FIG. 3
METHOD AND APPARATUS FOR PRODUCING COPPER FOIL BY ELECTRODEPOSITION

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8 Claims

ABSTRACT OF THE DISCLOSURE

Copper foil is produced by electrolytically depositing copper on a rotating titanium drum internally supported by an electrical conductive metallic structure having a greater thermal expansion characteristic than the titanium cathode drum. The supporting structure has a mating surface engaging the inner surface of the cylinder to provide an even electrical distribution on the cathode surface.

The invention relates to producing copper foil by electrodeposition on a moving cathodic surface and then stripping the electrodeposits from the surface. The invention is particularly directed to the provision of an improved method of carrying out the electrodeposition operation so as to produce an electrodeposited copper sheet of improved surface quality, of increased purity and of improved uniformity of gauge across the width of the cathode drum on which it is formed. The invention also provides improvements in the apparatus used for producing electrodeposited copper sheet in accordance with the new method.

Numerous proposals have been made heretofore for producing a variety of metals in sheet form by electrodeposition on a rotating drum cathode and sheet copper has been thus produced on a commercial scale for many years. The electrodeposition method has the advantage that sheets of wide width, thin gauge and indefinite long length can be produced. Heretofore, in the production of commercial grade copper foil, lead drums have been utilized extensively as cathodes upon which the copper was electrodeposited. The use of lead drums has a number of inherent disadvantages. For example, the oxide formed on the cathode surface during the plating process must be removed by grinding or polishing. Such operation increases the labor requirement and contributes substantially to the final costs of the copper foil. The grinding or polishing also accelerates the wear of the drum surface, leading to periodic resurfacing requirements; thus increases the down-time and the replacement costs. More particularly, the small lead particles generated from the grinding or polishing operation cause contamination of the copper foil and makes it unsuitable for application in electronic industry, such as for the production of printed circuits where only the high purity copper foil can be used.

Attempts to overcome the deficiencies of the electrodeposition process that use lead drums have not met with complete success. Prior attempts include the utilization of different types of cathodic surfaces such as stainless steel and chromium. The use of stainless steel as a cathode drum surface for copper foil production requires special electrolyte solution and operates at a comparatively low temperature not exceeding 105°F. Higher costs for the electrolyte and lower plating efficiency because of the temperature limitation offset the advantages that a stainless steel drum offers; consequently its use has yet to gain complete commercial acceptance. More recently, special chrome-plated drums are used for the production of premium grade copper foil suitable for the manufacture of printed circuits. This type of drum has a surface coating of unoxidized crack-free chromium. Successful plating of pure, thick solid copper foil by this drum is dependent on the chrome surface. Special preparation and frequent maintenance of the chrome surface of the drum is of extreme importance, not only that the proper type of chrome plating must be used and that the chrome plating is dressed just right, but the drum must also be specially maintained or it will cease to produce copper foil of suitable quality. Hence, chrome-plated drums of this type have only a limited application in the production of copper foil due to high costs of preparation and maintenance and cannot compete favorably with the existing lead drums for the production of commercial grade products.

I have now found that the disadvantages of the prior process can be substantially overcome by the method of this invention. In accordance with the present method, it is possible to produce high grade copper foil by electrodeposition of copper on a drum which is provided by engaging the inner surface of a titanium cylinder which has a substantially non-porous and smooth outer surface with a mating surface of an electrically conductive metallic structure. Advantageously, the outer surface is greater thermal expansion characteristics than titanium which enables the structure to expand at a higher temperature, such as the temperature used for the electrodeposition of copper, thereby forcing the mating surface to engage tightly and in substantially complete electrical contact with the inner surface of the titanium surface. In this method, the cathode drum is immersed partially in an electrolyte containing copper value and is connected to an electrical source to render the outer surface of the drum cathodic with respect to an electrode thereby forming an electrolytic cell. The rotation of the drum and the moving cathodic surface upon which the copper is electrodeposited. The copper foil thus formed is stripped from the cathodic surface. Preferably, the metallic structure is made of lead, which provides a number of advantages that will be apparent from the description presented hereinbelow.

Since titanium will not form oxide in the copper electrolyte, grinding or polishing is no longer required. The saving of labor by the method of this invention is further enhanced by the advantages of the drum which can be used with conventional copper plating baths at elevated plating temperatures in the range of 120°F. to 140°F. The resultant copper foil has high electrical conductivity, uniformity of gauge across the width and is substantially free of defects.

Preferably, the method of this invention is carried out in an apparatus comprising a cathode drum mounted for rotation on a horizontal axis, an anode mounted in a closely spaced relation with the cathode drum, means for providing an electrolytic solution between the anode and cathode to form an electrolytic cell for electrodeposition, and means for rotating the cathode drum to provide a continuous moving cathode surface. The cathode drum comprises an electrically conductive metallic supporting structure having a cylindrical mating surface and a titanium cylinder having an inner surface engaging the mating surface and a substantially non-porous and smooth outer surface serving as the continuous moving cathode surface.

