, partly in section and partly diagrammatically, apparatus which may be used for coating wire or filamentary material with thorium.

The tank 1, preferably coated on the inside with wax or some material not acted on by hydrofluoric acid, may be used for holding the plating solution of thorium 2. The spool 3 may be wound with wire or filament 4 of tungsten or the like, which wire may be drawn through the solution over pulley 5, rods or the like 6 and 7, of suitable material, pulley 8 and wound up on spool or pulley 9. Any suitable mechanism may be employed for driving the spool 9 at a uniformly slow rate of speed to draw the wire from the solution 2. An electrode 11 of carbon or the like is inserted in the solution 2 and an electrical potential established between the electrode 11 as an anode and the filament as a cathode by means of battery 12 or other suitable source of direct current. An ammeter 13 and a rheostat 14 may be inserted in the circuit for the purpose of indicating and adjusting the plating current to the desired strength.

Although only one end of the wire need be electrically connected to the battery 12, it is preferable, especially where wire of small size and therefore of high resistance is used, to connect the same to the battery at points adjacent where the wire goes into and emerges from the plating solution.

In the drawing, the wire is shown electrically connected to the battery 12 by means of conductors 15 and 16, respectively, connected to pulleys 5 and 8 by means of which electrical contact is made with the wire to be plated. A switch 17 may be provided for making or breaking the circuit from the battery 12.

By means of the aforesaid apparatus, wire of tungsten or the like may be plated or electrolytically coated with thorium preferably, in the form of an alloy or mixture thereof, after first receiving a thin coating of copper or the like, which is preferably applied to make the coating of thorium adhere more strongly to the wire. The thorium solution 2 may be prepared in any one of several ways, that is, it may be a fluoborate solution of thorium in the presence of lead, a fluosilicate solution of thorium in the presence of lead or a mixture of a lactate with salts of thorium and iron or lead. A small amount of glue or other suitable colloid is preferably added to the solution for the purpose of making the deposit more firmly adherent to the wire or article being plated.

An example of the formation of a plating solution by the fluoborate method may be as follows. Freshly precipitated thorium hydroxide together with a lead compound such as the hydroxide, carbonate or basic carbonate is added to a mixture of 32 grams of hydrofluoric acid (50%HF.) and 14.8 grams of boric acid (H_3BO_3). Thorium hydroxide may be added wet so that the resultant volume of the mixture is about 100 cubic centimeters. Some of the thorium added as hydroxide will precipitate as thorium fluoride and should be filtered off and the clear liquid used.

In order that an excessive amount of thorium fluoride will not be precipitated, an excess of boric acid is preferably present in the solution, over that needed to form fluoboric acid, and this excess also tends to make the fluoboric acid more stable.

One-quarter gram of glue or other similar colloid, may then be added so that the electrolytic deposit formed from the solution will be coherent and adherent. Without the glue the deposit is spongy and readily falls off from the cathode. It is preferable that the article or wire to be coated with thorium is first coated or plated very thinly with copper. With a copper sulphate solution containing 15% blue vitriol and 5% sulphuric acid, an exposure of about 1 or 2 minutes with a current density of about 10 to 50 milli-amperes per square centimeter of cathode surface may be used. The rate of deposit may easily be varied to suit conditions either by using other concentration of electrolyte, time of deposition or current density.

A wire of tungsten, for example, when copper plated as above described, which plating may be performed with apparatus such as illustrated in the accompanying drawing, may then be washed with water and placed in and passed through the fluoborate solution prepared as heretofore described where it is then plated with a mixture or alloy of thorium and lead by means of the apparatus hereinbefore described.

The time for depositing thorium may be varied according to the thickness of the coating desired and the strength of the current used. A higher current density requires a shorter length of time but the deposit will not adhere as well as when deposited more slowly. According to this method a 3 mil tungsten wire was increased in size to 4 mils, that is, a half mil coating was applied thereto, although thicker or thinner deposits may be made to suit the need. Such a wire, when used as a hot cathode in suitable electron-emission apparatus, the gas therein being removed by suitable well known means, showed the characteristic electron-emission of thorium. A few readings of this wire are given here to verify this statement.

