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METHOD OF CHEMICALLY PLATING METALS

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The present invention relates to the production of metal products by chemical plating; and, more particularly, the invention relates to a novel method for chemically plating to readily-oxidized, difficultly-soldered base metals, low melting metals which are below the base metal in the electromotive series. In a specific aspect the invention relates to a novel method for "tinning" base metals which are ordinarily difficult to solder to provide on the base metal article a coating of a metal more easily soldered than the base metal.

In many industries today, particularly in the manufacture of electronic equipment, it is desirable to provide a coating of such metals as indium, tin, lead, zinc, thallium, cadmium, indium-cadmium alloys, cadmium-tin alloys, cadmium-lead alloys, and the like, on base metal articles comprising aluminum, titanium, magnesium, zirconium or beryllium. This is particularly so in the fabrication of electronic equipment where it becomes necessary to solder parts onto an aluminum-, titanium-, magnesium-, zirconium- or beryllium-containing part. These latter metals are notoriously difficult to solder, the principal difficulty being due to the oxide film. Generally, no fluxes are satisfactory without mechanical means, such as abrasion, or ultrasonic vibration, to remove oxides from the metal surface. Mechanical abrasion is impractical for small areas and fragile parts, such as aluminum electrodes of low-power semi-conductor devices, and ultrasonic vibration may fracture the semi-conductor itself, causing an open or noisy device. Hence, some means of displacing at least a portion of the metal base with another metal more readily soldered would be highly advantageous.

Attempts to coat the aluminum, titanium, magnesium, zirconium or beryllium part by immersing it in a molten bath of the coating metal covered by a suitable flux resulted in coatings the thickness of which cannot be controlled. Moreover, the nature of the surfaces of these metals renders them difficult to wet by molten metal simply by immersing the article in the molten metal. Prior to the invention forming the subject matter of copending application Serial No. 572,828, filed March 21, 1956, the electroplating on aluminum, titanium, magnesium, beryllium or zirconium of metals of the type discussed above for the purpose of providing a readily soldered coating has not been practiced due to the fact that, during subsequent soldering, the coating will not adhere to the base metal.

It is the principal object of the present invention to provide a novel method for chemically plating certain metals onto readily-oxidized, difficultly-soldered metals.

Another object of the present invention is to provide a novel method for chemically displacing aluminum, magnesium, titanium, zirconium or beryllium from base metal articles containing one or more of these metals by a low melting metal more noble than the stated base metal.

Other objects, including the provision of a novel method for "tinning" parts containing aluminum, titanium, magnesium, zirconium or beryllium preparatory to soldering to the part, 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 base metal article in a molten salt bath comprising salt of a metal melting substantially lower than the stated base metal and more noble than the base metal, at a temperature substantially below the melting point of the base and above the melting point of the metal being deposited until the desired amount of more noble metal in molten form has formed on said base article.

The present procedure is based upon the discovery that the immersion of metals, which are readily-oxidized and thus difficult to solder and to coat by immersion in molten metal or by conventional electroplating, particularly aluminum, magnesium, titanium, zirconium, and beryllium, in a molten salt bath comprising salt of a metal having a melting point substantially lower than the stated base metal and more noble than the stated base metal and at a temperature substantially below the melting point of the base metal and above the melting point of the more noble metal, results in a relatively rapid displacement of the stated base metal by the more noble metal in molten form. Since the process depends upon the dissolution of the base metal, there is no problem concerning the oxide film on the base metal since the dissolution of the underlying metal loosens the oxide film and results in its removal.

The process of the present invention is thus a chemical plating procedure. The ions of the low-melting, more noble metal in solution in the molten salt bath are replaced by ions of the particular readily-oxidized, difficultly-soldered base metal, and the more noble metal initially in the bath plates out at the site of the base metal. If there is at least an equivalent amount of more noble metal ions in the bath initially, in time, all of the base metal can be replaced by the more noble metal. The procedure can be halted short of complete displacement where only a film or coating of the more noble metal on the base metal is desired. As will be pointed out more in detail hereinafter, there are instances when it may be advantageous to completely replace all of the base metal by the more noble metal.

