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METHOD OF ELECTRODEPOSITING METALS

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This present invention relates to a novel method for electrodepositing low melting metals onto readily-oxidized, difficultly-soldered metals, especially aluminum, titanium and magnesium; and, more particularly, the invention relates to a novel method for "tinning" the surfaces of metals ordinarily difficult to solder preparatory to soldering to such surfaces.

Soldering to aluminum, titanium or magnesium surfaces is, as is well known, very difficult. Because there is presently no flux capable of effectively removing the oxide film from these metal surfaces at ordinary soldering temperatures, such oxide film has, in the past, been mechanically scraped from the surface in preparation for the soldering operation. This is not only difficult generally, but becomes almost impossible with complex or very fine articles. Attempts to "tin" the stated metal surface with another, more readily solderable metal, by conventional means have failed in the past. Thus, attempts to coat the surface of the difficultly-soldered metal by immersing the article in a molten bath of the metal covered by a suitable flux resulted in coatings the thickness of which cannot be controlled. Moreover, the nature of the surfaces of aluminum, titanium and magnesium renders it difficult to wet them by molten metal simply by immersing the article in the molten metal.

A significant advance in this regard forms the subject matter of copending application Serial No. 572,827, filed March 21, 1956, wherein is disclosed and claimed the chemical plating of lower melting metals, in molten form upon certain metal surfaces including aluminum, magnesium and titanium.

What has been said above applies also to germanium, silicon, hafnium, beryllium and zirconium, although the problem is not as common with these metals as aluminum, magnesium and titanium.

It is the principal object of the present invention to provide a method for coating difficultly-solderable metals, principally aluminum, titanium and magnesium, with a lower melting metal.

Another object of the present invention is to provide a method for electrodepositing a low melting metal onto the surface of readily-oxidized, difficultly-soldered metals, such as aluminum, titanium and magnesium, whereby smooth, dense, homogeneous coatings are provided.

A further object of the present invention is to provide a novel method for "tinning" the surfaces of readily-oxidized, difficultly-soldered metals preparatory to soldering to such surfaces.

Other objects will become apparent from a consideration of the following specification and the claims.

The method of the present invention comprises immersing the readily-oxidized, difficultly-soldered metal to be coated as an electrode in a molten salt bath comprising ions of metal having a melting point below that of the metal to be coated, iodide ions and fluoride ions at a temperature above the melting point of the lower-melting metal but substantially below the melting point of the base metal to be coated, providing another electrode, com-

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pleting the circuit with the base metal to be coated as anode whereby the metal to be coated is electrolytically etched and oxide on the surface thereof is removed, then reversing the current with the metal to be coated as cathode whereby the lower melting metal deposits thereon in molten form, until the desired amount of the lower-melting metal has been so deposited.

The method of the present invention is particularly applicable to the coating, by electrodeposition, of metals whose oxides are not soluble in the conventional acid type fluxes and which, therefore, present particular difficulty in soldering. Such metals include aluminum, titanium, magnesium, germanium, silicon, hafnium, beryllium and zirconium. Of these, aluminum, magnesium and titanium, especially aluminum, are the most common metals and will be the metals most generally treated in accordance with the present process. The process is broadly applicable in providing a coating on the stated metals of lower melting metals, and such coatings may be deposited on the base metal for a wide variety of purposes. One of the present principal uses for the present method is as a "tinning" operation preparatory to the soldering of another metal article to the treated base metal. The deposited, lower-melting metal adheres readily to the base since the initial step of the process rapidly and completely removes the oxide film on the surface of the base metal and, due to the nature of the bath, there is no opportunity for an oxide film to reform by the time electrodeposition takes place.

The metal electrodeposited in accordance with the present process will have a melting point substantially lower, generally at least 100° C. lower, than that of the particular base metal. Generally the metal deposited will have a melting point between about 100° C. and about 450° C. Examples of the lower melting metals which are particularly suitable, are indium, tin, lead, zinc, cadmium, bismuth, thallium, alloys of two or more of these metals, such as tin-lead alloys (the eutectic of which melts at 180° C.), indium-cadmium alloys (the eutectic of which melts at 122.5° C.), tin-indium alloys (the eutectic of which melts at 117° C.) and the like. The composition of alloys may vary widely from those containing substantial proportions of each constituent to those containing only a minute proportion, such as about 0.1%, by weight, of one constituent. From the standpoint of "tinning," indium, tin, lead, zinc, cadmium and the stated alloys are particularly advantageous, and of these, indium is preferred.

