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ELECTRODEPOSITION OF COPPER

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1

This invention relates to improvements in the electrodeposition of copper using soluble copper anodes, whereby copper losses due to the build-up of copper in the electrolyte and due to sludging are reduced, and whereby the surfaces of the corroding anode and the deposited cathode are both maintained in exceptionally smooth condition, particularly when using acid copper sulfate electrolytes. The invention involves the use of an anode composed essentially of a phosphorus-bearing copper which, during use, acquires an adherent film which seems to prevent release of cuprous ions into the adjacent electrolyte during the cource of the electrolysis.

In copper electroplating operations it has heretofore been considered the best practice to use copper of the highest purity available as the anode. However, even with such anodes, the surfaces of thick cathode deposits become rough due to the formation of nodular growths, and the anodes corrode irregularly with the result that there is a considerable loss of copper in the "fish" (anode remnant) which must be discarded when the anode has been dissolved to the maximum practical extent. Also in the course of the usual electroplating operation there is a substantial build-up, or increase in concentration, of copper in the electrolyte employed. As a result, part of the electrolyte must periodically be withdrawn from the electrolytic cell and replaced with copper-free electrolyte, or insoluble anodes must be used along with soluble anodes in such proportion as to bring the rate at which copper dissolves from the soluble anodes into balance with the rate of copper deposition.

In addition to copper losses in the discarded anode "fish" and due to the build-up of copper in the electrolyte, there is also, especially when using an acid electrolyte, a substantial loss of copper due to the formation of a sludge consisting chiefly of finely divided copper particles. Most of the sludge settles to the bottom of the cell tank, but some of the fine copper sludge particles are carried to the cathode by the normal circulation of the bath and settle on the cathode surface. We have found that such particles nucleate and are responsible for the formation of most if not all of the nodular growths characteristic of rough, uneven cathode deposits. Thus the copper sludge is objectionable not only on account of the loss of copper which it represents, but also because of its adverse effect on the character of the cathode deposit.

We have discovered that if anodes composed essentially of copper containing a substantial

2

amount of phosphorus are used instead of high purity copper anodes, a clearly visible adherent black film forms upon the surfaces of the anodes as soon as a normal deposition voltage is applied to the cell, and remains throughout the useful life of the anodes. The film-coated anodes corrode very smoothly and evenly, with little or no loss of copper due to sludge formation or copper build-up in the electrolyte, and with the formation of very smooth cathode deposits even when such deposits are produced to considerable thickness. The necessity of placing a bag around the anode, which is a common practice, is thereby eliminated.

It is, therefore, characteristic of the present invention that in a process for the electrodeposition of copper in which an electric current is passed from a soluble copper anode through an aqueous electrolyte to a cathode, the anode is composed essentially of a phosphorus-bearing copper containing 0.01% to 0.1% phosphorus and the balance copper save for impurities normally present in commercial refined copper and save for the optional inclusion therein of 0.0005% to 0.01% of silver, selenium, tellurium, and arsenic, singly or in any desired combination. When such an anode is used, an adherent black film forms on its surface, and its surface remains smooth throughout its useful life. Also the presence in the electrolyte of minute particles of undissolved copper is minimized and the formation of a smooth cathode deposit substantially free of nodular growths is promoted.

The lower limit of 0.01% on the amount of phosphorus present in the anode metal is quite critical, as any substantially smaller amount does not lead to the formation of an adherent film on the anode surface or to the benefits of the invention. The upper limit of 0.1% phosphorus is much less critical and is dictated primarily by elements of cost and by the difficulty with which high-phosphorus copper is worked in forming hot-rolled anodes. Even much larger amounts of phosphorus than 0.1% can be used (and, in the case of cast anodes, can be incorporated without substantial technical difficulty), but no particular advantage is gained thereby, and the cost is unnecessarily increased when such large phosphorus content is employed. We have found that in general a copper containing 0.015% to 0.025% phosphorus is optimum for use as anode metal in accordance with the invention. A phosphorus content in this range is sufficient to yield substantially the full benefits of the invention, is small enough so that rolled, cast, or extruded

anodes may be made by conventional methods for working copper, and does not add significantly to the cost of the metal. An amount of phosphorus in this range is appreciably more than is present as residual phosphorus in phosphorus-deoxidized copper of the "low residual phosphorus" type, but it substantially corresponds with the amount present in such copper of the "high residual phosphorus" type. Hence "high residual" phosphorus deoxidized copper as now commercially made is an excellent copper for use in accordance with this invention.

We have found that some advantage may be gained by including up to 0.01% of extraneously introduced silver, tellurium, selenium, or arsenic in the anode metal. These elements are commonly present as impurities in commercial refined copper, but an additional amount may be added to that normally present as an impurity to bring the total quantity of each of them to an upper limit of about 0.01%. Such additions are not necessary in order to secure the benefits of the invention, but under some conditions they have the advantage of making the black anode film adhere more tightly to the anode surface, and of making it somewhat more dense. At any rate no harm is done by making a small extraneous addition of any one or more of the metals silver, tellurium, selenium and arsenic to the phosphorus-bearing copper anode metal, and the invention contemplates doing so on an optional basis.