The present process, being a chemical plating procedure based on the phenomenon of simple chemical displacement due to relative differences in position in the electromotive series, does not rely on any flow of current, as in electroplating, nor in any extraneous reducing agent. By the present procedure, the more noble metal can be plated evenly and smoothly over all types of irregular surfaces and the shape of the base is immaterial. Moreover, there is no need to maintain electrical contact as in the case of electroplating so that the fineness or complexity of the parts is immaterial. In addition, other metals, such as silicon, germanium, nickel, copper, silver and gold, which are more noble than the lower melting metals, are not affected by the bath, and these may be part of the assembly treated without danger of coating them if they are not in electrical contact with the base metal.

In view of the availability of aluminum and magnesium, particularly the former, the present process is most generally utilized in the treatment of base metal articles comprising one or more of these metals. For example, in the preparation of a silicon-aluminum diode, a dot of aluminum is applied to an n-type silicon wafer and the assembly heated alloying the aluminum and silicon at the interface between the two metal bodies so that upon cooling silicon in the intermediate phase recrystallizes to form a p-n alloyed junction within the silicon wafer

and overlaid with the remaining, unalloyed aluminum. A lead wire must then be soldered to this electrode, and it has been the practice in the past to solder the wire to the overlying aluminum. The soldering of the lead wire to the aluminum electrode is very difficult for the reasons mentioned hereinabove. By the process of the present invention, the diode assembly can be simply immersed in the described bath to provide selectively over the aluminum a coating of the lower-melting metal. This lower-melting metal is much more readily soldered than is aluminum so that the coated electrode can be soldered by conventional methods using conventional rosin or "acid" type fluxes. All of the overlying unalloyed aluminum metal in the electrode can be replaced by the lower-melting metal. In this case, the junction between the n-type silicon base and the p-type recrystallized silicon will not be affected, and the lower-melting metal serves as the metallic contact with the recrystallized silicon. A structure of this type has advantages over the aluminum electrode in that the diode assembly can be electrolytically etched in alkaline solutions with no appreciable attack on the lower-melting metal electrode. The lead wire can, in this type of structure, be soldered directly to the lower-melting metal.

Referring to the lower-melting metal, it may be selected from a wide variety of such metals, including alloys, so long as the metal is more noble than the base metal. In other words, by the process of the present invention any metal, including combinations of metals (alloys), melting substantially below the particular base metal and more noble than the base metal can be applied to the base. Such metals include indium, tin, lead, zinc, cadmium, thallium, alloys of two or more of these metals, such as indium-cadmium alloys (the eutectic of which melts at 122.5° C.), tin-lead alloys (the eutectic of which melts at 180° C.), tin-indium alloys (the eutectic of which melts at 117° C.), and the like. In the case of the alloys, the compositions may vary widely from those containing substantial amounts of each constituent to those containing only minute amounts, such as 0.1%, by weight, of one of the constituents. As stated, such metals must melt below the base metal, and preferably the plated metal has a melting point at least 100° C. below that of the particular base metal. Generally the more noble metal will have a melting point between about 100° C. and about 450° C. The preferred lower-melting metals are indium, tin and thallium, especially the former.

As stated, the procedure comprises simply immersing the base metal into the defined molten salt bath comprising salt of the more noble, lower-melting metal to be deposited. The bath may consist substantially entirely of molten salt of metal to be deposited. When an alloy is to be deposited, the bath may consist substantially entirely of a mixture of salts of the metals to form the alloy deposit. Of the salts of the more noble, lower-melting metals, the halides, especially the chlorides and bromides, are especially suitable. Examples of suitable salts are stannous chloride, zinc chloride, indium monochloride, indium dichloride, indium trichloride, thallous chloride, plumbous bromide, cadmium chloride, and the like. In systems containing ammonium or hydrogen ions it is preferred that multivalent metals like indium, lead and tin be in a lower valent state in the bath.

In addition to salt of the more noble, lower-melting metal to be deposited, the fused salt bath may contain other salts serving principally as diluents or solvents. Such other salts may be ammonium salts or salts of metals more electropositive than the base metal. For example, other chlorides, such as lithium chloride, potassium chloride and mixtures thereof, such as the eutectic mixture, may be included in the bath to control the concentration of ions of the metal to be deposited. Salts of metals which would ordinarily deposit on certain of the base metals may be employed as diluents or solvents in baths containing ions of metal which is substantially more noble than such metal. For example, in the deposition of lead onto magnesium, the bath may also contain zinc chloride to serve as a diluent, the zinc, in this case, not depositing on the magnesium. In this case, a particularly suitable diluent salt mixture for use with magnesium is the zinc chloride-ammonium chloride eutectic, composed of three parts of zinc chloride to one part of ammonium chloride, by weight, having the melting point of 180° C.