The treatment of the present invention takes place in a molten salt bath comprising ions of the lower-melting metal to be deposited, iodide ions and fluoride ions. Referring to the ions of the metal to be deposited, these may be provided by a salt of the metal. Of the metal salts, the halides, that is, the chlorides, iodides, bromides, and fluorides, are particularly advantageous. Examples of other salts that may be used are the borates and phosphates. In the case of the multivalent metals, such as indium, lead and tin, it is preferred, in systems containing ammonium or hydrogen ions, that the metal ions be in a lower valent state in the bath. In addition, plumbic and stannic salts are more volatile, at the operating temperature, than the corresponding plumbous or stannous salts. Hence, stannous salts are generally preferred over stannic salts, plumbous salts are generally preferred over plumbic salts, and indium mono-salts, like indium monochloride, are generally preferred over indium di-salts, like indium dichloride, the latter being generally preferred over indium tri-salts, like indium trichloride. When an alloy is to be deposited, a combination of salts, the cations of which are the constituents of the alloy it is desired to plate, is employed. In this case, the proportion of metal salts is selected to provide, under the conditions of op-

eration, principally current density and temperature, deposition of a mixture of metals in molten form forming the desired alloy.

The fluoride ions in the molten salt bath serve as etchant for the removal of the oxide from the base metal during the etching and oxide-removal portion of the process. These ions may be provided in whole or in part through the use of a fluoride, having a cation other than metal to be deposited, especially an ammonium or an alkali metal fluoride, such as sodium fluoride, or may be provided in whole or in part by a fluoride of the lower-melting metal to be deposited. The fluoride ions promote etching by the formation of stable complex metal fluoride ions, for example, in the case of aluminum, by the formation of AlF_6^{3-} ions. The term "fluoride" as used herein includes acid fluorides, such as sodium bifluoride.

The iodide ions present in the bath prevent reformation of the oxide film. These ions may be provided through the use of an iodide having a cation other than metal to be deposited, especially an ammonium or an alkali metal iodide, such as sodium iodide, or may be provided in whole or in part through the use of an iodide of the lower-melting metal to be deposited.

It will be seen from the foregoing that the bath may comprise an iodide and a fluoride of the lower-melting metal to be deposited. The bath may consist entirely of a combination of such salts to provide the necessary constituents, or some or all of the lower-melting metal may be provided by another salt, such as the chloride or bromide, and some or all of the iodide and/or fluoride ions may be provided by salts other than the iodide and/or fluoride of the lower-melting metal to be deposited.

In addition, there may be present in the bath another salt or salts, serving principally as diluent or solvent. In this case, such salts may be metal salts, the metal of which is sufficiently less noble than the metal being deposited, that under the conditions of operation it will not become deposited, or may be an ammonium salt, or a mixture of such metal salt and ammonium salt. Examples of such diluent or solvent salts are the alkali metal borates, chlorides, and bromides, ammonium borate, ammonium chloride, and, in some cases, zinc salts, like zinc chloride, and the like.

Referring to the amount of ions of the lower-melting metal in the bath, the concentration thereof may vary widely. When the bath is made up essentially of salt, including fluoride and an iodide, of the lower-melting metal to be deposited, such metal ions make up 100 atomic percent of the cations of the bath. On the other hand, where other salts are employed, such as other fluorides and/or iodides and other diluent or solvent salts, and there is no danger of the cation of any of these salts plating out, the concentration of the lower-melting metal to be deposited may be as low as about 0.2 atomic percent of the cations of the bath. In general, the higher the concentration of ions of the lower-melting metal in the bath, the less voltage required to deposit the metal and the less danger of evolving hydrogen from systems containing ammonium or hydrogen ions during the electrodeposition stage of the process. The concentration of such metal ions may also depend upon other materials present in the bath. For example, when a zinc salt is present in a bath as a diluent or solvent and it is desired to deposit another metal more noble than zinc, such as indium, it is desirable to have sufficient ions of the metal to be deposited, such as at least about 2 atomic percent of the cations, to insure against the plating out of zinc.