Anodes of phosphorus-bearing copper of the composition described above are employed in the usual manner in electroplating and other electrolytic operations. When the phosphorized anode has been in use a short time in a conventional aqueous electrolyte, it acquires a dull black coating which adheres tenaciously to its surface. As corrosion of the anode proceeds its surface remains smooth and free from pits and other surface irregularities that ordinarily characterize partially corroded anodes. About the only departure that is made from its original shape as the anode dissolves is that any initially sharp corners tend to become smoothly rounded. Such smooth surface is maintained until the anode has dissolved to the extent where the residual "fish" must be discarded; consequently the danger that the anode may deform and short-circuit with the cathode, and the danger that irregular corrosion may enable chunks of anode metal to drop off, are both greatly reduced. Hence corrosion of the new phosphorized anode may be allowed safely to proceed much farther than when conventional high purity anodes are used, with the result that the amount of copper lost in the discarded "fish" is considerably decreased.

The cathode deposit produced when using the phosphorus-bearing anode described above is fine-textured, smooth, and essentially free from nodular growths when a normal amount of glue or other sprout-inhibiting addition agent is present in the electrolyte. Cathode deposits of copper an eighth of an inch or more in thickness which possess a surface free from any pronounced pits or growths can be made using simply the phosphorized anodes in a conventional aqueous electrolyte. The cathode deposit is substantially pure copper, and is as free from phosphorus as is electrolytic copper generally.

Our present explanation as to why the phosphorized copper anodes are more satisfactory than high purity copper anodes, and the observations on which such explanation is based, insofar as anode dissolution and cathode deposition in acid electrolyte is concerned, are as follows: When ordinary high purity copper anodes are corroded in a conventional aqueous electrolyte solution of sulfuric acid and cupric sulfate, a large number of very loosely adherent fine metallic copper particles are formed at the anode. During the course of the electrolysis these particles become detached from the anode and form a sludge which mostly settles to the bottom of the electrolytic cell tank. Some of the fine copper particles, however, are carried in the electrolyte to the cathode, where they settle out on its surface. We have found that wherever one of these particles settle on the cathode, a nodular growth tends to appear. Contrary to general belief, we have definitely established that the size or number of such copper particles bears no relation to the grain size of the anode. However, comparison of photomicrographs of these particles with photomicrographs of the sludge formed by digesting cuprous oxide in sulfuric acid indicates that the copper particles formed under both sets of circumstances are the same in physical appearance and structure. From this and other evidence we conclude that the metallic copper sludge produced when conventional anodes are employed in an acid electrolyte is formed in the electrolyte adjacent to the anode by a reaction between the cuprous ions that are produced at the anode,

$$2Cu^{+} \rightarrow Cu^{\circ}\downarrow + Cu^{++}$$

(That such cuprous ions exist is proven by the fact that anode current efficiency with high purity copper anodes is commonly in excess of 100%.)

The foregoing reaction converts half of the cuprous copper entering the electrolyte into cupric ions, and converts the other half into finely divided metallic copper sludge. When anodes of phosphorized copper are used in accordance with the invention, no anode sludge of metallic copper particles is observed to form. Evidently the black adherent film on the face of the corroding anode holds back any cuprous ion or cuprous compound that is formed electrolytically, or, at any rate, inhibits the entry into the electrolyte of cuprous ions. This, it now seems, is the reason why the cathode deposit is so much superior, and why the copper losses are so much lower, when using phosphorized anodes than when using conventional high-purity anodes. Also, the film coating on the phosphorized anodes seems to inhibit more rapid dissolution of the anode at the grain boundaries or in other localized regions of the metal surface than elsewhere, except at sharp corners and edges where anode current densities are exceptionally high. In this manner the film seems to be responsible for the maintenance of a smooth surface, with nicely rounded edges, on the anode as it corrodes.

It is believed that the build-up of copper content in the electrolyte, characteristic of a cell using high purity anodes, results from the oxidation of copper by air dissolved in the acid electrolyte, and the consequent solution of the oxide in the acid. Most of this action probably takes place on the surface of the finely divided sludge particules, but attack on the anode itself probably also occurs. With phosphorus-bearing anodes, no sludge is produced and the anode is protected by a film; hence there is no source of copper to contribute to solution build-up.

However, whether or not these explanations be correct, the fact remains that the use of phosphorus-bearing copper anodes in electroplating and like operations using acid electrolytes leads

to the foregoing advantages. Also, although the chemistry of sludge formation as set forth above is not applicable to electroplating operations using an alkaline cyanide electrolyte, the herein described phosphorized copper anodes may nevertheless be employed successfully in operation using a cyanide electrolyte.