The concentration of ions of the more noble, lower-melting metal in the molten salt bath is relatively immaterial since the deposition is selective and quantitative. In other words, all of the more noble, lower-melting metal in the bath will eventually plate out, and, hence, the bath can contain just that amount of metal to be plated. When treating only a single or a limited number of very small structures, for example, the ions of the more noble, lower-melting metal may make up as little as about 0.01 atomic percent of the cations of the bath. Preferably, for general purposes when a bath of reasonable life is desired, the concentration is at least about 0.2 atomic percent of the cations of the bath. Of course, when the bath is made up entirely of salt of the metal to be deposited, the ions of the more noble, lower-melting metal make up 100 atomic percent of the cations of the bath. The rate of deposition is a function of the concentration of ions of the more noble, lower-melting metal, and the concentration can be easily adjusted through the addition of diluent salt, as mentioned above, to provide, in conjunction with other conditions, such as temperature, any desired rate of deposition.

During operation, the bath will be at a temperature substantially below the melting point of the base metal, preferably at least 100° C. below, but above the melting point of the more noble, lower-melting metal. The exact temperature of the bath will thus depend upon the exact system employed, particularly upon the more noble, lower-melting metal. Where the more noble, lower-melting metal formed on the base is a single molten metal, the temperature of the bath will be above the melting point of that metal. Where, however, an alloy is formed on the base metal, the temperature of the bath will be above the melting point of the alloy although it may well be below the melting points of each of the individual metals making up the alloy. In addition, the temperature of the bath may depend somewhat upon the size of the article immersed therein, since the cold metal article will have a cooling effect locally. Therefore, in practice, the melting point of the bath is generally held at least 10° C. above the melting point of the deposited metal or the liquidus point of the bath, whichever is higher, to allow for any local cooling effect due to the immersion of the metal article. The higher the temperature the more vigorous the action, due to the greater solubility of the base metal in the molten, lower-melting metal coating and the resulting greater availability of base metal at the interface between the molten, lower-melting metal coating and bath, and the higher the conductance of the bath, whereas fuming becomes an increasing problem as the boiling or subliming point of the salt or salts in the bath is approached. Accordingly, the exact temperature selected may be a compromise between these factors. For the systems under consideration, as a general matter, the temperature of the bath is usually at least about 150° C., preferably at least about 200° C., and may go up as high as about 500° C. when aluminum is the base metal and even as high as about 1000° C. when titanium is the base metal.

As will be apparent from the foregoing, the process of the present invention is a function of time, temperature, concentration of ions of the more noble, lower-melting and relative difference in positions of the base metal and more noble metal in the electromotive series. Accordingly, any or all of the first three variables can be con-

trolled to provide for any particular system a desired rate of deposition and amount of deposit as well as extent of replacement of the base metal.

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

One gram of plumbous chloride is added to ten grams of zinc chloride-ammonium chloride eutectic (3:1 parts, by weight, melting point, 180° C.) and the mixture heated at 400° C. The immersion of magnesium metal in this bath results in the displacement of the magnesium and the formation of a smooth, uniform coating of molten lead on the magnesium at a rate of about 200 mils per minute. Removal of the assembly from the bath before complete replacement of the magnesium results in solidification of the lead and a lead coated magnesium article.

Example II

Ten grams of zinc chloride-ammonium chloride eutectic (3:1 parts, by weight, melting point, 180° C.) are heated at 450° C. Aluminum metal immersed in this bath results in the rapid displacement of aluminum by zinc until the desired coating of zinc is formed on the aluminum.

Example III

One gram of indium trichloride is added to ten grams of lithium chloride-potassium chloride eutectic (5:6 parts, by weight, melting point, 352° C.) and the mixture maintained at a temperature of 420° C. The immersion of aluminum metal in this bath results in the replacement of the aluminum by molten indium and the coating of molten indium on the remaining base aluminum metal at the rate of about 100 mils per minute.