The concentration of iodide ions in the bath may vary widely, and may range from about 0.2 up to about 99.5 atomic percent of the anions of the bath. The concentration of fluoride ions in the bath may also vary widely, and may range from about 0.5 up to about 99.8 atomic percent of the anions of the bath. The iodide and fluoride have a bearing on the melting point of the bath so

that the amount of iodide and fluoride salts selected, relative to the other constituents, may depend upon the particular melting point desired for the bath.

During the present process, the temperature of the bath will, of course, be such to maintain all the materials of the bath in molten condition, and will be above the melting point of the lower-melting metal to be deposited. In addition, the temperature of the bath will be substantially below, that is to say at least about 100°C . below, the melting point of the base metal onto which the lower-melting metal is deposited. Other considerations may determine the exact temperature of the bath. For example, the higher the temperature the more vigorous the etching during the oxide-removal portion of the treatment, and the higher the conductance of the bath. However, fuming also increases with increased temperature as it approaches the boiling or sublimation point of the salt or salts employed. Hence, the operating temperature selected may be a compromise between these factors. In addition, it may be desirable to dissolve a small portion of the base metal in the molten metal deposit, for example, to increase wettability. Since the solubility of the base metal in the molten metal deposit is a function of the temperature of the molten deposited metal, this may be considered in selecting an operating temperature. In practice, the temperature of the bath is maintained somewhat above, generally at least 10°C . above, the solidification point of any part of the bath including the lower melting metal, that is to say above the melting point of the lower melting metal or the liquidus point of the bath, whichever is higher, since the immersion of the cold base metal article may cause local chilling. For most purposes the temperature of the bath will generally be at least about 180°C ., preferably at least about 200°C ., and may go as high as about 500°C ., especially when aluminum is being coated, and even as high as about 1000°C ., particularly when titanium is being coated.

The current density during the process may vary widely. During the etching stage it will depend upon the nature of the base metal article, including the degree of oxidation of the surface thereof and whether or not it is smooth or rough, and upon the results desired during etching, e. g. whether only a light etch, a heavy etch or electropolishing is required. During the plating stage, the current density employed will depend upon the nobility of the lower-melting metal being deposited. In any event during etching and plating the voltage employed will be above the decomposition potential of the system during etching or plating which can readily be determined for any of the systems employed in accordance with the present invention. There is no definite critical upper limit of voltage, although in a particular system the heat generated or, in the deposition of an alloy, the well known favoring of deposition of the less noble metal with increasing current may impose limitations on the maximum amount of current employed.

The present procedure is a stage-wise electro-etching and electrodepositing procedure. In practicing the process, the metal to be coated is immersed in the defined molten salt bath and is connected, in an electrical system, to another electrode which is also immersed in the bath. The other electrode may be inert in the bath, and carbon is an example of a suitable material for this purpose. The other electrode may also be a metal corresponding to that deposited. In this case the electrode is actually in molten form, and a conducting wire, suitably insulated from the bath, such as a nickel wire in a glass sleeve, may be used to make contact with the pool of molten metal. The first portion of the procedure involves etching of the base metal and the removal of oxide therefrom, and, hence, the base metal to be coated, during this stage, serves as the anode in the system. Upon the completion of the circuit, the base metal to be coated serving as anode, the stated base metal becomes etched, the oxide loosening and falling away therefrom and dissolving in

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the bath. This treatment is continued until the base metal to be coated is clean and the surface is free of oxide. The flow of current is then reversed so that the base metal to be coated becomes the cathode in the system. When this is done, the lower-melting metal ions in solution in the bath plate out upon the base metal forming a coating of molten metal thereon. When a coating of the desired thickness has been built up, the coated article is removed from the bath, and, upon cooling, the molten coating solidifies.

