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METHOD OF ELECTRODEPOSITING METALS

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The present invention relates to a novel method of electrodepositing metals, including metal alloys; and, more particularly, the invention relates to a novel method of electrodepositing metals, especially relatively low melting metals, which method possesses important advantages over electrodepositing procedures heretofore known. This application is a continuation-in-part of my application, now abandoned, Serial No. 510,537, filed May 23, 1955.

The conventional electrodepositing procedures involve the use of aqueous electrolytes. The limitations of such electrodepositing procedures are well known. For example, using aqueous electrolyte systems at ordinary pressure it is not possible to electrodeposit the metal at temperatures above about 100° C. As will appear hereinafter, there are certain advantages in electrodepositing metals at temperatures substantially above 100° C., especially at temperatures resulting in the electrodeposition of the metal in molten form. In addition, in electrodepositing out of aqueous systems, hydrogen is frequently evolved, especially in electrodepositing metals above hydrogen in the electromotive series. Because of this, low current densities are usually employed, and even with these low current densities, low current efficiencies are sometimes obtained. As a result, electrodeposition is very slow. Likewise, with most of the metals, only relatively thin films can be deposited. In many cases the films are of very poor quality.

In order to avoid the above-discussed limitations of aqueous systems, there have been suggestions concerning the use of molten salt or salt mixtures as the electrolyte solvent. These suggestions have generally dealt with the deposition of certain specific metals, and the salts suggested have included cryolite, sodium chloride, sodium tetraborate, and the like. Even with molten salt systems, difficulties are encountered. For example, the salts and salt mixtures heretofore used or suggested have possessed relatively high melting points necessitating high operating temperatures, and many of them are basic in nature resulting in precipitation of certain metals sought to be deposited therefrom. Operation with many of them has been found to result very shortly in the formation of a crust on the surface of the bath. In addition, the deposits obtained through the use of such suggested fused salt baths have not been as bright as desired.

It is the principal object of the present invention to provide a novel method for electrodepositing metals, including alloys.

It is another object of the present invention to provide a novel method for electrodepositing metals, by which method are obtained important advantages over prior suggested electrodeposition procedures.

Still another object of the present invention is to provide a novel method for electrodepositing metals wherein relatively high current efficiencies are obtained with substantially higher current densities than has been possible in aqueous systems, and wherein deposition takes place at a much faster rate.

A further object of the invention is to provide a novel method for electrodepositing metals employing a fused salt bath system which has a relatively low melting point and which is acid in nature insuring the presence of the metal sought to be deposited as ions therein, wherein

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the resulting deposit is unusually bright and clean, and wherein little or no crust formation takes place.

A further specific object of the invention is to provide a novel method for electrodepositing relatively low melting metals, including relatively low melting metal alloys, in molten form, by which deposition takes place at a very rapid rate and with the formation of very bright deposits.

Other objects, including a novel method for forming small controlled amounts of metals, including metal alloys, involving electrodeposition of the metal at a cathode and recovery of the metal therefrom, will become apparent from a consideration of the following specification and claims.

The method of the present invention comprises electrolyzing, between an anode and a cathode, salt of the desired metal to be deposited in solution in a molten salt bath comprising said salt and other salt at least a substantial proportion of which is a zinc halide, whereby the metal of said metal salt is deposited at the cathode. In one embodiment, the molten salt bath consists essentially of the said metal salt and said zinc halide, and in another embodiment the molten salt bath consists essentially of said metal salt, said zinc halide and an ammonium halide.

Of the halides, the chlorides and bromides are of more general applicability than the iodides and fluorides. And as between the chlorides and bromides, the chlorides are particularly preferred. Hence, the invention will be further described herein with particular emphasis on the use of zinc chloride, as the zinc halide, and of ammonium chloride, as the ammonium halide, although it will be understood that what is said may also be applicable to the other halides.