Example IV

One gram of stannous chloride is added to ten grams of the lithium chloride-potassium chloride eutectic and the mixture maintained at a temperature of 420° C. The immersion of aluminum metal in this bath results in the replacement of the aluminum by molten tin and the formation of a molten tin coating on the remaining aluminum metal at the rate of about 50 mils per minute.

Example V

One gram of plumbous chloride is added to ten grams of the lithium chloride-potassium chloride eutectic and the mixture maintained at a temperature of 450° C. Immersion of aluminum metal in this bath results in the replacement of aluminum by the molten lead and the formation of a molten lead coating on the aluminum base metal at the estimated rate of about 50 mils per minute.

Example VI

Indium monochloride is melted and maintained at a temperature of 250° C. Aluminum metal immersed in this molten indium monochloride is gradually replaced by molten indium metal with the formation of a coating of molten indium on the aluminum.

Example VII

Aluminum metal is immersed in molten 2:1, by weight, indium monochloride-zinc chloride mixture at 230° C. The aluminum is gradually replaced by molten indium metal forming a smooth, uniform coating of molten indium on the aluminum.

Example VIII

Stannous chloride is melted and maintained at a temperature of 260° C. Aluminum metal immersed in this molten stannous chloride is gradually replaced by molten tin, forming a smooth, homogeneous coating of molten tin on the aluminum.

Example IX

A 30:10:3, by weight, zinc chloride-ammonium chloride-plumbous chloride mixture is melted and maintained at 360° C. Aluminum metal immersed in this bath is gradually replaced by molten lead forming a smooth, homogeneous coating of molten lead on the aluminum.

Example X

A 4:6:1, by weight, zinc chloride-indium monochloride-cadmium chloride mixture is melted and maintained at a temperature of 230° C. Aluminum metal immersed in this bath is gradually replaced by a cadmum-indium alloy forming on the aluminum a smooth, homogeneous coating of molten cadmium-indium alloy.

Example XI

A silicon-aluminum diode assembly consisting of an n-type silicon wafer having a p-n alloyed junction therein overlaid with aluminum metal(prepared by placing a small body, or "dot," of aluminum on the silicon wafer, heating to melt the aluminum with the dissolution of silicon in the molten aluminum at the interface and cooling to recrystallize the silicon from the silicon-aluminum phase) is immersed in a molten 2:1, by weight, mixture of indium monochloride and zinc chloride at 230° C. The diode is held in the bath until all of the overlying aluminum is replaced by molten indium. Removal of the assembly from the bath results in solidification of the indium providing an indium electrode directly in contact with the recrystallized silicon.

In none of the above baths are germanium or silicon affected so that composite structures comprising one of the stated base metals, and germanium and/or silicon can be immersed in the bath without affect on the latter and with preferential and selective replacement and coating of the desired base metals.

Considerable modification is possible in the selection of the base metals and lower-melting more noble metals as well as in the exact techniques followed without departing from the scope of the present invention.

I claim:

1. The method of coating a readily-oxidized difficultly-soldered metal with a cadmium-indium alloy which comprises immersing said readily-oxidized difficulty-soldered metal in a molten salt bath comprising a halide of zinc, a halide of cadmium and salt of indium in a valent state below 3, at a temperature below the melting point of said immersed metal but above the melting point of the cadmium-indium alloy deposited on said immersed metal, until the desired amount of alloy in molten form has deposited on said immersed metal through displacement of said immersed metal.

2. The method of claim 1 wherein the temperature of said bath is above the melting point of said alloy but below the melting points of each of the individual metals making up such alloy.

3. The method of coating aluminum with a cadmium-indium alloy which comprises immersing said aluminum in a molten salt bath comprising zinc chloride, cadmium chloride and a chloride of indium in which the indium is in a valent state below 3, until at least a portion of said aluminum has been displaced by cadmium-indium alloy in molten form, said molten salt bath being at a temperature below the melting point of the aluminum but above the melting point of said cadmium-indium alloy displacing said aluminum.

