United States Patent Office 2,923,671 Patented Feb. 2, 1960



2,923,671

# COPPER ELECTRODEPOSITION PROCESS AND ANODE FOR USE IN SAME

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No Drawing. Application March 19, 1957
Serial No. 646,985

4 Claims. (Cl. 204—52)

This invention relates to the electrodeposition of metal using a consumable anode and to a new and novel anode for use in an improved process therefor. More particularly this invention relates to a copper electrodeposition process and to a high purity oxygen-free copper anode of modified crystalline structure for use therewith. The invention is particularly useful in connection with either cyanide or acid bath compositions for enabling more efficient utilization of the anode while minimizing sludge formation and further resulting in the formation of an improved copper deposit on the cathode.

In copper electrodeposition processes commonly referred to as copper electroplating, the problem of roughness of the cathode electrodeposit i.e. the copper deposit on the cathode is of extreme importance. Although the use of various addition reagents to the bath composition has proven helpful for improving the properties and characteristics of the copper deposit on the cathode, this approach has not proved entirely satisfactory as a solution of the problem.

A major cause of rough cathodic deposits is considered to be the formation and presence of anode sludge which occurs during the course of the electrodeposition process. The formation of such sludge is thought to be due to a combination of factors including electrochemical action at the face of the anode, and a preferential attack by the electrolyte solutions on the boundaries between the crystals of the copper constituting the structure of the anode. Such attack has the result that loose particles of the anode are detached from the body of the anode, particularly when the crystals are small, and are carried into the electrolyte forming a sludge which settles mostly in the bottom of the tank. During the process, however, some of these loose particles are mechanically carried to the cathode where they produce a deleterious rough plate upon the cathode. Another effect of such intercrystalline attack is an uneven anode dissolution which results in excessive losses of copper in terms of the anode remmant which must then be prematurely discarded.

Several methods have been suggested to overcome the undesirable effects of such sludging or to reduce the formation of anode sludge. One proposal involves bagging of the anode whereby the sludge is caught in the bags. Others have proposed the addition of elements to copper anodes made of ordinary that is, oxygen bearing or "tough pitch" copper whereby chemical films are formed on the surfaces of the anode to inhibit sludge formation. All these proposals, however, have entailed certain disadvantages. The placing of bags around the anodes not only complicates the actual carrying out of the plating process, but also materially decreases current efficiencies in the bath and promotes polarization or passivation of anodes particularly when operating at high current densities. Moreover, the use of bags does not overcome the other disadvantages which arise due to uneven anode dissolution. Although the use of copper anodes containing addition elements as, for example, phosphorous possess



certain advantages in some instances, such anodes have generally been found to possess limited applications with respect to the bath compositions suitable for use therewith.

In order to obtain more uniform anode dissolution, there is evidence to indicate that dissolution should occur through the metal crystal rather than at the crystal boundary. For best results, it becomes accordingly apparent that the consumable copper anode should possess a substantially uniformly dense crystal structure as well as clean crystal boundaries. The need for these requirements are obvious since non-uniform density of the copper would incur more rapid dissolution through the less dense portion resulting in uneven overall dissolution of the anode. Then too, the presence of oxygen or oxides and other impurities in the grain boundary which are usually more soluble than copper lead to grain boundary corrosion which ultimately causes increased sludge formation.

In view of the above, the improved plating characteristics and more efficient utilization of the anode made possible by the more recently increasing use of high purity, oxygen-free, high conductivity copper anodes in conventional acid type and alkaline cyanide electrodeposition processes are not surprising since such anodes are characterized by (1) higher purity, (2) more uniform and increased density and (3) the absence in the copper crystal boundaries of oxygen or oxygen in combination with a chemical deoxidant as is normally found in anodes composed of tough pitch or chemically deoxidized copper.

In accordance with the foregoing, it will be seen that a single, pure, dense crystal of copper would be ideal for the purpose of electroplating. Since this is presently impossible commercially, a feasible approach to the problem consists of making available a copper anode which possesses the combination of (1) larger crystal size, (2) uniform density of the crystals, and (3) minimum number of crystal boundaries which should be as clean as possible particularly of oxide inclusions.

I have now found that by the addition of extremely small quantities of lithium to oxygen-free high conductivtiy copper, a substantial average enlargement of the crystal structure is obtained whereby it becomes possible to reduce in anodes of equivalent size the overall number and extent of crystal boundaries presented to the sludge-forming preferential attack of electrolyte solutions during the electrodeposition process. Moreover, I have found that none of the other desirable properties connected with the use of oxygen-free, high conductivity copper anodes in either an acid sulfate or fluoborate as well as a cyanide copper electroplating process are in any way adversely affected by such lithium additions.

It is the principal object of this invention to provide a copper electrodeposition process utilizing an oxygen-free, high purity copper anode having an enlarged average crystal structure whereby preferential attack during electroplating is minimized and the more uniform dissolution of the anode results in reduced sludge formation and improved smoothness of the copper deposit on the cathode.

Another object of this invention is to provide an oxygen-free, high purity copper anode having a relatively enlarged crystal structure which is conducive to improved results in copper electrodeposition processes.

Other specific objects and advantages of the invention will become apparent as this specification proceeds.

