

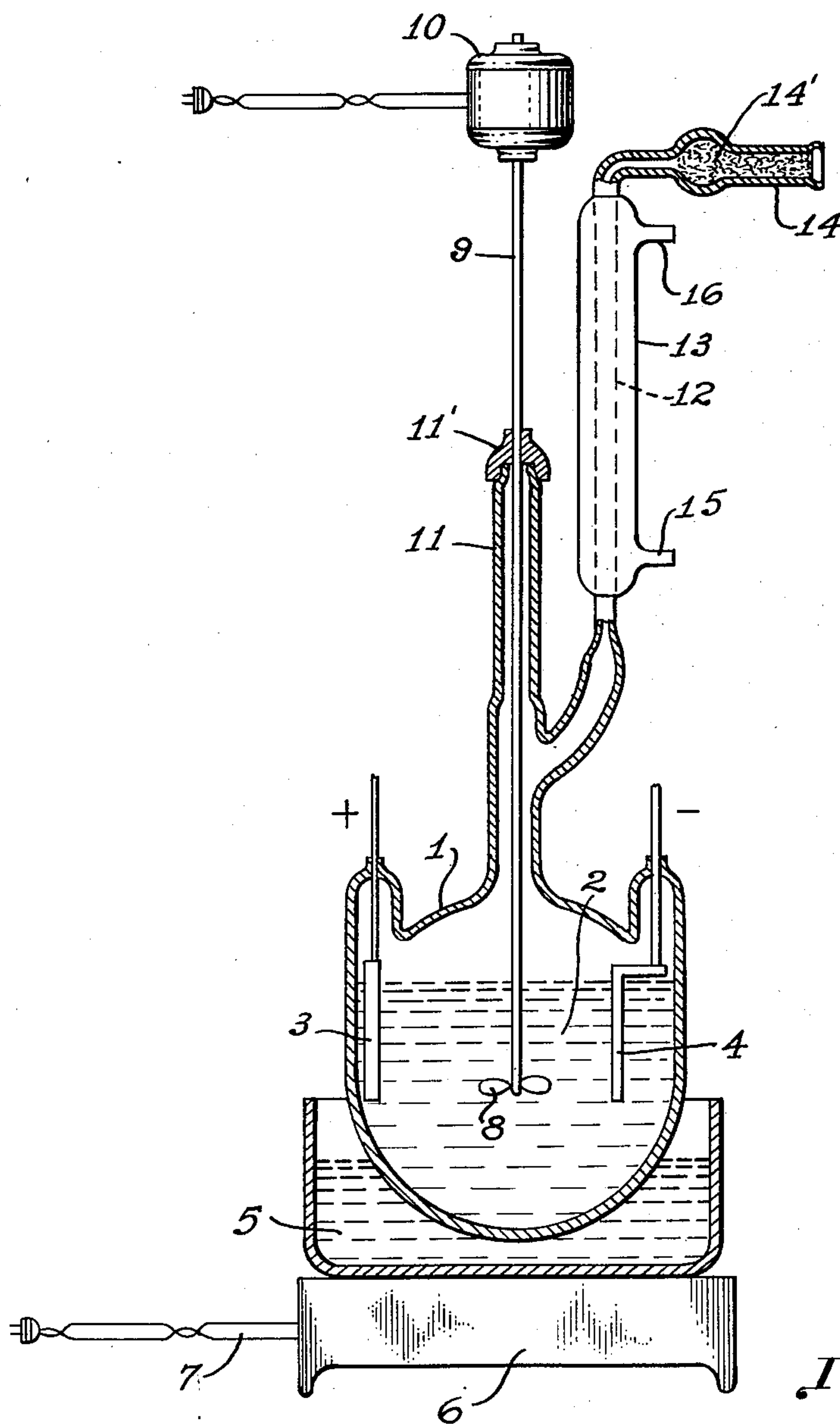
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METHOD OF PLATING METALS WITH ZIRCONIUM

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METHOD OF PLATING METALS WITH ZIRCONIUM

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1

This invention relates to the electroplating of metals and alloys with other metals.

