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METHOD FOR ELECTRODEPOSITING CADMIUM-INDIUM ALLOYS

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The present invention relates to a novel method for electro-depositing a cadmium-indium alloy; and, more particularly, the invention relates to a novel method for electrodepositing a cadmium-indium alloy plating having a controlled uniform composition throughout the electrodepositing operation. The present invention also relates to a novel electroplating bath from which which can be deposited a cadmium-indium alloy with a controlled uniform composition.

In copending application Serial No. 510,536, filed May 23, 1955, is disclosed and claimed the use of a cadmium-indium alloy as solder. In copending application Serial No. 510,164, filed May 23, 1955, is disclosed and claimed a novel method for forming and attaching a body of solder, including the stated cadmium-indium alloy, at the end of a relatively fine, elongated metal member, such as a wire or strip. In each of these applications it is pointed out that the cadmium-indium alloy solder may be formed in situ by electrodepositing the cadmium-indium alloy, in molten form, from a bath comprising both cadmium and indium in the form of ions.

The cadmium-indium may contain as low as about 40% and as high as about 85%, by weight, of indium, with the preferred alloys having a composition of between about 60 and about 80%, by weight, of indium. A particularly suitable cadmium-indium alloy is the eutectic containing about 75%, by weight, of indium.

The electrodepositing of a cadmium-indium alloy having a uniform composition presents problems. For example, from a bath containing both indium and cadmium ions under normal conditions, the electrodepositation of cadmium, on a weight basis, is favored, resulting, over a period of time, in a deposit having a widely varying composition. Attempts to overcome this, by increasing the proportion of indium in the bath, leads to erratic results.

It is particularly desirable to have the proportion of the indium to the cadmium in the bath the same as those desired in the deposit so that there is no non-uniform depletion of the bath. However, for the reasons stated above, in conventional baths this is impossible.

It is the principal object of the present invention to provide a novel method for electrodepositing a cadmium-indium alloy having a controlled uniform composition.

Another object of the present invention is to provide a novel method for electrodepositing a cadmium-indium alloy having a controlled uniform composition from a bath in which the proportions of cadmium to indium are the same as those in the resulting deposit.

Other objects, including the provision of a novel bath whereby the foregoing objects may be realized, will be apparent from a consideration of the following specification and the claims.

In accordance with the process of the present invention, the indium-cadmium alloy is electrodeposited out of a bath maintained at an elevated temperature and comprising an acidic solution of indium and cadmium salts in a polar organic liquid boiling above the temperature of operation and having dissolved therein a poly-basic acid

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compound forming soluble complexes with indium and cadmium in the solution, especially those selected from the group consisting of ethylene diamine tetraacetic acid, citric acid and tartaric acid. In the bath the proportion of indium to cadmium will be the same as that desired in the resulting deposit. As is usual in electrodepositing operations, an anode and a cathode will be provided, the indium-cadmium alloy depositing at the cathode, and the circuit will be completed for electrodepositation to take place.

The method comprises, therefore, electrolyzing, between an anode and a cathode and at an elevated temperature, an acidic solution of salts of cadmium and indium in a polar organic solvent the proportion of cadmium to indium in said solution being substantially the same as that of the alloy deposited, and said solution having dissolved therein a polybasic acid forming soluble complexes with said indium and cadmium in solution.

By the process of the present invention it is possible to form by electrodepositation an alloy of indium and cadmium having a controlled uniform proportion throughout the entire deposition procedure. Moreover, this electrodepositation takes place out of a bath in which the proportion of indium to cadmium is the same as that in the resulting deposit so that a fixed bath composition, with respect to proportion of indium ions to cadmium ions throughout the electrodepositing procedure, is insured. Although indium is reported to be the more noble metal as between indium and cadmium in aqueous systems, and should therefore tend to plate out first from a bath of inorganic salts of both indium and cadmium, it has been found that in polar organic solvent systems, the electrode potentials are sufficiently close together that both metals plate out at the same time under ordinary conditions. In glycols, for example, glycerol or ethylene glycol, deposition of cadmium, on a weight basis, is favored. The improved results obtained as the result of the present process, however, wherein the indium and the cadmium are deposited in a fixed and controlled proportion, the same as that existing between the cadmium and indium in the plating bath, is believed to be due to a combination of factors. In the first place, it is believed that, in the present bath, deposition of indium relative to cadmium is favored by virtue of a stronger complexing of the cadmium as compared to the indium so that, in effect, the concentration of cadmium ions is lowered relatively more than the indium ions. In addition, the acidity of the bath, coupled with the relatively high operating temperatures permitted through the use of the high boiling polar organic solvent, also play a part and are believed to favor deposition of the indium. At any rate, in accordance with the present invention, a bath can be prepared comprising indium and cadmium in any desired ratio to provide an alloy having the desired composition corresponding to the ratio of indium to cadmium in the bath, and the alloy is deposited, in accordance with the present process, with a uniform composition throughout the deposition operation regardless of the extent of depletion of the metal ions. In addition, the presence of the polybasic acid compound renders less critical fluctuation in operating conditions such as temperature and current density.