The effectiveness of phosphorus-bearing anodes quite clearly is not due to the fact that the copper is deoxidized. A small residual amount of phosphorous of the order of 0.005% in phosphorous-deoxidized copper of high purity does not yield a satisfactory anode metal, even though such metal is quite fully deoxidized. Also, deoxidizing agents such as silicon, cesium, boron, and calcium boride, when added to copper in sufficient amounts to effect substantially complete deoxidation of the metal and to leave a small residue of unconsumed deoxidizer, have all proved to be quite ineffective for forming any adherent film on anodes made of such copper, or for obtaining the above-described advantages of the invention. As a matter of fact, OFHC (oxygen-free high conductivity) copper has all the disadvantages of high purity tough pitch copper when employed as an anode.

In experimental runs employing the method of this invention using anodes having a phosphorus content of about 0.02% in a conventional acid electrolyte consisting fundamentally of an aqueous solution of cupric sulfate and sulfuric acid, and operating at an average current density of approximately 25 amperes per square foot, very smooth cathodes were produced with negligible copper loss due either to sludging or to build-up of copper sulfate in the electrolyte solution. Control runs made under the same conditions but employing commercially pure copper anodes on which no adherent film was formed resulted in a copper loss due to sludging and to copper build-up in the electrolyte of about 15% by weight of the original anodes. It was also found that owing to the extremity uniform corrosion of the phosphorized anode, it could be consumed until the residual "fish" remaining after the anode had been corroded to the maximum practical extent was much smaller than when commercially pure copper anodes were employed.

As hereinbefore noted, the addition of silver, arsenic, selenium, or tellurium in amounts up to 0.01% appears to make the black film which develops on the anode during the electrolytic operation somewhat more tenacious and somewhat denser. Accordingly the inclusion of a small amount of at least one of these metals extraneously added to the copper in an amount in excess of its normal impurity limit and up to 0.01% is within the scope of the invention.

The greater smoothness of thick cathode deposits produced according to the process of the invention as compared with similar deposits produced using commercially pure refined copper as the anode is quite striking visually. The smoothness of a partially or fully corroded phosphorized copper anode as compared with a correspondingly corroded anode of commercially pure copper is equally striking. These advantages, coupled with the considerable reduction or substantial elimination of copper losses due to sludge formation and to build-up of copper sulfate in the electrolyte, and the smallness of the residual anode "fish", make the process of this invention much more economical to carry out than a procedure involving the use of commercially pure copper anodes, which heretofore has been considered to represent the best practice in the electroplating of copper.

We claim:

1. A process for the electrodeposition of substantially pure phosphorus-free copper in which an electric current is passed from a soluble copper anode through an aqueous electrolyte to a cathode, characterized in that the anode is composed essentially of a phosphorus-bearing copper containing 0.01% to 0.1% phosphorus, impurities normally present in commercial refined copper, and the balance copper, whereby an adherent film forms upon the surface of the anode and the surface of the corroding anode remains smooth throughout its useful life.

2. A process for the electrodeposition of substantially pure phosphorus-free copper in which an electric current is passed from a soluble copper anode through an acid electrolyte to a cathode, characterized in that the anode is composed essentially of a phosphorus-bearing copper containing 0.015% to 0.025% phosphorus, impurities normally present in commercial refined copper, and the balance copper, whereby an adherent film forms upon the surface of the anode with the result that the presence in the electrolyte of minute particles of undissolved copper is minimized and the formation of a smooth cathode deposit substantially free of nodular growths is promoted.

3. A process for the electrodeposition of substantially pure phosphorus-free copper in which an electric current is passed from a soluble copper anode through an acid electrolyte to a cathode, characterized in that the anode is composed essentially of a phosphorus-bearing copper containing 0.01% to 0.1% phosphorus, impurities normally present in commercial refined copper, from 0.0005% to 0.01% of at least one of the elements selected from the group consisting of silver, tellurium, selenium, and arsenic, and the balance copper, whereby an adherent film forms upon the surface of the anode with the result that the presence in the electrolyte of minute particles of copper is minimized and the formation of a smooth cathode deposit substantially free of nodular growths is promoted.

4. A process for the electrodeposition of substantially pure phosphorus-free copper in which an electric current is passed from a soluble copper anode through an aqueous electrolyte to a cathode, characterized in that the anode is composed essentially of a phosphorus-bearing copper containing 0.015% to 0.025% phosphorus, impurities normally present in commercial refined copper, from 0.0005% to 0.01% of at least one of the elements selected from the group consisting of silver, tellurium, selenium, and arsenic, and the balance copper, whereby an adherent film forms upon the surface of the anode and such surface remains smooth throughout the useful corroding life of the anode.

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