ABSTRACT: This invention relates to apparatus and methods for continuously producing a strip or sheet of metal by depositing metal from an electrolyte upon a moving, cathodic surface and stripping the deposited metal as a strip or sheet from said surface, wherein in addition to the cathode, anode and electrolyte supply means, there is also provided a nonconductive, hard particle activating means which contacts the surface of the initially electrodeposited metal film to activate the surface of the electrodeposited metal allowing the use of very high current densities to rapidly deposit an increased thickness of dense, compact, smooth and bright metal on the initially deposited film.
ELECTRODEPOSITED METAL FORMATION

FIELD OF THE INVENTION

Production of metal sheet by electrolytically depositing metal on a moving cathodic surface has been a slow and tedious process associated with such problems as the forming of a porous, rough, spongy metal deposit, electrodepositing metal at the edges of the drum which interferes with the removal of the metal film from the drum, and extremely slow rates of metal deposition which economically limits the product to a very thin sheet. The present invention relates to an improved method and apparatus for forming continuous metal strips and sheets by so electrodepositing metal on a moving cathodic surface as to produce thick dense, bright and smooth metal strips at rates many times faster than heretofore possible.

DESCRIPTION OF PRIOR ART

Processes of making metal sheet or foil, wherein a metal such as copper is deposited from an electrolytic plating bath on a moving cathodic surface such as a drum or endless belt, have long been known. However, various difficulties have arisen in the practical operations of such processes which have greatly limited their usefulness.

Because of the extremely slow rate of metal deposition, the metal film thickness of the prior art processes have been limited to a practical upper limit of approximately 0.0015 inch. See for example, U.S. Pat. No. 2,587,630 where it is said to take 72 hours to produce a 19 feet linear strip of iron metal having a thickness of 0.0034 inch; U.S. Pat. No. 2,203,253 which demonstrates a construction suitable for production of copper foil whose thickness ranged below 0.0003 inch; U.S. Pat. No. 2,944,954 which demonstrates production of zinc metal sheets of 0.003 inch thickness corresponding to a current density of 588 amperes per square foot at a linear advance of 1.75 inches per minute; and U.S. Pat. No. 3,151,048 which shows the production of copper foil having a thickness of 0.0014 inch corresponding to a current density of 135-145 amperes per square foot at a linear advance of 12 inch per minute. Thus, prior art production of even 0.0015 inch thickness metal sheets was a slow, time-consuming process which was economically feasible only where there was no alternative process available for the production of the sheet metal.

Other problems plagued the prior art processes in addition to the above. The copper foil of U.S. Pat. No. 2,203,253 had a rough, spongy surface which had to be polished and rolled in order to produce a suitable product. An improved foil product is described in U.S. Pat. No. 3,151,048 but the improvement relies on an elaborately prepared plating drum whose surface requires special maintenance techniques to prevent the drum from quickly deteriorating in its ability to produce an acceptable product, and thus one problem is replaced with another.

The prior art processes utilizing a drum were hampered by metal plating near the edges and on the ends of the drum which resulted in the possibility of tearing the metal sheet during stripping from the drum due to the edge of the metal sheet adhering to the edge of the drum. Several methods have been suggested to avoid or reduce the metal plating near the edges of the drum (for example see U.S. Pats. Nos. 2,429,902 and 2,944,954) but have proven not to be completely successful and the problem still persists.

SUMMARY

The present invention is directed towards a process of producing metal strips and sheets by electrolytically depositing metal on a moving cathodic surface such as a drum or continuous belt, wherein the initial metal layer is deposited under normal electroplating conditions, and thereafter, the surface of the metal layer is continuously and repetitively contacted at extremely short time intervals by what is termed herein as "dynamically hard" particles. By this term is meant that the combination of the hardness of the particles, the contact pressure of the particles on the surface of the metal layer and the speed at which such particles are moving relative to the metal layer surface is such as to produce an action on such surface sufficient to mechanically "activate" the surface. "Activating" the surface of the metal layer within the meaning of the present invention means the removal of any polarization layer and reaction product layer from the metal layer surface and the disarrangement of the atoms in the metal layer surface to a degree sufficient to cause increased activity. This process is fully described in my copending application, Ser. No. 718,468, filed Apr. 3, 1968 entitled "Electrodeposition" now abandoned and the entire contents of such copending application incorporated herein in entirety.