The bath during operation will comprise a solvent which, at the temperature of operation, is a liquid having a boiling point above the temperature of operation, and in which ionic conduction occurs. Any high boiling polar organic compound meeting these requirements, and in which the components of the bath are soluble at the temperature of operation, may be employed. Examples of polar organic compounds that may be employed are the polyhydric alcohols, such as glycerol; the glycols, for instance ethylene glycol, propylene glycol, and the like;

the polyethylene glycols, like diethylene glycol; 1,2,4-butanetriol, and the like; glycol derivatives, such as ethylene glycol monobutyl ether, and the like; high boiling amines, such as triethanolamine, N,N,N',N'-tetrakis (2-hydroxy propyl) ethylene diamine, and the like; amides, such as acetamide; hydroxy aromatic compounds, such as phenol; phthalic anhydride; benzoic acid; and the like. As is the case with certain of the materials mentioned above, the organic material may be solid at ordinary temperatures. Of the organic materials mentioned, the polyhydric alcohols, particularly glycerol, are preferred.

In preparing the bath for operation, salts of cadmium and indium will be dissolved in the organic solvent. In this connection, the halides have been found to be particularly suitable, especially the bromides and chlorides. Cadmium chloride and indium trichloride are the preferred salts. Since it is desirable to maintain anhydrous conditions in the bath, anhydrous salts are preferably employed.

There is also included in the bath, as stated, a compound forming a soluble complex with the indium and cadmium in solution. Examples of such compounds are polybasic acids, especially the polybasic acids selected from the group consisting of ethylene diamine tetraacetic acid, citric acid and tartaric acid. The free acid itself may be added to the bath or salts thereof may be added. If the polybasic acid compound is added in the form of a salt, the acidity of the bath may be adjusted so that the polybasic acid will exist in acid form therein. Of the polybasic acids, ethylene diamine tetraacetic acid is highly preferred.

Referring to the acidity of the bath, if the polybasic acid itself is added to the bath, this material, along with the indium and cadmium salts, may provide the requisite acidity. However, if it is necessary to adjust the acidity of the bath, any conventional acid or acid salt, for example ammonium chloride, may be added. In general, the acidity of the bath should be such that a sample thereof diluted ten times with water should provide a pH of below about 5, preferably below about 4.

In the preferred embodiment of the present invention ammonium chloride will be included in the bath. This material increases the conductivity of the bath, acts as a buffer and exerts a fluxing action causing the deposited molten metal to have a high surface tension.

Referring specifically to the cadmium-indium alloy, a combination of 25%, by weight, cadmium and 75% indium forms a eutectic having a melting point of 122.5° C. Alloys with a solidus point as low as this temperature can readily be prepared with widely varying proportions of indium and cadmium. Cadmium-indium alloys containing up to 82% indium, by weight, form the eutectic, and thus have a solidus temperature of 122.5° C. Cadmium-indium alloys containing more than 82% indium form solid solutions having progressively higher melting points, and alloys containing above about 85% indium have melting points so high, and such increase in softness, as to offer little advantage over indium alone. In cadmium-indium alloys containing less than about 75% indium, the cadmium is in suspension in the molten eutectic mixture. Alloys prepared in accordance with the process of the present invention may contain as low as about 40% indium, by weight. The cadmium-indium alloys containing between about 60 and about 80% indium, by weight, are particularly suitable, especially as solders, and constitute the preferred alloy prepared by electrodeposition in accordance with the present invention. The present process is particularly suitable for electrodepositing the cadmium-indium eutectic. Hence, in the bath, the proportion of indium to cadmium therein will be adjusted to that ratio corresponding to the desired alloy composition within these ranges.