The resulting product, therefore, comprises the stated base metal having thereover a smooth, uniform coating of the lower-melting metal. The deposited metal adheres tenaciously to the base metal inasmuch as the oxide film originally on the surface of the base metal has been completely removed, and the lower-melting metal in molten form readily wets the oxide-free surface. The coated metal article is ideally suited for direct soldering, the coating serving as the "tinning" through which other metal articles may be soldered by conventional means using conventional rosin or "acid" type fluxes to the tinned base metal article.

The present process 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 mixture containing 15 parts of anhydrous zinc chloride, 5 parts of ammonium chloride, 4 parts of indium monochloride, 8 parts of ammonium bifluoride and 2 parts of sodium iodide (all by weight) is heated and maintained at a temperature of about 200° C. forming a clear melt. Aluminum wire (#20) is immersed in the bath and a carbon rod (about 1/8" in diameter) is also immersed in the bath as an electrode. The carbon rod and the aluminum wire are connected electrically, the aluminum wire to serve initially as the anode in the system. Within about 20-30 seconds after the completion of the circuit, 6 volts direct current being employed, the aluminum is etched and the oxide film thereon is removed. The current is then reversed making the aluminum the cathode in the system for about 30 seconds and molten indium metal deposits thereon. The molten indium metal readily wets and coats the aluminum. Upon removal of the indium-coated aluminum from the bath, the indium metal solidifies, forming a smooth, uniform coating. A wire can readily be soldered to the indium-coated aluminum using conventional soldering procedures and conventional rosin or "acid" type fluxes.

In place of aluminum, magnesium or titanium can be used and coated in the same manner.

Example II

A mixture containing 15 grams of the lithium chloride-potassium chloride eutectic (5:6 parts, by weight), 1 gram of indium trichloride, 0.5 gram of sodium fluoride and 0.2 gram of sodium iodide is heated and maintained at a temperature of 430° C. A #20 aluminum wire and a carbon rod (1/8" in diameter) are immersed in the bath as electrodes. The carbon rod and aluminum wire are connected electrically, the aluminum wire to serve initially as anode in the system. Within about 2-5 seconds after the completion of the circuit, 6 volts direct current being employed, the aluminum is etched and oxide film removed. The current is then reversed making the aluminum wire the cathode in the system, and after about 5-10 seconds a coating of molten indium is formed thereon. Upon removal of the indium-coated wire from the bath, the indium solidifies forming a smooth, uniform coating.

In place of the aluminum, magnesium or titanium can be used and coated in the same manner.

Example III

In this example the bath of Example II is employed, 75

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except that 0.2 gram of sodium fluoride is used instead of 0.5 gram, and the bath is maintained at 430° C. A 1/8" carbon rod is immersed in the bath, and a strip of germanium (3 ohm-cm. n-type) about 1 inch long, 60 mils wide and 10 mils thick is also immersed to a depth of about 250 mils. The carbon rod and germanium strip are connected electrically, the germanium serving initially as the anode. Within about 20 seconds after the completion of the circuit, 6 volts direct current being employed, the germanium is etched and oxide is removed. The current is then reversed making the germanium the cathode in the system. After about 15 seconds, a coating of molten indium forms on the submerged germanium, which solidifies to a smooth, uniform coating upon removal of the germanium strip from the bath.

Example IV

A mixture of 20 grams of stannous chloride, 1 gram of ammonium fluoride and 1 gram of ammonium iodide is heated and maintained at 310° C. A small amount of tin is added to the bath, forming a molten globule in the body thereof, and the end of a nickel wire shielded from the bath by a glass sleeve is immersed in the molten tin. The molten tin serves as an electrode. A germanium strip of the same type and size as employed in Example III is also immersed in the bath. The nickel wire leading to the molten tin and the germanium strip are electrically connected, the germanium to serve initially as anode in the system. Within about 10 seconds after the completion of the circuit, 12 volts D. C. being used during this stage, the germanium is etched and oxide removed. The current is then reversed, with 6 volts D. C. being used during the plating stage, and within about 60 seconds a coating of molten tin is formed on the submerged germanium. This tin solidifies to a smooth, uniform coating upon removal of the strip from the bath.