The invention is of particular utility in the electroplating of zirconium and other similar getter functioning metals on copper, nickel and other metals and conducting materials used in the manufacture of electrical incandescent lamp bulbs, thermionic tubes and the like, although certain features of the invention are of broader application. For example, the interior support and mount wires of such bulbs and tubes under this invention may be coated or electroplated in accordance with the invention to obtain active surfaces of the gettering material on the exterior of the nickel, copper or other metallic or conducting support and mount wires utilized.

An object of the invention is a novel and improved method of electroplating metals and other conducting materials with metals of the above indicated character.

A further object of the invention is a novel non-aqueous medium containing in solution a compound of the metal to be deposited which compound upon being subjected to electrolysis gives off the metal for deposit upon the negative electrode of the plating cell.

A further object of the invention is the electroplating of the metal to be deposited by utilizing a non-aqueous electrolyte consisting of an organic solvent carrying in solution an electrolytically reducible compound containing as a constituent the metal to be deposited or plated upon the cathode.

A further object of the invention is a novel and improved method for electrolytically producing a getter or other metallic plating on other metallic or conducting substrata at temperatures readily obtainable in laboratory or factory-scale equipment and sufficiently low as to be relatively non-hazardous and readily controlled.

A further object of the invention is a non-aqueous electrolyte composed of a mono-hydroxy aliphatic alcohol as a solvent carrying in solution an electrolytically reducible compound containing the metal for deposit.

A further object of the invention is the electroplating of metals or other conducting materials with the getter or other metal utilizing a non-aqueous electrolyte of the above indicated character.

2

More particularly, and with specific reference to zirconium, the electrolytically reducible compound of zirconium may be any of those embodying fluorine, chlorine, bromine, iodine, etc. such, for example, as the zirconium halides, zirconium oxy-halides, etc., or nitric acid salt of zirconium, namely zirconium nitrate $Zr(NO_3)_4$ or zirconium oxy-nitrate. As examples, good results have been obtained by the use of either zirconium oxy-chloride ($ZrOCl_2 \cdot 8H_2O$) or zirconium tetrachloride ($ZrCl_4$), as the zirconium-containing compound, which is to be reduced by electrolysis and the metal plated upon the cathode.

As the non-aqueous carrying medium or solvent for the getter or other metal compound, aliphatic alcohols may be used as described above, such, for example, as the butyl alcohols. Of the butyl alcohols, n-butyl alcohol has given good results, particularly when using zirconium oxy-chloride as the zirconium compound. The n-butyl alcohol, referred to as normal butyl alcohol, has a boiling point of 117–118° C. (increased slightly by material in solution) and during the electroplating process is heated to the boiling point of the solution.

The concentration of solute in the non-aqueous electrolyte may be varied within limits but good results have been obtained with a saturated solution in the presence of excess solid. As one example, a non-aqueous electrolyte which may be used to advantage contains 20 parts by weight of n-butyl alcohol and 1 part by weight of zirconium oxy-chloride. This gives a saturated solution of the zirconium oxy-chloride and an excess of solid which is indicated by the turbid character of the non-aqueous electrolyte. Best results are obtained when the solution is saturated with excess solid and the turbid appearing character of the solution indicates the presence of the excess solid and the saturated character of the solution.

The zirconium tetrachloride is quite soluble in the n-butyl alcohol and we have obtained successful results with from 1 to 10% by weight of the tetrachloride dissolved in the butyl alcohol.

We have found the solubility of zirconium oxy-chloride to be considerably less than that of zirconium tetrachloride in the same solvent.

namely butanol. The solubility of zirconium oxy-chloride in refluxing butanol, as determined by us, is of the order of magnitude of 0.5 to 1.0% by weight. However, when only that quantity by weight of the zirconium oxy-chloride is added the results are unsatisfactory, which fact may be due to the low conductivity of the electrolyte. Accordingly when using zirconium oxy-chloride we need to introduce into the butyl alcohol a quantity of the compound substantially greater than the 0.5 to 1.0% by weight and we have found that particularly good results, with the low voltages available, the temperature used, etc., may be obtained by introducing zirconium oxy-chloride to the extent of 5% by weight of the solvent.

