electrolytes used in electroplating of aluminum, which modifier results in the deposition of a smooth, even plating of aluminum upon a metallic cathode.

A further object of the invention is to provide an improved aluminum electroplating process in which high current efficiency is attained in plating aluminum upon the metallic substrate from an organoaluminum complex electrolyte.

Other objects and advantages of the invention will become apparent as the following detailed description of the invention is read.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The metals plated with aluminum by the process of this invention can be substantially any dissimilar metal such as steel, copper, iron, lead, tin, zinc, brass or bronze. The metal is shaped to correspond to an article which it is desired to aluminum plate, and is made the cathode positioned within the cell for immersion in the electrolyte bath. The anode employed consists of aluminum which is preferably of relatively high purity to avoid undesirable alloying in the plate which is deposited, unless such alloying should be desired, in which event an aluminum alloy can be usefully employed as the anode.

The electrolyte bath used in the invention consists essentially of an electrically conductive organoaluminum complex containing from about 1 weight percent to about 10 weight percent, based on the total weight of the electrolyte system, of a deposit modifier of the formula RX, where R is an alkyl radical, and X is selected from the group consisting of chlorine, bromine and iodine.

Various electrically conductive organoaluminum complexes are useful in the process of the invention, and the utility of many of these as major components of aluminum plating baths has been heretofore recognized. Examples of organoaluminum complexes which are electrically conductive and thus suitable for use in the invention are lower aluminum trialkyl metallic complexes of the formula MeX₃·MAIR, where Me is a metal—preferably an alkali metal, X is halogen, and R is a lower alkyl radical containing from 1 to 5 carbon atoms; lower aluminum dialkyl metallic complexes of the formula Me₂X·AIR·X', where Me, X and R have the meanings set forth above, and X' is halogen which may be identical to, or different from, X; and complexes of the formula MeAIRX₄₋ₓ where Me, R and X have the meanings set forth above, and x is an integer of from 0 to, and including, 4. Ethereal complexes of organoaluminum compounds are also electrically conductive and suitable. In preparing such ethereal complexes, a wide variety of ethers may be utilized, such as ethyl ether, propyl ether, butyl ether, octyl ether, etc.

Of the types of organoaluminum complexes useful in the invention, the alkali metal aluminohalide complexes are preferred. These compounds have the formula MeAIRX₄₋ₓ as defined above. Sodium aluminum ethyl trichloride functions especially well in conjunction with the alkyl halide deposit modifiers hereinafter described in greater detail.

The deposit modifier utilized in the electrolyte system is selected from the group consisting of alkyl chlorides, alkyl bromides and alkyl iodides. The alkyl radical, though not so limited, is preferably of straight chain configuration, and preferably contains from 2 to 8 carbon atoms. Examples of useful deposit modifiers include ethyl chloride, propyl bromide, octyl iodide, isobutyl chloride, and tertiary amyl bromide. The modifier constitutes from about 1 weight percent to about 10 weight percent of the total weight of the electrolyte system, and preferably from about 1 weight percent to about 5
3 weight percent is employed, and is distributed evenly throughout the organoaluminum complex.

In some circumstances, such as where it is desirable to reduce the melting point of the bath, or to reduce its viscosity, it may be desirable to add an inert diluent to the electrolyte. Typical materials which can be employed for this purpose include aromatic hydrocarbons, tetrahydrofuran and various ethers such as diphenyl ether and diethyl ether. β,β-dichloroethy ether may be used in small amounts to improve the smoothness and hardness of the plating.

The electroplating bath is maintained at temperatures which are, in general, above that required to maintain the electrolyte in a molten, or relatively low viscosity state (where a diluent is used). The upper temperature limit is dictated by the decomposition temperature of the complex. I have found that temperatures in the range of from about 0°C to about 100°C can be effectively utilized with most systems, and operation at room temperature offers economic advantages in a number of instances. Since the electrical conductivity of the electrolytes increases sharply with temperature, it is often desirable to use bath temperatures of about 100°C or above where the specific conductivity of the complex in use is relatively low.

As is well understood in the art, it is desirable to protect the heated melts of the organoaluminum complex electrolyte from contact with air. This may be accomplished by covering them with a small amount of paraffin oil, but is preferably accomplished by blanketing the bath with an inert gas, such as nitrogen. The electroplating bath should also be prepared and maintained under anhydrous conditions.

