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(54) PROCESS FOR PRODUCING COPPER FOIL BY ELECTROLYTIC DEPOSITION OF COPPER

(57) The invention relates to a process for producing copper foil by electrolytic deposition of copper metal on a rotating drum cathode and, in particular, to the means for dissolving the copper to be deposited in the process. In the process, copper is electrolytically deposited on a rotating drum cathode, which is partially immersed in an electrolyte solution contained in a plating tank; the deposited copper layer is peeled off the part of the drum cathode that is not immersed in the electrolyte solution to obtain the copper foil; an insoluble anode is used as counterelectrode to the drum cathode; the electrolyte solution contains copper ions, organic additives and an Fe^{2+}/Fe^{3+} redox system; the concentration of copper ions in the electrolyte solution is maintained constant by passing the electrolyte solution through a copper dissolution unit; in the copper dissolution unit, the electrolyte solution is in contact with an auxiliary anode and an auxiliary cathode; copper metal and an oxygen-containing gas are introduced into the copper dissolution unit; the auxiliary anode is in contact with the copper metal; the oxygen-containing gas contacts the surface of the copper metal; the copper metal continuously dissolves into the electrolyte solution by being oxidized by the Fe^{3+} component of the Fe^{2+}/Fe^{3+} redox system.

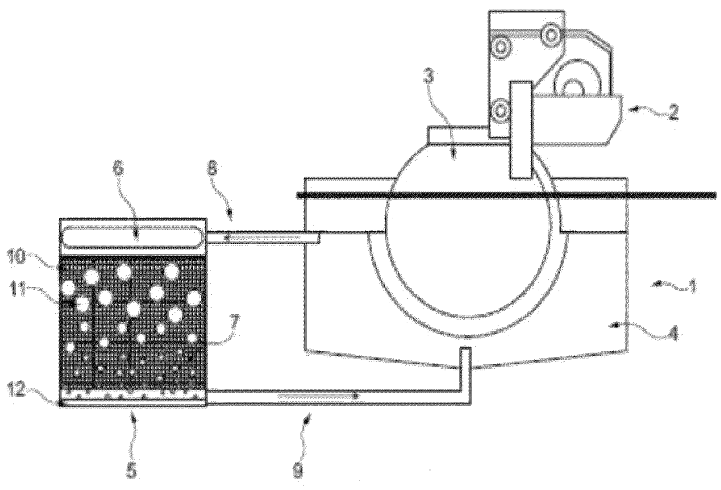

FIG. 2

Processed by Luminess, 75001 PARIS (FR)

Description

Field of the invention

[0001] The present invention relates to a process for producing copper foil by electrolytic deposition of copper metal on a rotating drum cathode and, in particular, to the means for dissolving the copper to be deposited in the process.

Prior art

[0002] It is known to produce copper foil by a continuous process, wherein copper is electrolytically deposited (plated) on a rotating drum cathode, which is partially immersed in an electrolyte solution contained in a plating tank, the copper layer deposited on the drum cathode is peeled off the part of the cathode that is not immersed in the electrolyte solution to obtain the copper foil, and an insoluble anode is used as counter-electrode to the drum cathode. Such a process is described, for example in US 2002/0064019 A1, which relates to a cathode electrode material and rotating cathode drum for electrolytic copper foil production.

[0003] In such a process, the electrolyte solution typically contains copper sulfate, sulfuric acid, chloride and organic compounds. Current densities are in the range of 50 to 80 A/dm^2 and treatment times around 60 seconds at 50 °C. Drum speeds vary between 7 m/min (for copper foils for lithium batteries) and 25 m/min (for copper foils for printed circuit boards). Copper foils manufactured in this way can have lengths of several kilometers.

[0004] In such a process, titanium anodes coated with MOX are typically used as insoluble anodes. During plating, oxygen is created at the anode surface and turns the electrolyte into a milky blue solution. The oxygen bubbles can lead to plating defects and the damage of the anodes.

[0005] The copper deposited from the electrolyte solution onto the drum cathode needs to be replaced continuously so as to keep the copper concentration in the electrolyte solution constant.