In certain cases we have obtained good zirconium plating by merely the solution formed when the zirconium oxy-chloride is added to and dissolved in the solvent, but the results are not uniform, which lack of uniformity may be due to variations in the character of the particular zirconium compound used or to variations in the solvent, etc. For example, it is believed that the solution of a zirconium salt in butyl alcohol is usually not sufficiently acid for a satisfactory plating result. In any event, we have found that this difficulty may be overcome and uniformly good results obtained by the addition to the plating solution or electrolyte of small amounts of anhydrous hydrogen chloride (HCl) and the like. A convenient way of adding the anhydrous hydrogen chloride to the plating solution is to form a saturated solution of the hydrogen chloride in butyl alcohol and then add this saturated solution to the plating solution. We have also found that better and more uniform results are obtained with zirconium tetrachloride when a similar small quantity of the butanolic HCl is added to the solution. Comparatively small quantities of this butanolic hydrogen chloride solution are usually sufficient to bring the acidity of the plating solution to a satisfactory working level and, as indicated above, with certain plating solutions none need be added. With the particular materials, factors and other conditions present, we have found that the addition of from 0% to 5% by volume of the saturated butanolic hydrogen chloride solution to the plating solution containing the zirconium oxy-chloride compound renders the results more certain and uniform. We have found that when using the zirconium tetrachloride compound it is sometimes desirable to add slightly larger quantities. In no case should it be necessary to add as much as 10% by volume. We have obtained satisfactory plating over a wide range of acidities in the plating solution and the present preferred acidity is an "effective pH" of from 2.35 to 2.60, applying a direct current of unvarying character to the cathode. The phrase "effective pH" is an arbitrary standard of acidity comparison which we have set up for the purposes of this invention. It involves the measurement of a 1.00 milliliter sample of the plating solution and the dilution of this sample with 49.00 milliliters of distilled water to form an aqueous test solution. This aqueous test solution, which consists of a single phase after mild shaking, is checked in a conventional type glass electrode pH meter which has been standardized with buffers of known pH value. The resulting meter reading is the "effective pH." The "effective pH." thus defined, of the original plating solutions is usually above the preferred range, and accordingly we add to them, when needed, sufficient

butanolic hydrogen chloride solution to bring the acidity within this range.

As indicated above, the electrolyte is heated during the electroplating process to the boiling point of the solution. This heating is externally applied but the heat energy resulting from the reaction during the electroplating process, makes possible a reduction of the external heat applied in order to maintain a given temperature. The heating of the electrolyte to a temperature above room temperature makes it possible to obtain the desired current density with a comparatively low voltage, i. e. 35 to 75 volts with the particular materials used and other factors present for getting the desirable results, two examples of which are given below. With higher voltage sources available it is possible to obtain with any particular electrolyte and set-up as to volumes of container, spacing of electrodes, etc., satisfactory results at lower temperatures of operation, even at room temperature, but with the method above described, including the maintenance of the temperature at the boiling point of the plating solution, the lower available voltages may be utilized to obtain the desired results while the temperatures are within the range which does not require special heating apparatus ordinarily not available in factories. An operation at or near room temperature would require cooling due to the heat energy liberated in the plating solution.

By varying the current density and other factors, there occur variations in the plated product which range from a bright lustrous plated surface through a black amorphous, adherent surface to a black to brown powdery non-adherent surface. The latter product is less desirable than the smooth polished surface and the black amorphous adherent plate, and preferably the adjustment is such as to preclude the formation of the less desirable plating product. In the Example No. 1 given below, the plated surface was a bright, lustrous surface while in the Example No. 2 the plated surface was less bright and less lustrous. These plated surfaces, where needed, may be polished by mechanical treatment after being formed to assume surface characteristics very closely resembling those of polished ductile zirconium. Thus the character of the plated surface may be varied by varying the current density and other factors. For example, if at any particular current density the bright polished surface is obtainable, an increase in current density tends to produce a less polished surface with the same plating solution. By adding more anhydrous hydrogen chloride to the plating solution with an increase of current density, the tendency to produce the less polished plating is reduced, and as a variant of the process the gradual addition of anhydrous hydrogen chloride or other anhydrous source of hydrogen ion is contemplated in order to stabilize cell resistance and avoid depletion of the plating solution by precipitation of zirconium hydroxide or other basic oxy-chlorides of zirconium.