The supporting structure has a greater thermal expansion characteristic than titanium, whereby during electrodeposition at an elevated temperature, thermal expansion of the metallic structure provides substantially complete electrical contact of the mating surface with the inner surface of the titanium cylinder thus providing an even electrical current distribution on the continuous moving cathode surface.

The use of titanium as a cathode for electrodeposition of copper has been suggested in the past. Its utilization as a
cathode drum, however, has been considered impractical because of the high cost of the metal and the inactivity in the platinum on other metals, particularly lead. The relative scarcity of the metal makes it too costly to be used solely for the construction of a cathode drum. Its low electrical conductivity further renders the cathode drum constructed completely from titanium metal undesirable. The low electrical conductivity of the metal requires more electricity and is not able to distribute the current evenly across the width of the drum surface causing unevenness of gauge in the copper foil. Attempts to solder titanium on other metals have not been too successful. Silver solder, for example, that can be used for soldering lead and titanium is not suitable because of its solubility in the copper electrolyte.

In contrast, the method of this invention not only successfully utilizes a titanium cathode surface, but also produces high quality copper foil of uniform gauge because of the even current distribution. The uniform distribution of electric current on the cathodic surface is contributed by higher electrical conductivity of the supporting structures and by the total engagement of the mating surface of the supporting structure and the inner surface of the titanium cylinder. The better conductive metallic supporting structure further reduces the power consumption. Since a lead drum has been used principally for the production of commercial copper foil, the present invention has still another advantage of utilizing as the supporting structure the used lead drums which require resurfacing. In such instances, only a thin sheet of titanium plate is required for the construction of the drum.

A preferred embodiment of the method and apparatus of the invention is described hereinbelow with reference to the accompanying drawings wherein:

FIG. 1 is an elevation, partially in section, through apparatus for producing sheet copper by electrolysis on a rotating drum cathode;

FIG. 2 is a vertical view partly in section taken along line 2—2 of FIG. 1; and

FIG. 3 is a sectional view of the drum taken along line 3—3 of FIG. 2.

The apparatus shown in FIG. 1 comprises a tank 10 of conical or other material which is provided internally with a lining 11 of lead and is supported on piers 12. An electrolyte conduit 13 provides for introducing electrolyte intermittently or continuously, as desired, into the tank, and an electrolyte outlet conduit 14 receives the overflow of electrolyte from the tank and provides for maintaining a desired level of electrolyte in the tank. A filled drain pipe 15 is provided for emptying the tank whenever necessary.

A cylindrical cathode drum 16 is supported by an axial shaft 17 which extends through bearings 18 mounted on the sides of the tank 10 (see FIG. 2). The drum is slowly rotated in the direction indicated by the arrows by means of a sprocket chain 19 engaging sprocket wheels 20 and 21 mounted respectively on the drum shaft 17 and on a drive shaft 22. The drive shaft is continuously rotated by a motor (not shown).

The cathode drum 16 extends about half into and half out of the tank 10. A pair of cylindrically curved anodes 23 and 24 are mounted in the tank, in close proximity to the two lower quadrants of the cylindrical face of the cathode. Only narrow annular electrolyte spaces 25 and 26 are left between the anodes and the adjacent face of the cathode. The heavy anodes are supported in place by vertical support plates 27 mounted on brick piers 28. Electrical connections to the anodes are made through bus bars 29.

When a direct electric current is passed (at sufficient voltage) from the anodes 23, 24 through copper-bearing electrolyte in the electrolyte spaces 25, 26 to the cathode drum 16, copper is electrodeposited on the cylindrical face of the drum. As the drum rotates, this deposit is carried to above the surface of the electrolyte in the tank 10. There it is separated as a sheet 30 from the face of the drum by passing it over a stripping roll 31 that is wound into a coil 32 on a coil core 33. The coil core is mounted on a shaft 34 which is continuously driven by a sprocket chain 35 from the drive shaft 22, in order to maintain the copper sheet 30 under tension as it is stripped from the drum.

A discharge manifold 36 is mounted between the spaced adjacent lower edges of the anodes 23 and 24, where it extends parallel to the surface of the cathode drum adjacent the line of deepest immersion thereof. The discharge manifold is supported in place by means of a pair of end brackets 37 (only one of which is shown in FIG. 1) and one or more center brackets 38. A solution inlet conduit 39 is provided for admitting electrolyte to the distribution compartment 40 of the distribution manifold 36 and deliver it to the discharge compartment 41.

As indicated in FIG. 1, the discharge manifold is so mounted that the solutions of electrolyte introduced in the discharge openings (not shown) are delivered into the narrow electrolyte spaces 25 and 26 between the anodes and the cathode face of drum 16. The solution inlet conduit 39 is connected to a valve supply pipe 42 through which electrolyte solution under pressure is delivered to the distribution compartment 41.