[0006] In the conventional process, this is done by withdrawing the electrolyte from the plating tank and transferring it to a copper dissolution tank as shown in Fig. 1. The two tanks on the lefthand side are the copper dissolving tanks (sometimes up to 250,000 l electrolyte), where the solution is heated up to 80 °C and air is blown into the electrolyte to enable/enhance the dissolution of copper metal.

[0007] Due to oxygen development at the anode, heating the solution to up to 80 °C and blowing air into the dissolution tank, the organic compounds contained in the electrolyte solution are destroyed and exist as undefined organic compounds which need to be removed. Therefore, the third tank (approx. 5,000 l) from the left (right to the two solution tanks) takes care of the destroyed organics. Here active carbon is mixed into the solution. The active carbon then absorbs the organic compounds and is subsequently removed by filtration. The spent active carbon must then be disposed of. After filtering the active carbon from the copper solution, the electrolyte is stored in another tank. Here, the electrolyte is cooled down to about 50 °C and the missing organic electrolyte compounds are added before the solution is transferred back into the plating tank of an apparatus containing the drum cathode and the device to peel off the copper foil.

[0008] WO 95/18251 A1 describes a process and device for the electrolytic deposition of metallic layers wherein insoluble anodes are used for the electrolytic deposition of uniform metallic layers having determined physico-mechanical properties, in particular copper layers. In the process, compounds of a redox system, comprising e.g. Fe^{2+}/Fe^{3+}, are added to the deposition solution and react at the insoluble anodes during deposition. The resulting compounds draw new metal ions out of part of a reservoir that contains the metal to be deposited in order to replace the metal ions deposited from the solution. In the process, the additive compounds are not destroyed (to a larger extent).

[0009] WO 01/68953 A1 describes a method and device for the regulation of the concentration of metal ions in an electrolyte for the electrolytic deposition of metals, the electrolyte containing additional substances of an electrochemically reversible redox system. According to the method at least a part of the electrolyte is passed through an auxiliary cell, comprising an insoluble auxiliary anode and at least one auxiliary cathode, between which a flow of current is generated by application of a voltage. Excess amounts of the oxidized material from the redox system are thus reduced at the auxiliary cathode and the formation of ions of the metal to be deposited is avoided. According to the method, pieces of the metal to be deposited are used as the auxiliary cathode.

[0010] The above conventional method to produce copper foil is disadvantageous in that it consumes large amounts of energy, it consumes large amounts of active carbon which, when spent, needs to be disposed of as industrial waste, and the device is relatively complex and, thus, requires significant maintenance effort.

[0011] Thus, it is an object of the invention to provide a continuous process for the production of copper foil wherein copper is electrolytically deposited on a rotating drum cathode, which process avoids the disadvantages of the prior art, in particular, which consumes lower amounts of energy and no significant amounts of active carbon and which can be carried out by means of a relatively simple device requiring reduced maintenance effort.

Summary of the invention

[0012] The invention relates to a continuous process for producing copper foil by electrolytic deposition of copper metal on a rotating drum cathode and, in particular, to the means for dissolving the copper to be deposited in the process; the process consumes low amounts of energy and no significant amounts of active carbon and can be carried out by means of a relatively simple device requiring reduced maintenance effort. In the process, copper is electrolytically deposited on a rotating drum cathode, which is partially immersed in an electrolyte solution contained in a plating tank; the copper layer deposited on the drum cathode is peeled off the part of the drum cathode that is not immersed in the electrolyte solution to obtain the copper foil; an insoluble anode is used as counter-electrode to the drum cathode; the electrolyte solution contains copper ions, organic additives and an Fe^{2+}/Fe^{3+} redox system; the concentration of copper ions in the electrolyte solution is maintained constant by passing the electrolyte solution through a copper dissolution unit; in the copper dissolution unit, the electrolyte solution is in contact with an auxiliary anode and an auxiliary cathode; copper metal and an oxygen-containing gas are introduced into the copper dissolution unit; the auxiliary anode is in contact with the copper metal; the oxygen-containing gas is introduced such that bubbles thereof contact the surface of the copper metal; the copper metal continuously dissolves into the electrolyte solution by being oxidized by the Fe^{3+} component of the Fe^{2+}/Fe^{3+} redox system and optionally the oxygen contained in the oxygen-containing gas.