At 10:30 a. m. an emission of 77 milliamperes per square centimeter of wire surface at about 1780° K. was obtained, on continuous service at 3 p. m. an emission of 70 milliamperes per square centimeter was obtained at about 1765° K.; while at 4.45 p. m. another reading showed 77 milliamperes per square centimeter at about 1780° K. (absolute).

Thorium in the presence of lead may also be electroplated or deposited from a fluosilicate solution prepared in a similar manner to that described for a fluoborate solution. It is to be understood that we do not restrict ourselves to the use of lead as a co-precipitator for causing thorium to deposit, for there are other metals as well, which we contemplate using, such as iron, nickel, copper and many others. The reason lead has been used to aid in the deposition of the thorium, is on account of the low electron-emission of lead and its oxide.

A tungsten wire, as above described, plated with lead alone will give no indication of electron-emission in any stage of its heating. The only emission observed from the mixture then is that of thorium alone, at any point below the emission temperature of tungsten.

Another method for successfully depositing or electroplating with thorium is that using a lactate solution, for example, a thorium-iron mixture or alloy may be deposited from a solution of the following composition using the same conditions regarding current density, anode and cathode surface as hereinbefore described with reference to fluoborate solutions.

First it is preferable to neutralize to litmus 7½ grams of 85% (U. S. P.) lactic acid with a strong solution (50%) of potassium hydroxide. A few cubic centimeters of a solution which contains 1.3 grams of thorium chloride and a few cubic centimeters of a solution of ferrous chloride and 2 grams of potassium chloride may then be added. The total volume of the solution is then preferably made up to 100 cubic centimeters and 5 drops of lactic acid added to acidify it slightly. When electrolyzed under the same conditions as heretofore described for a fluoborate solution, a gray-white deposit consisting of an alloy or mixture of thorium and iron may be obtained, which adheres well to the article or wire plated and may be made up to a considerable thickness. Such a deposit is less crystalline and more adherent than the lead alloys and a 3 mil wire thus prepared showed a constant emission of about 70 milliamperes per square centimeter of surface at about 1715° K. (absolute).

Since lead is more desirable than iron where there would be chance for confusion of the slight emission of iron with that of thorium, lead may be substituted for the iron in a lactate solution prepared as above described. A filament coated with a thorium-lead alloy or mixture by the lactate method when tested showed electron emission of 48 milliamperes per square centimeter of filament surface at about 1730° K.

It will be apparent that our invention may be used for many purposes, for example, the electron-emission of many elements may be determined by electroplating on a filament from a solution and testing the electron-emission of the plated filament. In this way the electron-emission of elements which have not yet been prepared in metallic form may be determined. We also have in mind the deposition of calcium, strontium and barium alloys and the subsequent oxidation of these for oxide-coated filaments for radio bulbs and the like. We also have in mind the deposition of pure metals which have not yet been prepared in this way from various aqueous solutions and some of which have never been prepared at all. With some of these materials, we may find it more desirable to plate from glycerine or alcoholic solutions or to use other salts than those heretofore mentioned.

According to our invention a mixture or alloy of a metal may be deposited with a more volatile one and the latter volatilized leaving the pure metal, or possibly the reverse method, to recover the desired metal plated as a mixture or alloy by distilling and condensing the same on a cold surface.

Although we have described what we now consider to be the preferred means of practicing our invention and have described specific embodiments thereof, it is to be understood that the same are merely illustrative and that our invention is limited only by the scope and spirit of the appended claims.

What is claimed is:

1. The method of forming thorium metal comprising preparing a solution thereof and depositing thorium therefrom electrolytically.

2. The method of preparing metallic thorium comprising forming an aqueous solution of a salt thereof and decomposing the same by electricity to deposit thorium therefrom.

3. The method of electroplating with thorium comprising dissolving a compound thereof and passing a current between an

anode and a cathode in the solution formed, whereby thorium is plated upon the cathode.

4. The method of forming thorium metal comprising preparing a solution of a thorium compound in water and decomposing said compound by passing electricity between an anode and cathode therein, whereby a coating of thorium is deposited on the cathode.

5. The method of coating with thorium comprising dissolving thorium hydroxide and inserting the material to be coated in the solution so formed as a cathode and depositing thorium thereon by electricity.