4. The method for selectively plating and displacing substantially only the overlaid aluminum of a silicon-aluminum diode comprising a silicon base and a recrystallized silicon p-n alloyed junction therein overlaid with aluminum, while not plating said silicon base and not affecting said recrystallized silicon p-n junction, which comprises immersing said overlaid aluminum as well as

at least a portion of said silicon base adjacent said overlaid aluminum in a molten salt bath comprising a salt of indium, until at least a portion of said aluminum is displaced by metal comprising indium, said bath being at a temperature above the melting point of said metal comprising indium and below the melting point of said aluminum.

5. The method of claim 4, wherein the temperature of said molten salt bath is at least 100° C. below the melting point of aluminum and at least 10° C. above the melting point of said metal comprising indium displacing said aluminum.

6. The method of claim 5 wherein said molten salt bath contains ions selected from the group consisting of hydrogen and ammonium ions and said salt of indium is a salt in which the indium is in a valent state below 3.

7. The method of claim 5 wherein substantially all of said immersed aluminum is displaced by said metal comprising indium.

8. The method of coating a readily-oxidized difficultly-soldered metal-containing article with a more noble metal comprising indium which comprises immersing said metal of said article in a molten salt bath established at a temperature below the melting point of said immersed metal but above the melting point of said more noble metal, said bath comprising salt of metal having a melting point substantially below that of said immersed metal and more noble than said immersed metal, metal of said salt comprising indium in a valent state below 3, said bath additionally comprising ions selected from the group consisting of hydrogen and ammonium ions; and maintaining said metal of said article immersed in said bath until the desired amount of more noble metal is deposited on said article through displacement of immersed metal.

9. The method of claim 8 wherein said readily-oxidized difficultly-soldered metal is selected from the group consisting of aluminum, magnesium, titanium, zirconium and beryllium.

10. The method of coating a readily-oxidized difficultly-soldered metal with a more noble metal comprising indium which comprises immersing said readily-oxidized difficultly-soldered metal in a molten salt bath established at a temperature below the melting point of said immersed metal but above the melting point of said more noble metal, said bath comprising salt of metal having a melting point substantially below that of said immersed metal and more noble than said immersed metal, metal of said salt comprising indium in a valent state below 3, said bath additionally comprising ions selected from the group consisting of hydrogen and ammonium ions; and maintaining said readily-oxidized difficultly-soldered metal immersed in said bath until the desired amount of more noble metal is deposited on said immersed metal as a coating.

11. The method of displacing a readily-oxidized difficultly-soldered metal with a more noble metal comprising indium which comprises immersing said readily-oxidized difficultly-soldered metal in a molten salt bath established at a temperature below the melting point of said immersed metal but above the melting point of said more noble metal, said bath comprising salt of metal having a melting point substantially below that of said immersed metal and more noble than said immersed metal, metal of said salt comprising indium in a valent state below 3, said bath additionally comprising ions selected from the group consisting of hydrogen and ammonium ions; and maintaining said readily-oxidized difficultly-soldered metal immersed in said bath until the desired amount of said immersed metal is displaced by said more noble metal.

12. The method of claim 11 wherein substantially all of said immersed metal is displaced by said more noble metal.

13. The method of tinning aluminum preparatory to soldering wherein the tinning metal is a metal more noble than aluminum, which comprises immersing said aluminum in a molten salt bath established at a temperature below the melting point of aluminum but above the melting point of said more noble metal, said bath comprising salt of metal having a melting point substantially below that of aluminum and more noble than aluminum, metal of said salt comprising indium in a valent state below 3, said bath additionally comprising ions selected from the group consisting of hydrogen and ammonium ions; and maintaining said aluminum immersed in said bath until at least a portion of said aluminum has been displaced by said more noble metal.

14. The method of coating a readily-oxidized difficultly-soldered metal-containing article with a more noble metal comprising indium which comprises immersing said metal of said article in a molten salt bath established at a temperature, between about 150° C. and about 1000° C., below the melting point of said immersed metal and above the melting point of said more noble metal, said bath comprising salt of metal having a melting point substantially below that of said immersed metal and more noble than said immersed metal, metal of said salt comprising indium in a valent state below 3, said bath additionally comprising ions selected from the group consisting of hydrogen and ammonium ions.

15. The method of claim 14 wherein said immersed metal comprises aluminum and wherein the temperature of said molten salt bath is between about 200° C. and about 500° C.

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