The activation of the metal layer results in a marked increase in the rate of electrodeposition as is reflected in the ability of the present process to operate at current densities in excess of 20,000 amperes per square foot as compared to the prior art methods mentioned earlier which had a maximum of about 388 amperes per square foot with the normal current density being about 100-150 amperes per square foot. This increase in activity results in the increase in plating rate, makes it possible to produce metal sheet by the present process having a thickness of 0.0015 inches at a theoretical rate of 7980 linear feet per hour in comparison to 60 linear feet per hour for the prior art practices disclosed in the references mentioned above.

As an inherent result of the activating process of the invention there is eliminated the need for both additives or pre-plating requirements to produce a dense and smooth sheet as exemplified by the burnishing roll of U.S. Pat. No. 2,203,253 and the additives and specially prepared chromium plated drum of U.S. Pat. No. 3,151,048. The present process produces a dense, smooth metal film using standard electroplating techniques which do not require use of additives although additives can be used if desirable nor the use of post plating treatment of any kind. There is, further, no necessity for pretreatment of the cathode as is required in prior art. Another inherent advantage of the activating step of the present process is that the problems of the prior art with respect to stripping the metal sheet from the drum or belt, as exemplified in U.S. Pats. Nos. 2,335,776, 2,429,902 and 2,944,954, are not encountered (the stripping process is fully described below). The thick metal sheet produced on the face of the drum or belt is some 100 to 150 times as thick as any metal film which is plated on the edges and sides of the drum or belt, and, therefore, during stripping any tear which is initiated by the thin metal film sticking to the edge or side of the drum or belt will not propagate into the much thicker film being stripped from the face of the drum or belt.

DRAWINGS

The present invention is explained hereinafter in greater detail by reference to the accompanying drawings which show the preferred embodiments of this invention. It should be understood, however, that the drawings and examples are given for purposes of illustration and that the invention in its broader aspects is not limited thereto.

In the drawings:

FIG. 1 is a side view of one preferred embodiment of apparatus employing this invention;

FIG. 2 is an end view partly in section of the apparatus of FIG. 1;

FIG. 3 is a side view of a second preferred embodiment of apparatus employing this invention;

FIG. 4 illustrates diagrammatically a portion of a cross section of one type of porous activating medium useful in the present invention;

FIG. 5 is an edge view of a curved surface drum which can be substituted for the drum of FIG. 1;

FIG. 6 is a side view of another preferred embodiment of apparatus employing this invention; and

FIG. 7 shows cross-sectional views of several shapes which the cathode element of FIG. 6 can take.
DESCRIPTION OF PREFERRED EMBODIMENTS

Referring now to FIG. 1, the apparatus of a preferred embodiment of the present invention comprises an electrolytic tank 10 fabricated of suitable electrical insulating material and filled with an electrolyte to the level shown by numeral 26, a semicircular anode 11, a cathodic drum 12, a dynamically hard particle-containing activating belt 13, pulley roller system 14, a pulley semicircular anode 11a and conventional means (not shown) for supporting said drum, anode and pulley system, for driving said cathodic drum and said belt and pulley system, and for collecting the metal sheet 15 being produced. As shown, the cathodic drum 12 rotates in a counterclockwise direction and the activating belt 13 can travel either in the counter-clockwise or clockwise direction and in addition can if desired be oscillated laterally with respect to the axis of the cathodic drum 12. As the cathodic drum 12 rotates from the point marked A in FIG. 1 (where the surface of the drum enters the plating bath) to the point marked B (where the surface of the drum comes into contact with the activating belt 13) the surface of the drum is plated as in ordinary electroplating processes with a thin film of metal. At the point marked B in FIG. 1, the thin metal film which has plated to the cathodic drum 12 comes into contact with the activating belt 13. The belt 13 travels either in the reverse direction to that of the cathodic drum 12, or if traveling in the same direction, it travels at a speed at least approximately 15 percent faster or slower than the drum so as to cause continuous relative motion between said activating belt and the surface of the thin metal film on the surface of the drum. The belt 13 has supported, at least on its surface, in closely spaced relationship to one another, a plurality of small, relatively inflexible particles, and as fully explained in my copending application, Ser. No. 718,468, mentioned earlier, the relative motion between the particle containing matrix and the surface of metal film activates said surface thereby markedly increasing the rate of electrodeposition upon said surface. The rate of electrodeposition in the area where the surface is in contact with the activating belt 13 is some 100-150 times as great as the rate of deposition in the area between points marked as A and B in FIG. 1. This marked increase in plating rate results in the ability of the present process to produce metal films or sheets of increased thickness and at markedly faster rates than the prior art processes.

