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Juda et al.

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[54] **METHOD OF ELECTRODEPOSITION USING CATALYZED HYDROGEN**

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[51] **Int. Cl.**..... **C22d 1/00**

[58] **Field of Search** ..... 204/263, DIG. 3, 252, 108, 204/105 R, 106, 109, 248, 52

[56] **References Cited**

UNITED STATES PATENTS

3,124,520	3/1964	Juda	204/86
2,578,839	12/1951	Renzoni	204/263
1,239,443	9/1917	Antisell	204/263
1,371,698	3/1921	Linder	204/263 X
3,103,474	9/1963	Juda	204/104
3,214,362	10/1965	Juda	204/255
3,271,279	9/1966	Poor	204/108
214,344	4/1879	Andre	204/263 X

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[57] **ABSTRACT**

This disclosure deals with the novel use of a hydrogen anode, diffusion barrier and anolyte circulation for the electrodeposition of a metal of oxidation potential below that of hydrogen from a salt solution thereof and in controlled locations maintained apart from the hydrogen catalyst surface at the anode which normally would plate out the metal thereon.

8 Claims, No Drawings

METHOD OF ELECTRODEPOSITION USING CATALYZED HYDROGEN

The present invention relates to method of electrodeposition of metals and other elements from solutions thereof being more particularly directed to such deposition aided by the action of catalyst-activated hydrogen.

For over a century, copper and similar metals have been electroplated by passing electroplating currents between anodes and cathodes disposed in appropriate salt solutions of these metals. These techniques have proven commercially successful though they have had disadvantages, including the restriction to locations where considerable electrical power has been available at low cost.

It has also been known, as described, for example, in "The Properties of Solutions of Copper Salts in Pyridine and Quinoline," by M. Parris and R. J. P. Williams — Discussions Faraday Soc. No. 29,240-7 (1960)— that catalysts such as cuprous salts in pyridine and quinoline catalyze homogeneously the reduction of Cu^{++} by molecular hydrogen. High temperatures and pressures are required to carry out the hydrogen reduction without catalyst, as shown, for example, in United States Letters Patent No. 2,813,020 (1957) by G. F. van Hare, Jr. While these have been interesting examples of hydrogen reduction, it has not been feasible to employ hydrogen reduction for the purpose of commercially recovering metals in compact form; the metal is obtained as a powder which has limited commercial value.

While it has previously been proposed to use hydrogen anodes in cathodic metal electrodeposition processes, as described in the prior United States Letters Patent No. 3,103,474 of the applicant Walter Juda, when such technique is applied to metals of oxidation potential below that of hydrogen, the process becomes self-arresting because the hydrogen anode becomes rapidly covered by the metal, part of which is chemically reduced at the anode, thus requiring removal of the anode and cleaning before re-use. In accordance with a discovery underlying the present invention, on the other hand, it has been found that by preventing contact between the metal in solution and the hydrogen anode, it can be insured that the anode will not be contaminated by reduced metal over prolonged periods of time. Through the confining of the metal solution to the cathode region only, with assurance of contacting the hydrogen anode only by hydrogen ions, and by diffusing the acid through an anode-cathode-separating diaphragm in a direction such as to maintain the metal ion in the cathode region, it has now been discovered that continuous electrodeposition of metals below hydrogen in oxidation potential (such as copper and the noble metals, as later discussed) can be achieved at high current efficiencies, since hydrogen and metals of oxidation potential above that of hydrogen, such as iron, nickel, etc., impurities are also prevented from depositing at the cathode. In addition, no external battery or other potential source, as described in said patent, is essentially needed to produce this phenomenon. For these reasons, the method of this invention is particularly suited for the recovery of copper or the like from dilute acid leach solutions of low grade ores, for example, or for recovery of copper from spent impurity-laden electrolyte of copper electrorefining, as another example.