Zinc chloride itself melts at about 280° C., and zinc chloride itself, in molten form, may serve with the metal salt as the molten salt bath. The equilibrium diagram of binary systems of metal salts and zinc chloride frequently has a eutectic having a melting point lower than that of one or both of the constituents. Hence, depending upon the particular metal salt or salts combined with the zinc chloride, the resulting bath may be operable at temperatures from about 150° C. to 280° C. and above. In the embodiment wherein a mixture of zinc chloride and ammonium chloride is employed with the metal salt, in some cases a ternary eutectic is formed which has a melting point lower than that of any of the possible binary eutectics. The eutectic mixture of about 49 mol percent ammonium chloride and about 51 mol percent zinc chloride has a melting point of 180° C. Hence, depending upon the proportions of zinc chloride and ammonium chloride and upon the particular metal salt or salts and amount thereof employed, the resulting bath may be operable at temperatures of about 150° C. to about 180° C. and above. As will appear hereinafter the bath may be operated at or above the liquidus point for any of the compositions, the composition defined herein being that of the melt itself, any excess, solid, metal salt present, for example, not being considered part of the bath and serving, at most, as a reserve supply of metal salt to replenish that in solution as it is being exhausted.

By the process of the present invention it has been found that a wide variety of metals, including alloys, can be electro-deposited at a relatively rapid rate. This is particularly true of lower melting metals which are deposited in molten form. Electrodeposition of metal in molten form results in a dense, homogeneous, non-porous deposit, as compared to the crystalline, porous, sometimes dendritic, and sometimes poorly adhering deposit produced by plating in solid form out of aqueous systems, which is unaffected by operating conditions, such

as acidity, concentration of metal ions, temperature, current density, and the like. By the present process substantially higher current densities may be employed than is the case with aqueous systems, and even at these higher current densities, much higher current efficiencies are realized. The highest current densities usable, and the highest current efficiencies realized, are in electrodepositing metals in the molten state. The hydrogen overvoltage on molten metals is much higher than on solid metals. Therefore, in electrodepositing molten metals by the present process there is much less tendency to evolve hydrogen, even in the embodiment wherein ammonium chloride is present, than when the metal is deposited in solid form. Even in the electrodeposition of metal in solid form in accordance with the present process, there is much less evolution of hydrogen than in electrodeposition from aqueous systems. In addition, the zinc chloride and the combination of zinc chloride and ammonium chloride, particularly the latter, have been found to act as a flux on the metal being deposited at the cathode, thereby insuring a bright clean deposit, and on the base metal, thereby insuring good wetting and improved adhesion. The quality of deposits formed by the present process has been found to be high, and heavy deposits may readily be built up. In fact, the present invention provides an advantageous method of forming small controlled amounts of metal by electrodepositing it at the cathode in molten form and removing it in, e. g. drops, as it continuously builds up. Moreover, it has been found that the bath employed in accordance with the present process does not readily form objectionable crusts during operation as is the case with prior fused salt baths. In fact when ammonium chloride is present, the bath may operate indefinitely without formation of crust. It is believed that this reduction or elimination of crust formation is due to the acid nature of the bath. When ammonium chloride is present, it serves as a buffer providing a reserve acidity by virtue of the ability of the zinc chloride and ammonium chloride to interact to form zinc chloride amines, which acidity is not destroyed through prolonged operation.

Whether or not ammonium chloride will be included in the bath will be determined largely by the type of metal being deposited, whether an alloy or a single metal is being deposited and the desired stability of the bath with time. Ammonium chloride increases the fluxing power of the bath, increases the solvent power of melt for certain metal salts, aids in lowering the melting point of the bath, buffers the melt and eliminates crust formation. On the other hand, it also introduces instability of the overall bath composition and fuming because of its tendency to sublime. This may cause a shift in the composition of an alloy being deposited. Thus where fuming is particularly objectionable, where bath stability over long periods of time in the deposition of alloys is required and where the zinc chloride alone is entirely satisfactory the advantageous features provided by the ammonium chloride may be sacrificed and that compound eliminated from the bath.