For any particular plating solution the adjustment of the current density, the temperatures, etc. are such as to obtain a preferential reduction of the metal for the deposit as distinguished from or over a preferential release of hydrogen gas. For example, with the current density below a certain value, assuming other conditions are the same, little or no getter metal is reduced and deposited while the hydrogen ions are depleted with no useful results.

The depletion of the plating solution may occur due to the precipitation of zirconium hydroxide $[\text{Zr}(\text{OH})_4]$, a reaction which is greatly accelerated by the presence of trace amounts of water. It is desirable therefore from an economic point of view to minimize the rate of this reaction and this may be effected by the elimination so far as practicable of the sources of moisture contamination. The apparatus described below for carrying out the process is sealed against the entry of moisture. Moisture may be present both in the butyl alcohol and in the zirconium oxy-chloride. In order to rid the butyl alcohol of all water content it may be treated as follows: A small quantity of metallic sodium (Na) is dissolved in butyl alcohol with the evolution of hydrogen gas and the formation of sodium butylate, the formula for which is NaOC_4H_9 . The solution of sodium butylate in butyl alcohol thus prepared is added to a larger quantity of butyl alcohol and the whole distilled at atmospheric pressure, removing that fraction of the distillate boiling above 115°C . as satisfactory material for use in our plating procedure.

The zirconium oxy-chloride crystallizes as an octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$). At a temperature intermediate between 150° and 300°C . it is possible to remove the water of crystallization from this compound. Amounts of water of this order of magnitude are apparently significant in the matter of precipitating zirconium hydroxide from the plating solution.

The plating result is obtained on the cathode whether its surface is entirely smooth or not but for best results it should be cleaned thoroughly as, for example, by etching the copper surface (when a copper cathode is used) in nitric acid and then washing thoroughly with distilled water and drying.

We have found that improved results are obtained by agitating the electrolyte during the plating process as, for example, by introducing a suitable stirrer which is operated during the process. The degree or rate of agitation affects the plating process. Generally speaking a too rapid agitation tends to result in uneven plating with areas devoid of plating or insufficiently plated. Less rapid agitation tends to result in an accelerated rate of cell polarization and a rise in the electrical resistance of the plating system due to the accumulation of zirconium hydroxide on the cathode. The speed of the stirrer is adjusted to obtain the optimum rate of agitation.

Under the conditions of mild agitation effective plating is achieved only on the surface of the cathode which is oriented in the direction of the anode and on the edges of the cathode, the probable reason for the latter being that there is a tendency toward a somewhat higher current density at these locations or points. It is possible however, by increasing the agitation and controlling the circulation of the electrolyte, to effect plating on the back surface of the cathode, namely the surface away from the anode. A more uniform plating of the whole metallic surface of the cathode exposed to the electrolyte may be effected by using a multiplicity of anodes oriented circumferentially with respect to the cathode and/or a rotating cathode, thereby uniformly presenting the entire cathode surface to the anode or anodes.

The following are examples of electrolytes and current densities used by us to obtain good plating with zirconium:

Example 1

With an non-aqueous electrolyte composed of 50 grams of n-butyl alcohol and 2.5 grams of zirconium oxy-chloride a cathode of copper was plated with zirconium utilizing direct current at a current density of approximately 12 milliamperes per square centimeter of cathode surface.