For the purpose of the present invention, it is essential that the copper used for the fabrication of the anodes be oxygen-free high conductivity copper. By the term "oxygen-free copper" is meant a high purity copper

which contains no oxygen by virtue of the process used in production in accordance with known methods therefor exclusive of the use of chemical deoxidizers such as phosphorus, and the like. Thus, copper which has been produced in a reducing atmosphere such as the commercially available OFHC brand copper may be used as well as copper prepared in an inert atmosphere or in a vacuum. Such copper is usually of 99.98% or even higher purity and the extremely small amount of impurities which may be present is not objectionable for the stated purpose. A typical analysis of the composition of OFHC brand copper with respect to the impurity content thereof is illustrated by the following:

| | Percent |
|---|---|
| Silver | 0.001 |
| Iron | 0.001 |
| Sulfur | 0.002 |
| Lead | 0.0003 |
| Tin | 0.0001 |
| Nickel | 0.0008 |
| Antimony | Less than 0.0005 |
| Bismuth | Less than 0.0001 |
| Zinc | Less than 0.0003 |
| Manganese | Less than 0.00005 |
| Oxygen | None |

The copper anodes for use in the electrodeposition processes as herein contemplated are made by the addition of extremely small amounts of lithium to the oxygen-free high conductivity copper using oxygen-excluding practices in accordance with known practices during the entire process. The amount of added lithium in the form of a master alloy or as lithium metal may be varied between 0.0001 to 0.001% by weight. Preferably, between 0.00015 to 0.0003% may be used with optimum results being achieved with the use of about 0.0002%.

The lower limit of 0.0001% for the amount of lithium to be added to the anode metal is determined by the observation that any smaller addition does not achieve the desired crystal enlarging effect. While the upper limit is less critical, it is desirable to keep the addition to the necessary minimum not only for cost considerations but also to ensure an anode of maximum copper purity. For this reason the use of about 0.0002% as previously indicated is most desirable in that adequate crystal enlargement is achieved without any appreciable impairment of purity, conductivity or density of the oxygen-free high conductivity copper.

Although the reasons for the unexpected grain enlargement achieved in oxygen-free high conductivity copper by the addition of such extremely small amounts of lithium are not clearly understood, it is believed that the highly efficient scavenging action of lithium serves in some manner to effect a reduction in the nucleation centers present in the copper. The effect is unique, however, since the effect associated with lithium addition to ordinary copper even in such small quantities is generally grain refinement as opposed to the actual grain enlargement obtained in the case of oxygen-free copper.

Lithium-treated oxygen-free copper anodes preferably made by the addition of the desired amount of lithium metal to a copper melt employing conventional oxygen-excluding practices during the melting, lithium addition and casting steps may be used in the usual manner using conventional bath compositions of the acid or alkaline type. By way of specific illustration, a conventional aqueous acid sulfate plating bath consisting essentially of cupric sulfate and sulfuric acid may be used utilizing, for example, a current density of about 100 amperes per



square foot of anode surface. Similarly the new and improved anode may be advantageously used in conventional cyanide plating processes utilizing an electrolyte bath composition, for example, which consists essentially of an aqueous solution of copper cyanide and sodium and/or potassium hydroxide with anode current densities averaging about 15 amperes per square foot.

Whether or not the advantageous results and improvements are attributable solely to the enlarged grain structure per se of the modified anodes herein described cannot be positively ascertained at this time. Whatever the reasons may be for the superior performance of the lithium-treated oxygen-free copper anodes of the type herein disclosed, the fact remains that, in addition to the adaptability of the anode to both acid and cyanide processes, smooth and fine-textured cathode deposits of substantially pure copper are consistently obtained which are substantially free from nodular growths notwithstanding the thickness of the deposited plate. Furthermore, the reduced sludge formation and minimized cathode roughness resulting therefrom entirely eliminates the need for bags or diaphragms around the anodes. The more uniform dissolution characteristics imparted to the anode in addition to reducing copper losses by sludge formation also permits a more complete utilization of the anode during the electrodeposition process whereby scrap losses are appreciably less.

Since certain changes may be made in the above invention and different embodiments of the invention may be made without departing from the scope hereof, it is intended that all matter contained in the disclosure shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. In a copper electrodeposition process wherein an electric current is passed from a consumable copper anode through an electrolyte to a cathode to provide a deposit of substantially pure copper on said cathode, the improvement which comprises subjecting to the action of said current an anode consisting of oxygen-free high conductivity copper to which is added from 0.0001% to 0.001% by weight of lithium to effect dissolution of improved uniformity of said anode with minimal sludge formation while forming a cathode deposit free of nodular growths.

2. In a copper electrodeposition process wherein an electric current is passed from a consumable copper anode through an electrolyte to a cathode whereby a deposit of substantially pure copper is effected on said cathode, the improvement which comprises subjecting to the action of said current an anode consisting of oxygen-free high conductivity copper containing the impurities normally present therein to which is added from 0.00015% to 0.0003% by weight of lithium to effect more uniform dissolution of said anode whereby less sludge is formed during the process.

3. The process of claim 2 wherein the electrolyte is an acid electrolyte comprising an aqueous solution of cupric sulfate and sulfuric acid.

4. The process of claim 2 wherein the electrolyte is of the alkaline cyanide type.


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