The electrolyte system employed in accordance with the present invention, is a melt solution comprising salt of metal to be deposited and either zinc chloride or a combination of zinc chloride and ammonium chloride.

When both ammonium chloride and zinc chloride are used, the proportion of ammonium chloride to zinc chloride may vary somewhat and advantageous features obtained through the use of ammonium chloride may be realized with as little as about 2 mol percent of ammonium chloride based on the combination of zinc chloride and ammonium chloride. It is found that the optimum proportions from the standpoint of bath operation, nature of deposits, and the like, are those between about 14 mol percent of ammonium chloride up to about 55 mol percent of ammonium chloride, on the same basis. A mixture containing about 14 mol percent of am-

monium chloride and the balance zinc chloride has a melting point of about 250° C. As the proportion of ammonium chloride to zinc chloride increases over this figure, the melting point of the resulting mixture decreases until the eutectic mixture, containing 49 mol percent of ammonium chloride and 51 mol percent of zinc chloride, is reached, having a melting point, as stated, of 180° C. The proportion of ammonium chloride to zinc chloride may be increased somewhat above the eutectic mixture, although proportions of ammonium chloride higher than about 55 mol percent provide mixtures which are not particularly satisfactory for use in the present process. A particularly advantageous combination of zinc chloride and ammonium chloride for use in accordance with the present process is one in the neighborhood of the eutectic referred to above.

In accordance with the present process, the metal which is to be deposited will exist in solution in the melt of itself and molten zinc chloride or zinc chloride-ammonium chloride mixture, in ionic form; that is to say, as a dissolved salt. The dissolved salt may be formed in situ, as by reaction between the elemental metal itself and the molten zinc chloride-ammonium chloride mixture; a salt of the desired metal may be added to and dissolved in molten zinc chloride or mixture of zinc chloride and ammonium chloride, or the various salts in solid form may be mixed together and the mixture heated to form the desired melt.

The amount of depositing metal salt combined with the zinc chloride or zinc chloride-ammonium chloride combination may vary widely depending upon the particular function or functions it must play. Simply as a source of metal ions for deposition, as little as 0.1 mol percent, based on the entire bath, is sufficient where a small amount of metal is to be deposited. The greater the concentration of such metal salt in the bath the greater the amount of metal that can be deposited. The metal salt may also play an important role in lowering or otherwise controlling the melting point of the bath, and for this purpose as high as about 90 mol percent, based on the entire bath, may be used. Generally, however, less than about 70 mol percent of such metal salt is present in the bath. The above figures refer to the total concentration of depositing metal salt in the bath. Thus, in the case of depositing an alloy where two or more different metal salts are employed, one or more of them may be present in a concentration below the lower figure given above.

Of the various metal salts for use as the source of the deposited metal, the halides, especially the chlorides, have been found to be particularly suitable. As stated, metal alloys may be deposited in accordance with the process of the present invention. In this case, a mixture of salts, the cations of which correspond to the metals making up the deposited alloy, will be dissolved in the bath.

A wide variety of metals, including metal alloys, can be deposited by the present procedure, and, in fact, any metal, a salt of which is soluble in molten zinc chloride or in a molten mixture of zinc chloride and ammonium chloride, and which is below zinc in the electromotive series, can be deposited by the present process. Hence, metals such as iron, cadmium, indium, thallium, cobalt, nickel, antimony, bismuth, tin, lead, copper, silver, and gold, as well as alloys of two or more of such metals, may be deposited. As stated, the present process is particularly applicable for the electrodeposition of metals in molten form. Since it is desirable to operate at temperatures below about 400° C., this means that the process is particularly applicable to the electrodeposition of the lower melting metals, operating at temperatures such that the metal is deposited in molten form. In this manner such metals as indium, cadmium, tin, lead, thallium, bismuth, and alloys of two or more such metals, such as cadmium-indium alloys, bismuth alloys, anti-

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many alloys, tin-lead alloys, tin-indium alloys, some silver-indium alloys, some gold-indium alloys, and the like, may readily be electrodeposited in molten form by the present procedure. One of the important features of the present process is the fact that the stated metals can be deposited without the deposition of even traces of zinc.