Example V

In this example the bath and procedure of Example IV is used except that a strip of silicon (4 ohm cm. n-type) 3/4" long, 80 mils wide and 20 mils thick is immersed to a depth of about 250 mils in the bath in place of the germanium. A tin coated silicon strip is prepared.

Example VI

A mixture of 15 grams of the lithium chloride-potassium chloride eutectic, 1 gram of sodium fluoride, 1 gram of indium trichloride and 0.5 gram of sodium iodide is heated and maintained at 520° C. The electrodes employed are the same as in Example III. Six volts direct current is employed for etching and plating, the etching time is 10-15 seconds and the plating time is 30 seconds. An indium-coated germanium strip is prepared.

Example VII

A mixture of 20 grams of anhydrous zinc chloride, 30 grams of indium monochloride, 5 grams of cadmium chloride, 1.5 grams of sodium iodide and 1 gram of sodium fluoride is heated and maintained at 320° C. A 1/8" carbon rod and a #20 aluminum wire are used as electrodes. Six volts direct current are used during etching and five volts during plating. The etching time is about 5 seconds, and the plating time is about 5 seconds. The aluminum wire is provided with a smooth uniform coating of indium-cadmium alloy.

Considerable modification is possible in the selection of plating metal and base as well as in the particular techniques employed without departing from the scope of the invention.

I claim:

1. The method of electroplating readily-oxidized, difficultly-soldered base metals which comprises immersing said base metal as an electrode in a molten salt bath comprising ions of metal having a melting point below the base metal, said metal ions being in a concentration of at least 0.2 atomic percent of the cations, iodide ions in a

concentration of at least 0.2 atomic percent of the anions, and fluoride ions in a concentration of at least 0.5 atomic percent of the anions, at a temperature above the melting point of the lower-melting metal but below the melting point of the base metal, providing another electrode, completing the circuit with the base metal as anode whereby the base metal is etched and oxide on the surface thereof is removed, reversing the current with the base metal as cathode in said molten salt bath whereby the lower-melting metal deposits thereon in molten form until the desired amount of lower-melting metal has been so deposited.

2. The method of claim 1 wherein the base metal is selected from the group consisting of aluminum, titanium, magnesium, germanium, silicon, hafnium, beryllium and zirconium.

3. The method of claim 1 wherein the lower-melting metal is selected from the group consisting of indium, tin, lead, zinc, cadmium, bismuth, thallium and alloys thereof.

4. The method of claim 2 wherein the lower-melting metal is selected from the group consisting of indium, tin, lead, zinc, cadmium, bismuth, thallium and alloys thereof.

5. The method of claim 1 wherein the base metal comprises aluminum.

6. The method of claim 1 wherein the base metal comprises titanium.

7. The method of claim 1 wherein the base metal comprises magnesium.

8. The method of claim 1 wherein the lower-melting metal comprises indium.

9. The method of electroplating readily-oxidized, difficultly-soldered base metals which comprises immersing

said base metal as an electrode in a molten salt bath comprising ions of metal having a melting point below the base metal, said metal ions being in a concentration of at least 0.2 atomic percent of the cations, iodide ions in a concentration of at least 0.2 atomic percent of the anions, and fluoride ions in a concentration of at least 0.5 atomic percent of the anions, at a temperature at least 10° C. above whichever is the higher of the melting point of the lower-melting metal and the liquidus point of the bath, but at least 100° C. below the melting point of the base metal, providing another electrode, completing the circuit with the base metal as anode whereby the base metal is etched and oxide on the surface thereof is removed, reversing the current with the base metal as cathode in said molten salt bath whereby the lower-melting metal deposits thereon in molten form until the desired amount of lower-melting metal has been so deposited.

References Cited in the file of this patent

UNITED STATES PATENTS

1,927,772	Chittum	Sept. 19, 1933
2,738,294	Spence	Mar. 13, 1956
2,786,809	Raynes	Mar. 26, 1957

FOREIGN PATENTS

10,705	Great Britain	Nov. 9, 1901
615,110	Great Britain	Jan. 3, 1948

OTHER REFERENCES

Handbook on Titanium Metal, 7th edition, Titanium Metals Corporation, 1953, page 92.