In operation of the above-described apparatus, the tank 10 is filled with a suitable electrolyte, e.g., an acidic aqueous solution of copper sulfate. A source of direct current is connected to the cathode drum 16 and to the anodes 23 and 24. The drive shaft 22 is set in operation, whereby the drum 16 is slowly rotated (in a counterclockwise direction as viewed in FIG. 1). The voltage between anodes and cathode is high enough so that copper is electrodeposited from the electrolyte in the spaces 25 and 26 between anodes and cathode on to the surface of the cathode drum. As the drum rotates, this electrodeposited is carried to above the surface of the electrolyte in the tank. Conventionally, the deposit on the drum is carefully washed to remove residual electrolyte (by washing means not shown in the drawings). The electrolyte then is stripped from the face of the drum in the form of the thin sheet 30 and is wound into the coil 32.

Electrolyte solution is introduced continuously and under pressure from the supply pipe 42 through the inlet conduit 39 to the discharge manifold 36. This electrolyte, which enters the distribution compartment 40 and is distributed thereby to the several discharge sub-compartments 41, is forcibly projected as a series of high velocity streams through the discharge outlets into the electrolyte spaces 25 and 26. The electrolyte of these streams, together with electrolyte present in the tank and which is set into circulation by the force of the streams, flows upwardly through the electrolyte spaces toward the surface of the electrolyte at each side of the drum. Thus the electrolyte between the anodes and the cathode is continuously maintained in fast flowing turbulent motion and is continuously renewed and replenished.

FIG. 2 and FIG. 3 show the sections of the cathode drum which comprises three lead spiders 46, 47 and 48 mounted on the drum shaft 17. Each of the spiders has 6 spoks 49 supporting a lead cylinder 50 which has an outer mating surface 51 engaging the inner surface 52 of a titanium cylinder 53. In a typical size, the drum measures 84" x 64". The titanium cylinder has a thickness of 0.333 inch and can be made of C.P. grade titanium.

Conventional operating conditions are applicable in practicing the method of this invention. Typical conditions for producing a 1 ounce foil with an 84" O.D. titanium drum and a plating bath which contains 50 g./l. copper and 180 g./l. H₂SO₄ are: a temperature about 130° F; current density 180 amps per sq. ft.; and a drum
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(rotational rate of 15 inches per minute. The electrolyte flow into the bank at a rate of 25 gallons per minute.

I claim:

1. A method of producing copper foil by electrolytically depositing copper on a moving cathodic surface which comprises providing a titanium cylinder having a substantially non-porous and smooth outer surface and an inner surface, engaging the inner surface of said cylinder with a mating surface of an electrically conductive metallic structure having a greater thermal expansion characteristic than said cylinder, partially immersing said cylinder in an electrolyte containing copper value, connecting said metallic structure to an electrical source to render the outer surface of said cylinder cathodic with respect to at least one additional electrode to form an electrolytic cell, rotating said cylinder to provide the moving cathodic surface, electrolytically depositing copper to said moving cathodic surface at a temperature sufficient to cause a substantially complete engagement of said mating surface and the inner surface of the cylinder, thereby providing an even electrical distribution on said cathodic surface and continuously stripping the resultant copper foil from said moving cathodic surface.

2. A method according to claim 1 wherein said metallic structure is lead.

3. A method according to claim 2 wherein the electrolytic deposition of copper is conducted at an elevated temperature in the range of 120° F. to 140° F.

4. Apparatus for producing copper foil by electrodeposition from an electrolytic solution containing copper value which comprises a cathode drum mounted for rotation on a horizontal axis, an anode mounted in closely spaced relation with the cathode drum, means for providing an electrolytic solution between said anode and cathode to form an electrolytic cell for electrodeposition and means for rotating said cathode drum to provide a continuous moving cathodic surface, said cathode drum comprising an electrically conductive metallic supporting structure having a cylindrical mating surface and a substantially non-porous and smooth outer surface serving as the continuous moving cathodic surface, said supporting structure having a greater thermal expansion characteristic than titanium whereby during the electrodeposition at an elevated temperature, thermal expansion of said metallic structure provides substantially complete electrical contact of said mating surface with the inner surface of said titanium cylinder thus providing an even electrical distribution or the continuous moving cathode surface.

5. Apparatus according to claim 4 wherein said electrically conductive metallic structure has a layer of lead in the form of a cylinder to provide said outer mating surface for engagement with the inner surface of said titanium cylinder.

6. Apparatus according to claim 4 wherein said cathode drum comprises:
   (a) an electrically conductive metallic structure having a central axle, lead spokes extending outwardly from said axle and a layer of lead in the form of a cylinder supported by said spokes, and
   (b) a titanium cylinder having an inner surface engaging the outer surface of said layer of lead and substantially non-porous and smooth outer surface serving as the continuous moving cathodic surface.

7. Apparatus according to claim 6 wherein said titanium cylinder is made of C.P. grade titanium.

8. Apparatus according to claim 6 wherein said metallic structure is made of commercial grade lead.

References Cited

UNITED STATES PATENTS

2,429,902 10/1947 Sternfels
2,646,396 7/1953 Dean
2,865,830 12/1958 Zoldas
3,151,048 9/1964 Conley et al.

FOREIGN PATENTS

395,002 7/1933 Great Britain.

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204—216