[0013] The object of the invention is achieved by the process according to claim 1; preferred embodiments thereof are defined in the dependent claims.

[0014] In the process according to the invention, relatively large amounts of copper per unit time are removed from the electrolyte solution due to deposition on the drum cathode and drag out. For example, when the drum cathode has a diameter of 2.0 m and a width of 1.5 m and a half thereof, i.e. a surface of 4.7 m^2, is immersed into the electrolyte and when the current density at the drum cathode is 65 A/dm^2, approximately 35.5 kg of copper will be deposited per minute; furthermore, at a relatively high rotation speed of typically 7 m/min, a significant amount of electrolyte solution is dragged out of the plating tank due to adhesion to the drum cathode (typically, 100 ml/m^2).

[0015] In order to keep the copper concentration in the electrolyte solution constant, fresh copper metal is continuously dissolved into the electrolyte solution by passing the electrolyte solution through the dissolution unit, into which copper metal is introduced.

[0016] The copper metal may be introduced into the dissolution unit in the form of copper clippings. The copper metal (e.g. clippings) may be placed in a basket made of an inert metal such as titanium. The basket then functions as the auxiliary anode.

[0017] The copper metal continuously dissolves into the electrolyte solution by being oxidized by the Fe^{3+} component of the Fe^{2+}/Fe^{3+} redox system. This dissolution process is described by the following chemical equation:

$$Cu^0 + 2\,Fe^{3+} \rightarrow Cu^{2+} + 2\,Fe^{2+}$$

[0018] The Fe^{3+} is generated predominantly by oxidation of Fe^{2+} at the insoluble anode used as counter-electrode to the drum cathode in the plating tank.

[0019] An oxygen-containing gas, e.g. air, is introduced into the dissolution unit such that bubbles thereof contact the surface of the copper metal, for example by bubbling the oxygen-containing gas, into the dissolution unit at a location beneath a basket containing the copper metal in the form of copper clippings to generate moderate gas agitation around the surface of copper metal.

[0020] This has two effects. First, turbulence at the copper metal surface increases, therefore the dissolving reaction increases in speed. Second, oxygen from the oxygen-containing gas acts as additional oxidizer (beside the anodic potential of the auxiliary anode which contacts the copper metal) to oxidize further Fe^{2+} to Fe^{3+}, which then dissolves additional copper metal.

[0021] However, the generation of excessive amounts of Fe^{3+}, which does not react with the copper metal and which is then transferred to the plating tank, should be avoided because Fe^{3+} contacting the drum cathode would reduce the copper deposition efficiency. Therefore, all Fe^{3+} should be transformed into Fe^{2+} after passing the copper metal in the copper dissolution unit.

[0022] To ensure this, the copper metal (e.g. copper clippings) in the dissolution unit is in electrical contact with the auxiliary anode. As the cathodic potential during copper deposition becomes higher, the anodic potential during copper dissolution increases. When leaving the dissolution unit, the electrolyte solution passes the auxiliary cathode, i.e. a metallic device (e.g., mesh), which has a positive potential; this potential has to be lower than the positive potential for copper deposition within the dissolving tank. Both, the copper metal at a negative potential and the auxiliary cathode with a positive potential will eliminate any existing Fe^{3+} ions. The current efficiency at the drum cathode will thus remain close to 100 %.

[0023] Both, (i) the anodic potential of the copper metal introduced into the dissolution unit and (ii) the gas agitation created by the introduction of the oxygen-containing gas such that bubbles thereof contact the surface of the copper metal, speed up the dissolution reaction of the copper metal. Thus, the copper concentration in the electrolyte solution can be effectively controlled and thereby kept within a narrow and high concentration range required for efficient and constant deposition of copper on the drum cathode by (i) controlling the potential applied to the auxiliary anode (i.e. the voltage between the auxiliary anode and the auxiliary cathode) and (ii), to a lesser extent, by controlling the intensity of the gas agitation.

[0024] In the process according to the invention, the electrolyte solution contains an Fe^{2+}/Fe^{3+} redox system, i.e. a combination of ferrous and ferric compounds. Fe^{3+} ions are generated predominantly by oxidation of Fe^{2+} at the insoluble anode and, after they are transferred to the dissolution unit, then act as an oxidant to oxidize copper metal to Cu^{2+} and thereby dissolve the copper metal into the electrolyte solution.