Example 2

190 ml. (154 grams)—Redist. n-butanol
7.6 gm.— $\text{Zr OCl}_2 \cdot 8\text{H}_2\text{O}$
1.0 ml.—Saturated HCl in n-butanol
26 m. a./cm.²

The desired degree of plating was obtained by carrying on the plating operation for from one to two hours.

It is understood that there is a considerable range of current densities which may be used as, for example, from the 12 milliamperes density for Example 1 and below to the 26 milliamperes density of Example 2 and above, and generally the current density should not exceed 100 milliamperes per square centimeter of effective cathode surface. Other things being equal and satisfactory, an increase in current density is accompanied by a decrease in necessary plating time to obtain a given amount of metal.

The drawing illustrates diagrammatically an apparatus which may be used in the zirconium plating process. This apparatus comprises a container 1 containing the non-aqueous solution 2 of the zirconium-containing compound in which are immersed an anode 3 and a cathode 4. These elements 3 and 4 have suitable electrical connections diagrammatically indicated with the positive and negative terminals of the D. C. power circuit. For maintaining the non-aqueous solution 2 at the boiling point the container 1 is immersed in an oil bath 5 which in turn is heated by an electric heater 6, the latter having an electrical terminal connection 7 for connection with a heating power circuit.

It may be desirable to keep the non-aqueous solution 2 in motion by a stirrer indicated at 8, this stirrer being in the form of a propeller blade mounted on a vertical shaft 9 driven by an electric motor 10. For convenience in accommodating the shaft 9 of the motor which extends down into the container 1 there is provided an upwardly extending tubular member 11 through which passes the shaft 9, said tubular member 11 having a vapor-tight bearing 11'. The container 1 is provided with a branch tubular member 12 which is surrounded by a cooling or condenser housing 13 for condensing the vapor rising from the boiling non-aqueous solution for returning the condensate to the container by gravity. The free end of the tubular member 12 is preferably formed into a breather cell 14 containing some suitable moisture absorbing agent 14' as, for example, anhydrous calcium chloride. The cooling or condensing housing is provided with an intake 15 and an outlet 16 for circulating any suitable cooling medium such, for example, as water.

The cathode 4 may be of nickel, iron, tungsten, molybdenum, copper or any metal below hydrogen in the electromotive series, or any alloys of such metals with themselves or other metals and as described above, good zirconium electroplating results were obtained with the use of copper as the cathode.

The anode 3 is preferably one which will not be

dissolved in the process and contaminate the non-aqueous plating solution. Good results have been obtained by the use of anodes of carbon. The anode may be made of platinum, palladium, etc., or zirconium.

This invention may be utilized in the isolation of zirconium or other metals as, for example, by utilizing initially a cathode of the pure metal to be electrolytically reduced and then using the invention to build up the pure metal upon this cathode. The product would be a sample of zirconium or other metal of extreme chemical purity limited only by the contaminants present in the metal-bearing compound and the solvent used.

As described above, particularly good results were obtained by the use of a non-aqueous solution of n-butyl alcohol and zirconium oxy-chloride with the proportions such that the solution is saturated, and with an anode 3 of carbon and a cathode 4 of copper and with direct current densities of 12 and 26 milliamperes per square centimeter of area (one side) of the copper cathode.

Of the other metals than zirconium which may be electroplated on metals in accordance with this invention, may be mentioned titanium, hafnium, tantalum and columbium, all of which have getter functioning qualities. Any suitable compounds of these metals may be utilized as the source of the metal to be electroplated, namely those embodying fluorine, chlorine, bromine, iodine, etc., such for example as the halides of the metals, the oxy-halides of the metals, etc. or the nitrates or oxy-nitrates of these metals. It is understood that certain features of the invention are applicable to the plating of other metals, such as those in the classes of the specifically mentioned getter metals as well as metals in other classes.

Generally speaking, with the procedure described above or one closely analogous to that outlined for zirconium, all metals any of whose halides, oxy-halides, nitrates or oxy-nitrates or any other inorganic or organic compound is sufficiently soluble in an organic solvent, can be electroplated by following this procedure.