In connection with certain multi-valent metals, it is desirable and sometimes necessary that the metal be in a lower valent state in the bath. If, for example, the indium is in the trivalent state in the bath comprising zinc chloride and ammonium chloride, it has been found that deposition does not take place. Thus indium must exist in such bath at a valence below three, that is one and/or two, preferably one. The maintenance of the multi-valent metal in a lower valent state will present no problem to those skilled in the art, and any one of several expedients serving to maintain the metal in a reduced ionic state may be employed. For example, the surface of the bath may be covered with a non-oxidizing, that is a neutral or reducing, atmosphere such as carbon dioxide, hydrogen, helium, argon, nitrogen, or the like. The multi-valent metal ions may also be prevented from oxidizing to the highest valent state by maintaining, in the bath, a body of the elemental metal as such.

Reference has been made above to the fact that the electrolyte bath consists essentially of salt of metal to be deposited and zinc chloride, and in some cases also ammonium chloride. It will be understood that this does not exclude the presence or inclusion of small amounts of other salts which do not deleteriously alter the advantageous features of the electrolyte bath. For example, small amounts, usually not over about 1-2 mol percent, of salts other than those of metal being deposited, such as sodium chloride or a fluoride may be included to help reduce the volatility of one or more of the constituents of the bath or to enhance fluxing action in a particular situation.

In practicing the process, the bath will be operated at a temperature at or above its liquidus point which may in certain cases go as low as about 150° C. The exact temperature conditions employed will depend, of course, upon the liquidus point of the bath as well as upon the metal deposited and upon whether the metal is to be deposited in the molten state or in solid form. When the metal is to be deposited in molten form, it is not always necessary that the temperature of the bath be at or above the melting point of the deposited metal. During electrodeposition, heat is evolved at the cathode, and the heat so evolved may be sufficient to maintain the deposited metal at or above its melting point in spite of the fact that the average temperature of the bath as a whole may be slightly below this melting point. Generally, however, when the metal is to be deposited in molten form, the bath is maintained at a temperature of at least, and preferably above, the melting point of the deposited metal.

As is usual in electrodepositing procedures, an anode and a cathode will be provided, each of which is connected to a suitable source of current. The anode may be any conducting material that is not deleterious to the bath at operating temperature. Metal corresponding to that deposited may serve as anode, or a metal or other material which is inert in the bath, such as platinum, tungsten, carbon, or the like, may be selected. The cathode, of course, is the site at which the metal is to be deposited. In general, the cathode may be any conducting material including the metals as well as non-metallic conductors such as carbon.

In carrying out the process, the anode and cathode are immersed in the stated bath, and connected to a suitable source of potential. Completion of the circuit results in electrolysis of the solution of the metal salt in the molten zinc chloride-ammonium chloride mixture with resultant deposition of the desired metal at the cathode.

The present process is, as stated, also applicable for the deposition of relatively heavy deposits of metal as

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contrasted to thin films. For example, the process may be employed in depositing a bead or body of low melting metal solder at the end of a relatively fine, elongated metal article, such as a strip or wire, which is specifically disclosed and claimed in my copending application Serial No. 510,164, filed May 23, 1955, now U. S. Patent No. 2,818,375.

In addition, the process is applicable to the formation of small finite bodies of metal. For example, sufficient metal may be accumulated at the cathode in molten form and removed or permitted to fall away from the cathode onto another surface.

The process of the present invention will be more readily understood from a consideration of the following specific examples which are given for the purpose of illustration only and are not intended to limit the scope of the invention in any way.