In accordance with this discovery, thus, the present invention enables obtaining the benefits of catalytically activated hydrogen while maintaining the metal ions or reduced metal from physical contact with the catalytic surface that activated the hydrogen — thus causing the metal or other elemental deposition not to occur upon the hydrogen catalyzing surface, but in predetermined areas where the recovery is highly commercial.

In summary, this result is effected through the interposition of a diffusion diaphragm or barrier between the metal salt or other solution and the catalytic surface, and the flowing of an appropriate generally acid solution through the diffusion barrier from the catalyst surface side thereof into the salt solution to prevent the flow of metal or other elemental ions or reduced metal in the opposite direction through the barrier toward the hydrogen catalyst surface. By the preferred technique of making the hydrogen catalyst surface a hydrogen anode and externally electrically connected with a conductive surface serving as a cathode in the salt solution, these ends are admirably served.

The invention will now be described with reference to certain preferred metals and elements, though its more general application will be evident from the description, it being deemed unnecessary in view of the simplicity and well-known character of the structure to illustrate the process steps by way of an apparatus figure or diagram.

Taking, for example, a preferred application to the deposition of copper in accordance with the present invention, this may be effected by inserting a cathodic copper or other conductive cathode surface which it is desired to plate, within a catholyte copper sulphate or similar preferably acidic salt solution of the copper, and externally electrically connecting the same by a direct connection to a platinum, palladium or similar conductive hydrogen catalyst surface, serving as an anode. A diffusion diaphragm or barrier separates the anode from the catholyte solution, with an acid such as, for example, sulphuric acid serving as an anolyte by being passed from the anode side of the barrier through the same toward the salt solution. This flow direction through the diffusion barrier has been found to prevent the reverse flow of copper ions back through the barrier toward the catalyst anode surface, though maintaining the anode in ionic contact with the salt solution, though out of physical contact therewith, and thus prevents the deposition of copper upon the catalyst as hydrogen is activated by the catalyst surface. Thus, the advantage of reducing the copper through the catalyst activation of hydrogen has been effected, but without the disadvantages of plating the copper upon the catalyst surface itself. Rather, the copper is deposited upon the cathode, preferably upon a copper cathode itself, positioned within the salt solution.

As a first example of an operational system of this character, approximately 21.3 milligrams of strongly adherent copper plate was deposited on the copper cathode surface in about 10 minutes from a 30 gram per liter copper sulphate catholyte and a 1.5 molar anolyte of sulphuric acid maintained at 55°–60°C. The anode was a 3.8 square centimeter platinum electrode having 4.5 milligrams of platinum per square centimeter, to which hydrogen gas was fed from one side. The before-mentioned sulphuric acid was introduced at the other side of the hydrogen anode and flowed under the influence of gravity through a glass frit diffusion bar-

rier, on the opposite side of which was disposed the copper sulphate solution containing the cathode. The diffusion barrier was about 2 to 3 millimeters thick and of such fine porosity that the gravity-fed flow of sulphuric acid into the salt solution was of the order of a few ml per minute. In the external electrical path between the anode and the cathode, which were connected through a resistor and an ammeter a current of 185 milliamps was measured, with the voltage developed in the cell across the electrodes being .08 volt, with an open-circuit voltage of 0.31–0.34 volts.

As a second example, increased plating was obtained by varying the resistance of the external direct electrical path or circuit. 185 milliamps was drawn, for example, with 0.050 volt appearing in the cell between the anode and cathode, with minimum external path resistance.

As a third example, in a system with the same concentration and operation, it was found that stirring the salt solution enabled increased plating to be produced. As an illustration, an increase up to 220 milliamps of current was obtained at 0.09 volts under the influence of such stirring action.