Organic solvents specifically useful from the point of view of this procedure are those in which one or more of the metal compounds referred to are sufficiently soluble to make the plating procedure feasible within reasonable limits. By feasible we refer to that set of conditions under which the plating procedure can be carried out on a basis which can be developed for factory use.

It is understood that the invention is not limited to these particular materials used or to the proportions used and that the claims hereto annexed are not to be construed as limited to the particular materials and relative proportions described except as may be rendered necessary by the language of the claims themselves.

We claim:

1. The method of plating metals with zirconium comprising the electrodeposition upon the cathode, of zirconium reduced by electrolysis in a non-aqueous solution of an aliphatic alcohol and an electrolytically reducible chloride of zirconium.

2. The method of plating metals with zirconium comprising the electrodeposition of zirconium upon a conducting cathode in a non-aqueous solution of a mono hydroxy aliphatic alcohol and an electrolytically reducible chloride of zirconium.

3. The method of plating metals with zirconium comprising the electrodeposition of zir-

conium upon a conducting cathode in a non-aqueous solution of butyl alcohol and an electrolytically reducible compound of zirconium.

4. The method of plating metals with zirconium comprising the electrodeposition of zirconium upon a conducting cathode in a non-aqueous saturated solution of butyl alcohol and an electrolytically reducible compound of zirconium while maintaining the non-aqueous solution at boiling temperature.

5. The method of plating metals with zirconium comprising the electrodeposition upon a cathode of zirconium reduced by electrolysis in a non-aqueous solution of zirconium oxy-chloride in an aliphatic alcohol.

6. The method of plating metals with zirconium comprising the electrodeposition upon a cathode of zirconium reduced by electrolysis in a non-aqueous solution of zirconium tetrachloride in an aliphatic alcohol.

7. The method of plating metals with zirconium comprising the electrodeposition upon a cathode of zirconium reduced by electrolysis in a non-aqueous solution of zirconium tetrachloride in an aliphatic alcohol while maintaining the solution at boiling temperature.

8. The method of plating metals with zirconium comprising the electrodeposition upon a cathode of zirconium reduced by electrolysis in a non-aqueous solution of a zirconium compound in n-butyl alcohol.

9. The method of plating metals with zirconium comprising the electrodeposition upon a cathode of zirconium reduced by electrolysis in a non-aqueous solution of zirconium oxy-chloride in n-butyl alcohol.

10. The method of plating metals with zirconium comprising the electrodeposition upon a cathode of zirconium reduced by electrolysis in a non-aqueous mixture of zirconium oxy-chloride and an aliphatic alcohol, the quantity of zirconium oxy-chloride present being sufficient to produce a solution containing a concentration of zirconium oxy-chloride ranging from 1/100 of 1% to 1%.

11. The method of plating metal with zirconium comprising the electrodeposition upon a cathode of zirconium reduced by electrolysis in a non-aqueous mixture of zirconium tetrachloride and an aliphatic alcohol, the mixture containing an aliphatic alcohol and zirconium tetrachloride in the proportion of 1 to 10% by weight of tetrachloride.

12. The method of plating metals with zirconium comprising the electrodeposition upon a cathode of zirconium reduced by electrolysis in a non-aqueous solution of butyl alcohol and electrolytically reducible zirconium oxy-chloride.

13. The method of plating metals with zirconium comprising the electrodeposition upon a cathode of zirconium reduced by electrolysis in a non-aqueous solution of n-butanol and electrolytically reducible zirconium oxy-chloride.

14. The method of plating metals with zirconium comprising the electrodeposition upon a cathode formed of a metal below hydrogen in the electromotive series, of zirconium reduced by electrolysis in a non-aqueous solution of butyl alcohol and electrolytically reducible chloride of zirconium.

15. The method of plating metals with zirconium comprising the electrodeposition upon a cathode formed of a metal below hydrogen in the electromotive series, of zirconium reduced by electrolysis in a non-aqueous solution of butyl

2,510,128

9

alcohol and electrolytically reducible chloride of zirconium, said cathode being formed of copper.

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