[0025] Thus, there is a continuous process in which copper metal is oxidized by Fe^{3+} in the dissolution unit, then transferred to the plating tank and reduced again to copper metal at the drum cathode while, at the same time, Fe^{3+} is reduced to Fe^{2+} by the copper mental as well as the auxiliary cathode in the dissolution unit and, after the Fe^{2+} has been transferred to the plating tank, it is oxidized to Fe^{3+} again.

[0026] This use of an Fe^{2+}/Fe^{3+} redox system as a means to dissolve copper metal in the large amounts required in a process for producing copper foil and in a well-controlled manner has the following advantages compared to conventional processes for producing copper foil:
Firstly, the oxidization of Fe^{2+} to Fe^{3+} at the insoluble anode competes with, and thus suppresses oxygen evolution and organic additive burning at the anode. Thus, consumption of organic additives (and the ensuing generation of contaminating decomposition products) is only due to the copper deposition processes at the drum cathode. Thereby, the total organic content (TOC) of the electrolyte solution remains low and extends the plating bath lifetime. Additionally, due to avoiding oxygen development at the anode, the lifetime of the anode is greatly increased.

[0027] Secondly, due to the oxidation of Fe^{2+} to Fe^{3+} at the insoluble anode and Fe^{3+} being an efficient oxidant for copper metal, there is no need to increase the temperature of the electrolyte solution for copper dissolution to temperatures of about 80 °C as is necessary in the conventional processes for producing copper foil. The Fe^{3+} generated at the insoluble anode will act as oxidant together with the oxygen-containing gas introduced into the dissolution unit and dissolves the copper metal. The temperature can remain at about 50 °C, i.e. the same as in the plating tank.

[0028] Thirdly, as lower amounts of organic compounds are destroyed, the use of active carbon to remove decomposition products becomes redundant.

[0029] Fourthly, a separate step of cooling the electrolyte solution down again to about 50 °C is not needed. Based on a simple online analysis, the organic compounds which were consumed during copper deposition only need to be replenished.

[0030] Fifthly, the addition of Fe^{2+}/Fe^{3+} lowers the required voltage to achieve a current density of 50 A/dm^2 by more than 25 %, as no oxygen bubbles are created at the insoluble anode. For example, in one experiment, 20 g/l of Fe^{2+} was added to a plating solution containing 60 g/l of Cu^{2+}, 150 g/l of H_2SO_4, 40 mg/l of Cl^-, 3 ml/l of conventional brightener, 11 ml/l of conventional carrier, and 5 ml/l of conventional levelling agent, at 50 °C with a cell current of 40 A; the cell voltage dropped after Fe^{2+} addition from 3.2 V down to 2.4 V.

Brief description of the drawings

[0031]

Figure 1 is a diagrammatic depiction of an apparatus for producing copper foil by a conventional process (Prior Art).

Figure 2 is a diagrammatic depiction of an apparatus for producing copper foil by the process according to the invention.

Description of embodiments

[0032] In the continuous process for producing copper foil according to the invention, copper is electrolytically deposited on a rotating drum cathode which is partially immersed in an electrolyte solution; the electrolyte solution contains copper ions, organic additives and an Fe^{2+}/Fe^{3+} redox system. The invention is explained by referring to an apparatus shown in Fig. 2, which can be used with the inventive process. The apparatus in Fig. 2 can be seen as an example. The apparatus is not necessarily limiting the inventive process.

[0033] As the electrolyte solution, an aqueous acidic copper plating bath is preferably used. Such baths are known from the prior art, for example from EP 0 690 934 A1. The basic composition of the electrolyte solution bath can vary within relatively large boundaries. In general, an aqueous solution of the following composition is used: copper sulfate ($CuSOa \cdot 5\ H_2O$): 20-250 g/l, preferably 80-140g/l or 180-220g/l; conc. sulfuric acid: 50-350 g/l, preferably 180-280 g/l or 50-90 g/l; iron (II) sulfate ($FeSOa \cdot 7\ H_2O$): 0.1-50 g/l, preferably 5-15 g/l; chloride ions (added for example as NaCl):

0.01-0.18 g/l, preferably 0.03-0.1 g/l. Instead of copper sulfate, other copper salts can be used at least in part. Even the sulfuric acid can be partly or wholly replaced by fluoroboric acid, methanesulfonic acid or other acids. That is, the electrolyte solution can be free or substantially free of sulfuric acid and/or sulfate salts. In particular, the electrolyte solution can contain methanesulfonic acid and the iron and/or copper salts thereof.