Example I

40 grams of a mixture of zinc chloride and ammonium chloride (25%, by weight, of ammonium chloride and 75%, by weight, of zinc chloride) are placed in a vessel and heated until a clear melt is obtained. The melt is then cooled to about 220° C., and 10 grams of indium metal are added thereto. The fused zinc chloride-ammonium chloride mixture slowly dissolves the resulting molten indium metal.

After several hours of heating at 220° C., most but not all, of the indium metal goes into solution in the form of indium monochloride.

With the bath at 220° C., a nickel wire coated with indium metal and having a loop of ½" in diameter at the end thereof is immersed in the bath so that the loop is imbedded in the molten indium metal. The molten indium metal thus serves as anode. The nickel wire is connected to the positive terminal of a direct current power supply.

A small steel strip is immersed in the bath and is connected to the negative terminal of the power supply. The circuit is completed with a potential of 4.5 volts, direct current, being employed.

Within a very short time a deposit of bright, clean molten indium metal forms on the immersed steel strip. Upon removal of the cathode from the bath, the indium solidifies to a bright, smooth coating.

Example II

Following the procedure of Example I, a fine nickel wire 5 mils in diameter is immersed as cathode in the described bath. Within about ½ second, a coating of molten indium 1 mil thick forms at the immersed end of the wire.

Example III

A bath is prepared by mixing and melting 16 grams of zinc chloride and 4 grams of ammonium chloride. The resulting melt is cooled to 240° C., at which time 24 grams of indium monochloride and 4 grams of cadmium chloride are dissolved therein.

Using 6 volts D. C. at 250° C., a carbon anode and a #26 copper wire cathode, a cadmium-indium alloy in molten form is deposited at the cathode.

Example IV

A mixture of 4 parts, by weight, of anhydrous zinc chloride, 6 parts of indium monochloride and 1 part of anhydrous cadmium chloride is heated at 250° C. for one hour under an atmosphere of dry nitrogen.

With the resulting bath at 230° C. in an atmosphere of dry nitrogen, and employing a tungsten wire as anode, a nickel wire cathode, and 6 volts D. C., cadmium-indium alloy of approximately eutectic composition is deposited at the cathode.

Example V

To 10 grams of a molten mixture of zinc chloride and ammonium chloride of the type employed in Example I is added 1 gram of thallous chloride.

With the resulting bath heated at 320° C., a #26 copper wire is immersed therein as cathode, and a 15 mil tungsten wire is immersed as anode. The circuit is completed with a potential of 1.5 volts, direct current, being employed. Molten thallium is deposited at the cathode.

Example VI

To 10 grams of a molten mixture of zinc chloride and ammonium chloride of the type used in Example I is added 1 gram of plumbous chloride.

With the resulting bath heated at 340° C., a #26 copper wire is immersed therein as cathode, and a 15 mil tungsten wire is immersed as anode. The circuit is completed with a potential of 1.5 volts, direct current, being employed. Molten lead is deposited at the cathode.

Example VII

To 10 grams of a molten mixture of zinc chloride and ammonium chloride of the type used in Example I are added 4 grams of anhydrous stannous chloride.

With the resulting bath at 320° C., a #26 copper wire is immersed therein as cathode, and a 15 mil tungsten wire is immersed as anode. The circuit is completed with a potential of 1.5 volts, direct current, being employed. Molten tin is deposited at the cathode.

Example VIII

A mixture of 10 grams of zinc chloride and 10 grams of stannous chloride is prepared and heated to 320° C. With the resulting bath at that temperature, a #26 copper wire is immersed as cathode and a 15 mil tungsten wire is immersed as anode. The circuit is completed using a potential of 1.5 volts, direct current. Molten tin is deposited at the cathode.

Example IX

To 10 grams of a molten mixture of zinc chloride and ammonium chloride of the type used in Example I are added 6 grams of bismuth trichloride.