As a fourth example, the same experimental techniques and procedures were used in connection with other variants of copper sulphate solutions; specifically, a 3.06 gram per liter copper sulphate solution obtained from the TIMNA copper mines of Israel having a pH of about 1.6 was used as catholyte. Over a four-hour period, hydrogen was introduced into the anode at the rate of about 100 milliliters a minute, and again with gravity flowing the sulphuric acid through the frit diffusion barrier. 44 percent of the copper was removed by plating from the solution at a current efficiency of 80–90 percent. This removal again was effected by electrodeposition upon a circular copper cathode 4 centimeters in diameter. The normal current produced in the operation of this cell was of the order of 40 milliamps at an anodic current density of 10 milliamps per square cm. Over the greater portion of time, the cell was held at about 56°C. In this example, as in the earlier ones, the pH of the sulphuric acid was approximately that of the salt solution, though variations were possible.

As a fifth example, another metal than copper, similarly of oxidation potential less than that of hydrogen and thus reducible by hydrogen, was plated in the same manner; namely, silver. The salt solution was silver acetate containing about 1.0 grams per liter and acidified to a pH of 1.6 of sulphuric acid. The cathode was a wire mesh silver screen of circular configuration about 4 centimeters in diameter. Successful plating was observed over a period of about 30 minutes with an external circuit current of about 57 milliamps.

It is evident that this same method is equally applicable to the other metals below hydrogen in oxidation potential, including the noble metals.

Further modifications will occur to those skilled in this art and all such are considered to fall within the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. A method of depositing a metal of oxidation potential below and thus reducible by hydrogen from an acidic salt solution thereof, that comprises, disposing a hydrogen-ionizing catalyst in ionic but not physical contact with said solution, passing hydrogen along said catalyst to activate the hydrogen, establishing an electrically conductive path external to said solution between said catalyst, acting as a hydrogen anode, and a conductive surface in said solution, acting as an electro-deposition cathode, in order to produce an electrochemical cell, generating an electric current within said cell without requiring an external power supply and passing said current along said path in order to deposit elemental metal upon said conductive surface within said solution while maintaining the metal ions of said solution and the reduced metal from physical contact with said catalyst, said maintaining step comprising interposing a porous diffusion barrier between said solution and said catalyst and flowing an acidic solution through said diffusion barrier into said salt solution from the catalyst side of the barrier to prevent the flow of metal ions and reduced metal in the opposite direction through the barrier toward said catalyst.

2. A method as claimed in claim 1 and in which the said metal is selected from the group consisting of copper, mercury and the noble metals.

3. A method of depositing a metal of oxidation potential below and thus reducible by hydrogen from a salt solution thereof, that comprises, disposing a hydrogen-ionizing catalyst anode surface in ionic but not physical contact with said solution, passing hydrogen along said surface to activate the hydrogen, disposing a conductive cathode surface within said solution, establishing an electrically conductive path between the anode and cathodic surfaces external to said solution to produce an electrochemical cell, generating an electric current within said cell without requiring an external power supply and passing said current along said path in order to deposit the metal from said solution with the aid of the action of said activated hydrogen, interposing a porous diffusion barrier between said solution and said anode surface, and flowing a solution across said barrier from the anode side thereof to prevent the flow of ions of the metal and the metal in the opposite direction through the barrier.

4. A method of depositing copper from an acidic copper salt solution, that comprises, disposing a hydrogen-ionizing catalyst in ionic but not physical contact with said solution, passing hydrogen along said catalyst to activate the hydrogen, causing the activated hydrogen to reduce the copper in said solution to elemental copper, and establishing external to the solution an electrically conductive path between said catalyst and a conducting surface in said solution in order to form an electrochemical cell, generating an electric current within said cell without requiring an external power supply and passing said current along said path in order to deposit the elemental copper upon said conductive surface within said solution, and maintaining the copper ions of said solution and the reduced copper from physical contact with said catalyst by flowing an acidic solution through a porous diffusion barrier into said salt solution from the catalyst side of the barrier.

5. A method as claimed in claim 4 and in which said conductive surface comprises a copper surface.

6. A method as claimed in claim 4 and in which said catalyst is selected from the group consisting of platinum and palladium.

7. A method as claimed in claim 4 and in which said acidic solution comprises sulphuric acid.

8. A method as claimed in claim 4 and in which said salt solution comprises copper sulphate and said conductive surface comprises a copper surface.

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