6. The method of electro-depositing thorium comprising preparing a fluoborate solution thereof in the presence of lead and inserting the material desired to be plated in said solution as a cathode and impressing a potential between the same and an anode of any suitable material such as carbon.

7. The method of coating material with thorium comprising perparing a fluosilicate solution of thorium and lead, inserting the material to be coated therein and depositing thorium thereon electrolytically.

8. The method of electroplating material with thorium comprising dissolving salts of thorium and iron in a lactate solution and inserting the material to be coated with thorium as a cathode therein.

9. The method of electro-depositing thorium comprising dissolving salts of thorium and lead in an acidified lactate solution and inserting material to be coated with thorium as a cathode therein.

10. The method of coating a wire continuously with thorium comprising passing it slowly through a fluoborate solution of thorium and lead while maintaining a potential between said wire as a cathode and an anode of any suitable material not attacked by the solution.

11. The method of continuously coating filamentary material or the like with a thorium alloy or mixture comprising preparing a solution of thorium and another metal and passing the material through said solution while maintaining a potential between the same as a cathode and a suitable anode immersed in said solution.

12. The method of plating metallic material with thorium comprising dissolving thorium hydroxide and lead hydroxide or the like in fluoboric acid containing an excess of boric acid, inserting the material therein as a cathode with a suitable anode and passing electric current therebetween.

13. The method of plating refractory metallic material with thorium comprising dissolving thorium hydroxide and lead hydroxide in fluoboric acid containing an excess of boric acid and glue or the like, copper plating the material and inserting it in the prepared solution as a cathode with a suitable anode and passing electric current therebetween.

14. The method of plating metallic material with thorium comprising dissolving thorium hydroxide and lead hydroxide or the like in fluosilicic acid, inserting the material therein as a cathode with a suitable anode and passing electric current therebetween.

15. The method of plating metallic material with thorium comprising dissolving thorium chloride and ferrous chloride in a solution of potassium lactate or the like, inserting the material therein as a cathode with a suitable anode and passing electric current therebtween.

16. The method of plating metallic material with thorium comprising dissolving thorium chloride and ferrous chloride in a solution of potassium lactate, acidulating it slightly with lactic acid, providing the metallic material with a surface of copper, inserting it in the solution as a cathode with a suitable anode and passing electric current therebetween.

17. Filamentary material for electron-emitting purposes comprising tungsten or the like electroplated with thorium.

18. An X-ray target electroplated with thorium.

19. Electron-emission material comprising a refractory metal, copper coated, upon which thorium has been electroplated.

20. Electron-emission material comprising tungsten or the like copper plated and then electroplated with an alloy of thorium.

21. Electron-emission material comprising molybdenum or the like, copper plated and electroplated with an alloy or mixture of thorium and iron.

22. Metallic material plated with an alloy or mixture of thorium and another metal.

23. Metallic material plated with copper and then electroplated with thorium.

24. Metallic material plated with copper and then electroplated with an alloy or mixture of thorium and lead.

25. Copper plated metallic material electroplated with an alloy or mixture of thorium and iron.

26. An X-ray target formed of refractory metal electroplated with thorium and another metal.

27. An X-ray target formed of tungsten or the like electroplated with thorium and another metal.

28. An X-ray target formed of tungsten copper-plated and then electroplated with thorium and another metal.

29. An X-ray target formed of tungsten or the like electroplated with thorium.

30. An X-ray target formed of refractory metal electroplated with thorium and lead.

31. An X-ray target formed of refrac-

tory metal electroplated with thorium and iron.

32. An X-ray target formed of refractory metal copper-plated and electroplated with thorium.

33. An X-ray target formed of tungsten or the like copper-plated and then electroplated with an alloy or mixture of thorium.

34. An X-ray target formed of tungsten or the like copper-plated and then electroplated with an alloy or mixture of thorium and another metal.

35. An X-ray target comprising refractory metal copper-plated and then electroplated with an alloy or mixture of thorium and lead.

36. An X-ray target formed of tungsten or the like plated with copper and then electroplated with an alloy or mixture of thorium and iron.

37. An X-ray target coated with thorium.

In testimony whereof, we have hereunto subscribed our names this 28th day of July 1922.

JOHN WESLEY MARDEN.
JOHN EDWARD CONLEY.
THOMAS PHILIP THOMAS.