With the resulting bath at 320° C., a #26 copper wire is immersed as cathode and a 15 mil tungsten wire is immersed as anode. The circuit is completed using 1.5 volts, direct current. Molten bismuth is deposited at the cathode.

Considerable modification is possible in the selection of the metals to be deposited and of the salts thereof employed, as well as in the particular technique followed in carrying out the process of the present invention without departing from the scope thereof.

I claim:

1. The method of electrodepositing indium metal which comprises electrolyzing, between an anode and a cathode, a salt of indium in which the indium is in a valent state below 3 in solution in a molten salt bath consisting essentially of said indium salt and other salt selected from the group consisting of a zinc halide and a combination of a zinc halide and an ammonium halide, whereby indium metal is deposited at the cathode.

2. The method of electrodepositing indium metal which comprises electrolyzing, between an anode and a cathode, a salt of indium in which the indium is in a valent state below 3 in solution in a molten salt bath consisting essentially of said indium salt and zinc chloride, whereby indium metal is deposited at the cathode.

3. The method of claim 2 wherein the bath is at a temperature at which the indium is deposited in molten form.

4. The method of electrodepositing indium metal which comprises electrolyzing, between an anode and a cathode, a salt of indium in which the indium is in a valent state below 3 in a molten salt bath consisting essentially of said indium salt, zinc chloride and ammonium chloride, whereby indium metal is deposited at the cathode.

5. The method of claim 4 wherein the ammonium

chloride is present in an amount between about 2 mol percent and about 55 mol percent based on the combined ammonium chloride and zinc chloride.

6. The method of claim 5 wherein the ammonium chloride is present in an amount of at least about 14 mol percent based on the combined ammonium chloride and zinc chloride.

7. The method of claim 5 wherein the ammonium chloride is present in the neighborhood of about 49 mol percent based on the combined ammonium chloride and zinc chloride.

8. The method of electrodepositing indium metal which comprises electrolyzing, between an anode and a cathode, a salt of indium in which the indium is in a valent state below 3 in solution in a molten salt bath consisting essentially of said indium salt and other salt selected from the group consisting of zinc chloride and a combination of zinc chloride and ammonium chloride at a temperature of at least the melting point of the deposited indium, whereby indium is deposited in molten form at the cathode.

9. The method of electrodepositing indium metal which comprises electrolyzing, between an anode and a cathode, a salt of indium in which the indium is in a valent state below 3 in solution in a molten salt bath consisting essentially of said indium salt, zinc chloride and ammonium chloride at a temperature of at least the melting point of the deposited indium, whereby the indium is deposited in molten form at the cathode.

10. The method of claim 9 wherein the ammonium chloride is present in an amount between about 14 mol percent and about 55 mol percent based on the combined ammonium chloride and zinc chloride.

11. The method of electrodepositing metal which comprises electrolyzing between an anode and a cathode, in a molten salt bath consisting essentially of a salt selected from the group consisting of zinc halide and a combination of zinc halide and ammonium halide, and a salt of metal to be deposited comprising at least in part a salt of indium in which the indium is in a valent state below 3 in solution in said bath, at a temperature of at least the melting point of the deposited metal, whereby a deposit comprising a metal selected from the class consisting of indium and alloys of indium is deposited in molten form at the cathode.

12. The method of claim 11 wherein said salt of metal to be deposited comprises said indium salt and a salt of cadmium, and wherein the salt selected for said salt bath is essentially zinc halide.

13. The method of electrodepositing metal which comprises electrolyzing between an anode and a cathode, in a molten salt bath consisting essentially of a salt selected from the group consisting of zinc chloride and a combination of zinc chloride and ammonium chloride, salt or metal to be deposited comprising indium monochloride and cadmium chloride, at a temperature of at least the melting point of the deposited metal, whereby an alloy of indium and cadmium is deposited in molten form at the cathode.

14. The method of claim 11 wherein the metal deposited is an alloy of indium and cadmium.

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