The actual concentrations of the components of the bath may vary widely. So far as the cadmium and

indium salts are concerned, the total concentration thereof may range from as low as about .05 mol per liter, up to the saturation point at the temperature of operation in the particular solvent selected. Preferably the concentration of indium and cadmium salts is at least about .4 mol per liter. The amount of polybasic acid employed will be at least sufficient to complex substantially the indium and cadmium ions in the bath. The complexing equivalents of the various polybasic complexing acids mentioned above with respect to various metal ions are known. For example, one mol of ethylene diamine tetraacetic acid will complex one mol of cadmium or of indium. Preferably, at least 20% excess of polybasic acid over that theoretically required is employed. No advantage is gained by employing over about 100% excess of polybasic acid. The concentration of the polybasic acid in the bath may thus vary widely depending upon the concentration of indium and cadmium therein, and upon the polybasic acid selected. Thus, with ethylene diamine tetraacetic acid, the concentration thereof may be as low as about .05-.06 mol per liter, preferably at least about .4-.5 mol per liter. When ammonium chloride is included in the bath in accordance with the preferred embodiment to increase its conductivity, the increase in conductivity is directly proportional to the amount of ammonium chloride added. To obtain a reasonable conductivity, the ammonium chloride will be employed in a concentration of at least about .5 mol per liter, preferably at least about 1 mol per liter.

The electrodeposition may be conducted at such a temperature that the cadmium and indium are electrodeposited as an intimate alloy mixture in solid form at the cathode. In this case the temperature of the bath may be substantially below the melting point of the alloy, even as low as about 100° C. However, the process is particularly suitable for depositing the cadmium-indium mixture in molten form. In this case the temperature of the bath will be sufficiently high to insure deposition of molten metal. During electrodeposition heat is evolved at the cathode and the heat so evolved may be sufficient to maintain the temperature of the metal being deposited at or above its melting point so that it will be deposited in molten form even when the average temperature of the bath is slightly below the melting point of the alloy. In most cases, however, the temperature of the bath will be maintained at least at the melting point of the cadmium-indium alloy and preferably above it. Since the eutectic has a melting point of 122.5° C. and since alloys having a solidus point as low as this temperature can readily be prepared, it will be seen that the bath is preferably operated at at least that temperature. The maximum temperature at which the bath is operated is dictated primarily by the nature, e. g. boiling point, decomposition temperature, and the like, of the organic solvent material employed, although no advantage is to be gained by operating at temperatures exceeding about 160° C. A particularly advantageous temperature range for electrodeposition is between about 130 and about 150° C.

As is usual in electrodeposition operations, an anode and a cathode are provided. A wide variety of materials may be employed as anode, such as carbon, tungsten, stainless steel, platinum, and the like. The cathode, of course, will be the metal surface onto which it is desired to electrodeposit the cadmium-indium alloy, and may be iron, steel, nickel, platinum, silver, gold, copper, and the like.

With the bath at operating temperature and the anode and cathode connected to a suitable source of current, the circuit is completed. The desired cadmium-indium alloy begins to deposit at the cathode. If the temperature of the bath is sufficiently high, the alloy deposits in molten form, so that, upon removal of the plated cathode from the bath, the deposit rapidly solidifies to a dense, homogeneous, alloy plating. If the temperature of the bath

is such that the metals deposit in solid form the deposit can subsequently be melted, if desired, to provide a more homogenous product.

The present method 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

A bath is prepared by dissolving 10 grams of ammonium chloride, 4.1 grams of cadmium chloride (anhydrous) and 14.5 grams of indium trichloride (anhydrous) in 100 grams of glycerin. The bath is heated to 140° C., after which 35 grams of ethylene diamine tetraacetic acid are dissolved therein. A carbon rod is provided as anode, and a piece of steel sheet is immersed as cathode, the anode and cathode being connected to a suitable source of current. A voltage of 15 volts is employed. Within a short time a plate of a molten eutectic alloy of cadmium and indium (75% by weight indium) forms on the surface of the steel sheet.

Example II

A bath is prepared as in Example I, using, however, 18 grams of tartaric acid in place of the 35 grams of ethylene diamine tetraacetic acid. The procedure of Example I is followed providing a deposit of indium-cadmium alloy having a constant, uniform composition at the eutectic.