[0034] The chloride ions are added as alkali chlorides, for example sodium chloride or in the form of hydrochloric acid. The addition of sodium chloride can be dispensed with wholly or partly if halogen ions are already contained in the supplements.

[0035] The electrolyte solution contains an Fe^{2+}/Fe^{3+} redox system. The Fe^{2+}/Fe^{3+} redox system can be formed from iron (II) sulfate heptahydrate. It is particularly suited to regenerating copper ions in aqueous, acidic copper baths. However, other water soluble iron salts, for example the iron salt of methanesulfonic acid and iron (III) sulfate nonahydrate, can also be used as long as the salts contain no biologically non-degradable (hard) complexing agents in the compound since the latter present problems during waste disposal (e.g. iron ammonium alum).

[0036] The organic additives contained in the electrolyte solution comprise, in particular, at last one brightener, at least one levelling agent and at least one carrier. Thus, the electrolyte solution generally contains copper ions (preferably, Cu^{2+} ions), Fe^{2+} ions, an acid, chloride ions, a brightener, a levelling agent and a carrier.

[0037] The brightener can be an organic sulfur-containing compound; this is preferably selected from one or more compounds selected from the group consisting of organic thiol, sulfide, disulfide and polysulfide compounds, preferably selected from the group consisting of 3-(benzthiazolyl-2-thio)-propylsulfonic acid, 3-mercaptopropane-1-sulfonic acid, ethylendithiodipropylsulfonic acid, bis-(p-sulfophenyl)-disulfide, bis-(w-sulfobutyl)-disulfide, bis-(w-sulfohydroxypropyl)-disulfide, bis-(ω-sulfopropyl)-disulfide, bis-(ω-sulfopropyl)-sulfide, methyl-(w-sulfopropyl)-disulfide, methyl-(ω-sulfopropyl)-trisulfide, O-ethyl-dithiocarbonic acid S-(w-sulfopropyl) ester, thioglycol acid, thiophosphoric acid O-ethyl-bis-(w-sulfopropyl) ester, 3-N,N-dimethylaminodithiocarbamoyl-1-propanesulfonic acid, 3,3'-thio-bis(1-propanesulfonic acid), thiophosphoric acid tris-(w-sulfopropyl)-ester and their corresponding salts. The concentration of all brightener compounds (in total) present in the electrolyte solution preferably ranges from 0.01 mg/l to 100 mg/l, more preferably from 0.05 mg/l to 10 mg/l still more preferably 0.1 to 5 mg/l.

[0038] The levelling agent can be a nitrogen-containing compound; this is preferably selected from one or more compounds selected from the group consisting of a ureylene polymer, polyethyleneimine, alkoxylated polyethyleneimine, alkoxylated lactams and polymers thereof, diethylenetriamine and hexamethylenetetramine, polyethylenimine bearing peptides, polyethylenimine bearing amino acids, polyvinylalcohol bearing peptides, polyvinyl alcohol bearing amino acids, polyalkyleneglycol bearing peptides, polyalkyleneglycol bearing amino acids, aminoalkylene bearing pyrroles and aminoalkylene bearing pyridines, organic dyes such as Janus Green B, Bismarck Brown Y and Acid Violet 7, sulfur containing amino acids such as cysteine, and phenazinium salts. The levelling agent is added to the electrolyte solution (in total) in amounts of 0.5 mg/l to 400 mg/l, preferably 0.1 mg/l to 100 mg/l.