The current densities and voltages employed are, of course, widely variable, and their selection will be dependent upon the electrolyte used, the amount, if any, of diluent used, the temperature of the bath, the electrode spacing and the specific type of plating desired. These considerations and their effect upon voltage and current density requirements are well understood in the art. The current densities utilized should, in general, however, range from about 1 ma/cm² to about 1 ampere/cm². It may also be stated as a general proposition that it is desirable, in most instances, to use the highest current densities possible for economic reasons.

The following working examples will serve to further illustrate the process of the invention. In the examples, a number of electroplating runs were carried out using various electrolyte systems within the scope of the present invention for accomplishing the deposition of aluminum metal on iron and platinum electrodes. The composition of several electrolyte systems used, and the electrical parameters employed, are set forth in Table I. It will be noted that the first run is a control run since the system did not include any deposit modifier in the electrolyte system. In each one of the runs, a Pyrex glass cell having a volume of 50 ml was utilized, and a medium-grade, glass-fritted disk was used for separating the anode compartment from the cathode compartment. The distance of separation of the electrodes was 2 inches. In Runs 3, 4, and 5 a platinum cathode was employed, and in Runs 1 and 2, an iron cathode was utilized. An aluminum anode was utilized in all of the runs.

The results obtained with the several electrolyte systems, and with the imposed electrical conditions identified in Table I, are set forth in Table II. It will be noted that where the electrolyte systems of the present invention were employed, very smooth plating was obtained as contrasted with the rough, mossy plating obtained when the deposit modifier of the present invention was omitted from the system.

Although certain preferred embodiments of the invention have been herein described in order to provide examples of the practice of the invention, it is to be understood that variations in the process conditions and quantitative amounts of the various ingredients of the electrolyte system can be employed without departing from the spirit and scope of the invention. Changes and innovations of this type are therefore deemed to be encompassed by the spirit and scope of the invention except as they may be necessarily limited by the accompanying claims or reasonable equivalents thereof.

What is claimed is:

1. A process for electroplating metals with aluminum comprising:
   providing the metal to be plated as a cathode, and
   providing an anode consisting essentially of aluminum metal, in an electrolyte consisting essentially of an electrically conductive organoaluminum complex, and containing an effective amount of an alkyl halide deposit modifier having the formula RX, where R is an alkyl radical, and X is selected from the group consisting of chlorine, bromine and iodine, said electrically conductive organoaluminum complex being selected from the group consisting of compounds having the formula MeX-2AIR, compounds having the formula MeX-AIRX, and compounds having the formula MeAIRX₄₋₅₋₆ wherein Me is a metal, X is halogen, R is a lower alkyl radical containing from 1 to 5 carbon atoms, and X is an integer of from 0 to 1, and including, 4, then passing an electric current between the electrodes to plate aluminum upon the cathode.

2. A process as defined in claim 1 wherein said alkyl halide deposit modifier is present in the electrolyte in an amount of from about 1 weight percent to about 10 weight percent of the total weight of the electrolyte system.

3. A process as defined in claim 1 wherein said bath is maintained at a temperature of from about 0°C to about 100°C during the passage of electric current between said electrodes.

4. A process as defined in claim 1 wherein said organoaluminum complex has the formula MeAIRX₄₋₅₋₆, where Me is an alkali metal, R is a lower alkyl radical containing from 1 to 5 carbon atoms, X is halogen, and X is an integer of from 0 to 1, and including, 4.

5. A process as defined in claim 1 wherein said alkyl radical contains from 2 to 8 carbon atoms.
trodes is from about 1 ma./cm.² to about 1 ampere/cm.² at the cathode surface.

7. A process as defined in claim 2 wherein said deposit modifier is present in the electrolyte in an amount of from about 1 weight percent to about 5 weight percent of the total weight of the electrolyte system.

8. A process as defined in claim 3 wherein said alkyl halide modifier is present in the electrolyte in an amount of from about 1 weight percent to about 5 weight percent of the total weight of the electrolyte system.

9. A process as defined in claim 4 wherein said organoaluminum complex is sodium aluminum ethyl trichloride.

10. A process as defined in claim 8 wherein said organoaluminum complex has the formula MeAlR₆X₄₋₆ₓ, where Me is an alkali metal, R is a lower alkyl radical containing from 1 to 5 carbon atoms, X is halogen, and x is an integer of from 0 to, and including, 4.

References Cited

UNITED STATES PATENTS

2,170,375 8/1939 Mathers et al. . . . . . . 204—14 N
2,849,349 8/1958 Ziegler et al. . . . . . . 204—14 N

OTHER REFERENCES


JOHN H. MACK, Primary Examiner
T. TUFAIELLO, Assistant Examiner

U.S. Cl. X.R.