Example III

A bath is prepared as in Example I using, however, 15 grams of citric acid in place of the 35 grams of ethylene diamine tetraacetic acid. The procedure of Example I is followed providing a deposit of indium-cadmium alloy having a constant, uniform composition at the eutectic.

Example IV

A bath is prepared by dissolving 5 grams of ammonium chloride, 4.1 grams of cadmium chloride (anhydrous) and 14.5 grams of indium trichloride (anhydrous) and 100 grams propylene glycol (1,2-). The bath is heated to 140° C., after which 30 grams of ethylene diamine tetraacetic acid are dissolved therein. The procedure of Example I is then followed, providing a deposit of indium-cadmium alloy having a constant, uniform composition at the eutectic.

Example V

A bath is prepared as in Example I using, however, 100 grams of ethylene glycol as solvent in place of the glycerin. The procedure of Example I is followed providing a deposit of indium-cadmium alloy having a constant, uniform composition at the eutectic.

Considerable modification is possible in the selection of the various ingredients of the bath and in the amounts thereof as well as in the exact techniques employed in practicing the present invention without departing from the scope thereof.

We claim:

1. The method of electrodepositing a molten cadmium-indium alloy having a controlled uniform composition which comprises electrolyzing, between an anode and a cathode and at a temperature at the cathode of at least the melting point of the alloy, an acidic solution of salts of cadmium and indium in a polar organic solvent therefor in which ionic conduction occurs and having a boiling point above the temperature of operation, the proportion of cadmium to indium in said solution being substantially the same as that of the alloy deposited, and said

solution having dissolved therein a polybasic acid forming soluble complexes with said indium and cadmium in solution in an amount at least sufficient to complex substantially all of the indium and cadmium ions in the solution, whereby a cadmium-indium alloy having a uniform composition is deposited in molten form at the cathode.

2. The method of claim 1 wherein said polybasic acid is selected from the group consisting of ethylene diamine tetraacetic acid, citric acid and tartaric acid.

3. The method of claim 2 wherein said polybasic acid comprises ethylene diamine tetraacetic acid.

4. The method of electrodepositing a molten cadmium-indium alloy having a controlled uniform composition which comprises electrolyzing, between an anode and a cathode and at a temperature at the cathode of at least the melting point of the alloy, an acidic solution of salts of cadmium and indium in a polyhydric alcohol solvent therefor in which ionic conduction occurs, and having a boiling point above the temperature of operation, the proportion of cadmium to indium in said solution being substantially the same as that of the alloy deposited, and said solution having dissolved therein a polybasic acid forming soluble complexes with said indium and cadmium in solution selected from the group consisting of ethylenediaminetetraacetic acid, citric acid and tartaric acid in an amount at least sufficient to complex substantially all of the indium and cadmium ions in the solution, whereby a cadmium-indium alloy having a uniform composition is deposited in molten form at the cathode.

5. The method of claim 4 wherein the temperature of the solution is maintained between about 122.5 and about 160° C.

6. The method of claim 5 wherein the temperature of the bath is maintained between about 130 and about 150° C.

7. The method of electrodepositing a molten cadmium-indium alloy having a controlled uniform composition between about 40% and about 85% indium which comprises electrolyzing, between an anode and a cathode and at a temperature at the cathode of at least the melting point of the alloy, an acidic solution of salts of cadmium and indium in a polar organic solvent therefor in which ionic conduction occurs and having a boiling point above the temperature of operation, the proportion of cadmium to indium in said solution being between about 40 and about 85 parts of the latter to between about 60 and about 15 parts of the former, said solution having dissolved therein a polybasic acid forming soluble complexes with said indium and cadmium in solution in an amount at least sufficient to complex substantially all of the indium and cadmium ions in the solution.

8. The method of claim 7 wherein the proportion of cadmium to indium in said solution is between about 60 and about 80 parts of the latter to between about 40 and about 20 parts of the former.

9. The method of claim 8 wherein the proportion of cadmium to indium in said solution is about 25 parts of cadmium to about 75 parts of indium.

10. The method of claim 7 wherein the solution also comprises ammonium chloride dissolved therein.

11. The method of claim 7 wherein said polar organic solvent is a polyhydric alcohol.

12. The method of claim 11 wherein said polyhydric alcohol is glycerol, and wherein said polybasic acid is ethylene diamine tetraacetic acid.

References Cited in the file of this patent

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