[0039] The carrier can be an oxygen-containing compound; this is preferably selected from one or more compounds selected from the group consisting of polyvinylalcohol, carboxymethylcellulose, polyethylenglycol, polypropylenglycol, stearic acid polyglycol ester, alkoxylated naphtoles, oleic acid polyglycol ester, stearylalcoholpolyglycol ether, nonylphenolpolyglycol ether, octanolpolyalkylenglycol ether, octanediol-bis-(polyalkylenglycol ether), poly(ethylenglycol-ran-propylenglycol), poly(ethylenglycol)-block-poly(propylenglycol)-block-poly(ethylenglycol), and poly(propylenglycol)-block-poly(ethylenglycol)-block-poly(propylenglycol). The concentration of the carrier compounds (in total) preferably ranges from 0.005 g/l to 20 g/l, more preferably 0.01 20 g/l, still more preferably from 0.01 g/l to 5 g/l.

[0040] The inventive process can be conducted in an apparatus, comprising a plating device **1** having a plating tank with the electrolyte solution **4** with a rotating drum cathode **3**, a peeling device **2** and a Cu dissolution unit **5**, as shown in Fig. 2. In the process for producing copper foil according to the invention, copper is electrolytically deposited on a rotating drum cathode **3**, which is partially immersed in an electrolyte solution **4** contained in a plating tank. The drum cathode typically has a diameter of 0.5 to 4.0 m, preferably 1.5 to 2.5 m. The drum cathode typically has a width of 0.5 to 3.0 m, preferably 1.0 to 2.0 m. The current density at the drum cathode is typically 20 to 100 A/dm^2, preferably 30 to 80 A/sm^2, more preferably 40 to 70 A/dm^2. The rotation speed of the drum cathode is typically 1 to 15 m/min, preferably 5 to 10 m/min. The amount of copper deposited on the drum cathode is typically 10 to 50 kg/min, preferably 30 to 40 kg/min. The thickness of the copper foil produced by the process according to the invention is typically 2 to 30 μm, preferably 5 to 20 μm, more preferably 7 to 12 μm.

[0041] In the process for producing copper foil according to the invention, an insoluble anode is used as counter-electrode to the drum cathode. The current density at the insoluble anode is typically > 20 A/dm^2.

[0042] In the process for producing copper foil according to the invention, copper is electrolytically deposited on a rotating drum cathode, typically at a temperature of 15 to 70°C, preferably 25 to 60 °C, more preferably 40 to 50°C.

[0043] In the process for producing copper foil according to the invention, the concentration of copper ions in the electrolyte solution is maintained constant by passing the electrolyte solution through a copper dissolution unit. Thereby, the concentration of copper ions in the electrolyte solution present in the plating tank is typically 80 to 90 g/l. The concentration of Fe^{3+} ions in the electrolyte solution present in the plating tank is typically < 5 g/l, preferably < 5 g/l.

[0044] That is, a part of the electrolyte solution present in the plating tank is continuously or periodically withdrawn from the plating tank and transferred to the dissolution unit.

[0045] Preferably, this is done such that the part of the electrolyte solution withdrawn according to Fig. 2 from the plating tank is introduced into the Cu (copper) dissolution unit **2** at a location that is closer to the auxiliary cathode as a cathode mesh **6** than to the auxiliary anode as an anode mesh 7 so that the withdrawn part comes into contact with the auxiliary cathode first.

[0046] The part of the electrolyte solution withdrawn from the plating tank contains Fe^{3+} ions at a relatively high concentration (Fe^{3+}rich solution **8**) and Fe^{2+} ions at a relatively low concentration. In the Cu dissolution unit, the Fe^{3+} plus ions contribute to the oxidation of copper metal (which thereby dissolves) and are thereby reduced to Fe^{2+} ions. Therefore, after it has passed through the Cu dissolution unit, the electrolyte solution contains Fe^{3+} ions at a relatively low concentration and Fe^{2+} ions at a relatively high concentration (Fe^{2+}rich solution **9**).

[0047] In the copper dissolution unit, the electrolyte solution **4** is in contact with an auxiliary anode **7** and an auxiliary cathode **6.** A voltage is applied between the auxiliary anode and the auxiliary cathode. This voltage is typically 1 to 9 V, preferably 2 to 4 V. The auxiliary anode is in contact with the copper metal **10.** The application of this voltage and the copper metal being in contact with the auxiliary anode promotes the dissolution of the copper metal introduced into the dissolution unit such that relatively large amounts of copper can be dissolved per time unit. This dissolution is also promoted by the introduction of an oxygen-containing gas into the Cu dissolution unit such that bubbles **11** thereof contact the surface of the copper metal. The oxygen-containing gas can be air, preferably is air, more preferably hot air bubbles. The air can be introduced by an air blower **12.**

[0048] The auxiliary cathode and anode can be made of any kind of conductive and dimensionally stable material. The size of the dissolution unit is not particularly limited and can be adapted to the requirements of the process for producing copper foil, especially the amount of copper foil to be produced per time unit.

Claims

1. A continuous process for producing copper foil, wherein

   copper is electrolytically deposited on a rotating drum cathode, which is partially immersed in an electrolyte solution contained in a plating tank;
   the copper layer deposited on the drum cathode is peeled off the part of the drum cathode that is not immersed in the electrolyte solution to obtain the copper foil;
   an insoluble anode is used as counter-electrode to the drum cathode;
   the electrolyte solution contains copper ions, organic additives and an Fe^{2+}/Fe^{3+} redox system;
   the concentration of copper ions in the electrolyte solution is maintained constant by passing the electrolyte solution through a copper dissolution unit;
   in the copper dissolution unit, the electrolyte solution is in contact with an auxiliary anode and an auxiliary cathode;
   copper metal and an oxygen-containing gas are introduced into the copper dissolution unit;
   the auxiliary anode is in contact with the copper metal;
   the oxygen-containing gas is introduced such that bubbles thereof contact the surface of the copper metal;
   the copper metal continuously dissolves into the electrolyte solution by being oxidized by the Fe^{3+} component of the Fe^{2+}/Fe^{3+} redox system and optionally the oxygen contained in the oxygen-containing gas.

2. The process according to claim 1 wherein the organic additives contained in the electrolyte solution comprise at last one brightener, at least one levelling agent and at least one carrier.

3. The process according to any one of the preceding claims wherein the electrolyte solution contains 20-250 g/l of copper sulfate pentahydrate, 50-350 g/l of sulfuric acid, 0.1-50 g/l of iron (II) sulfate heptahydrate, 0.01-0.18 g/l of chloride ions.

4. The process according to any one of the preceding claims wherein the electrolyte solution contains methanesulfonic acid and the iron and/or copper salts thereof.

5. The process according to any one of claims 1, 2 or 4, wherein the electrolyte solution is substantially free of sulfuric acid and/or sulfate salts.

6. The process according to claim 2 wherein the total concentration of brightener compounds present in the electrolyte solution is from 0.01 mg/l to 100 mg/l.

7. The process according to claim 2 wherein the total concentration of levelling agents present in the electrolyte solution is 0.5 mg/l to 400 mg/l.

8. The process according to claim 2 wherein the total concentration of carrier compounds in the electrolyte solution is 0.005 g/l to 20 g/l.

9. The process according to any one of the preceding claims wherein the current density at the drum cathode is 20 to 100 A/dm^2.

10. The process according to any one of the preceding claims wherein the amount of copper deposited on the drum cathode is 10 to 50 kg/min.

11. The process according to any one of the preceding claims wherein copper is deposited on the rotating drum cathode at a temperature of 15 to 70°C.

12. The process according to any one of the preceding claims wherein the concentration of copper ions in the electrolyte solution present in the plating tank is 80 to 90 g/l.

13. The process according to any one of the preceding claims wherein the concentration of Fe^{3+} ions in the electrolyte solution present in the plating tank is < 5 g/l.

14. The process according to any one of the preceding claims wherein the part of the electrolyte solution withdrawn from the plating tank is introduced into the dissolution unit at a location that is closer to the auxiliary cathode than to the auxiliary anode so that the withdrawn part comes into contact with the auxiliary anode first.

15. The process according to any one of the preceding claims wherein the voltage applied between the auxiliary anode and the auxiliary cathode is 1 to 9 V.

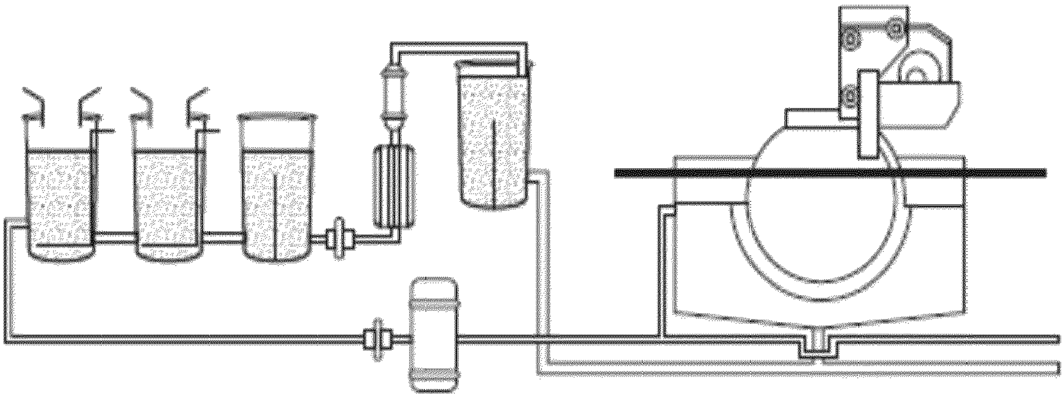

FIG. 1
(PRIOR ART)

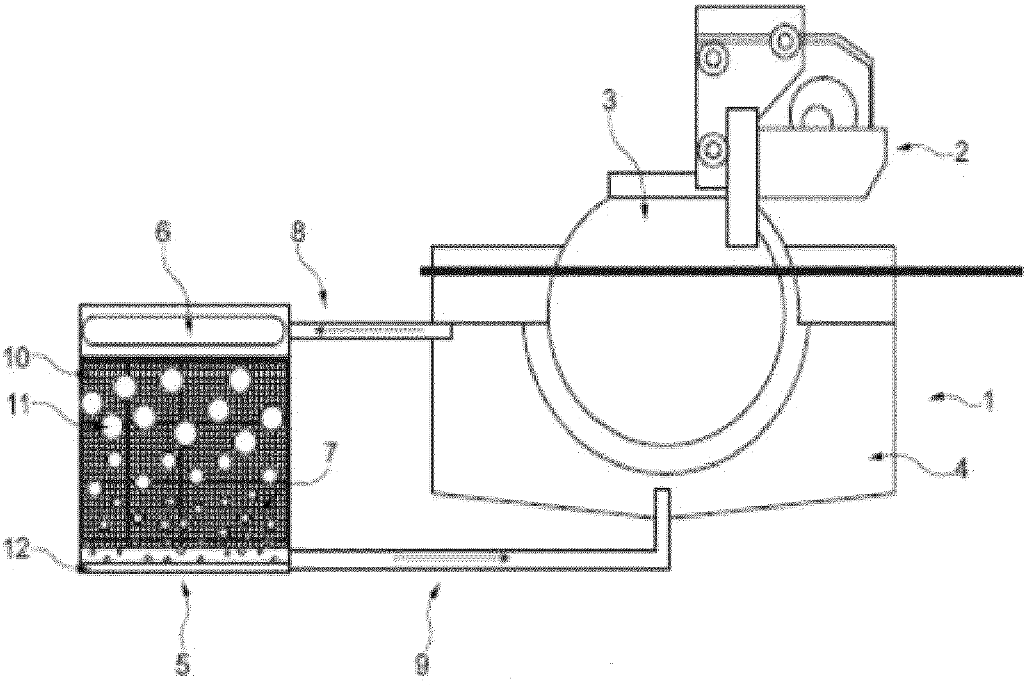

FIG. 2

Europäisches Patentamt
European Patent Office
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EUROPEAN SEARCH REPORT

Application Number
EP 23 15 1521

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y A	EP 0 862 665 B1 (ATOTECH DEUTSCHLAND GMBH [DE]) 15 March 2000 (2000-03-15) * abstract * * examples 1, 4 * * paragraph [0043] *	1-13,15 14	INV. C25D1/04 C25B9/01 C25C1/12 C25D3/38 C25D1/00
Y A	US 11 050 050 B1 (CHANG CHUN PETROCHEMICAL CO LTD [TW]) 29 June 2021 (2021-06-29) * abstract * * figure 1 * * examples 1-9 *	1-13,15 14	
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TECHNICAL FIELDS SEARCHED (IPC)

C25D
C25C
C25B

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	6 June 2023	Lange, Ronny

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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