The initial plating, which occurs between points marked as A and B of FIG. 1, is accomplished as in the prior art teachings because the adherence of the thin metal film deposited to the surface is much less using the prior art plating techniques than is the case with films plated on an activated surface provided by this invention. This facilitates the stripping of the final metal film or sheet from the drum. Also, the surface of the cathodic drum 12 is normally treated with a parting agent such as wax, resin, graphite or other substances used in the prior art, and the mild abrasive action of the activating belt would remove or impair the effectiveness of such parting agent. As shown in FIG. 1, an auxiliary anode 11a can be used to induce the initial thin film plating if so desired.

As was mentioned above, the prior art processes were plagued with the problem of stripping the film from the drum 12 (stripping occurs at the point marked 18 on FIG. 1). The metal film, in the prior art processes, adheres uniformly over all the surfaces including the end surfaces of the drum. The portion of the metal film plating on the edge and ends of the drum was as thick and, therefore, as intrinsically strong as the portion of the metal sheet formed on the surface of the drum. This, during the stripping step, tended to adhere firmly to the drum and surface of the drum resulting in a break in the metal film which would propagate to a much larger portion of the film. Many elaborate methods have been proposed to reduce to a minimum the electroplating of metal on the edge and ends of the drum which would result in a thinner and weaker film being formed at the edge and end of the drum. Then if, during stripping, the film at the edge of the drum should stick and fail to come free of the drum, the weaker film would simply break free of the thicker and stronger metal sheet formed on the surface of the drum rather than tear across the width of the metal sheet. The prior art methods were not completely satisfactory in this respect and the problem of tearing the sheet of metal during stripping has continued to be a big problem. Inherent in the present process, the activating belt 13, as shown in FIG. 2, can be varied in its width so as to produce varying widths of sheet metal product and, as explained earlier, the rapid metal plating takes place only where the activating belt 13 comes into contact with the metal film on the cathodic drum 12. When producing sheet which is not as wide as drum 12 an is designated by the number 30 in FIG. 2 of the surface of the drum 12 does not come into contact with the porous activating belt 13. The metal film formed in the area designated by the number 30 in FIG. 2 is some 100 to 150 times thinner and, therefore, weaker than the metal sheet formed on the surface of drum 12 which has been activated by the activating belt 13. Even when producing sheet as wide as the drum 12, the ends 31 of the drum do not come into contact with the activating belt 13 and again the metal formed on said ends 31 is much thinner and weaker that that formed on the drum. Thus, if during the stripping step of the present process, the thin weak metal film does stick to the edge or end 31 of the drum 12, it breaks free from the much thicker and stronger sheet rather than produce a tear across the width of the thick sheet.

FIG. 3 illustrates a variation in the apparatus of FIG. 1. The cathodic drum 12, of FIG. 1, has been replaced with an endless conducting belt 17, made, for example, of stainless steel extending over and between two cylindrical drums 16 made of or coated with a nonconductive material, such as rubber. The inner surface 19 of the endless belt 17 is coated with a nonconductive material, such as rubber. The electrolyte layer 27 of cell 10 is maintained such that the lower rectilinear section 21 of belt 17 is beneath the surface of the electrolyte and the upper rectilinear section 22 is above the electrolyte surface. A source of DC negative current is connected to the endless belt 17 by means of brushes 20 and thus the uncoated face of belt 17 becomes negatively charged and acts as the cathode. The activating belt 13 extends over and between three cylindrical drums 23 one of which is driven by a means not shown, whereas the upper and lower rectilinear sections 24 and 25 of belt 13 are in a horizontal plane parallel to the plane of the rectilinear sections 21 and 22 of endless belt 17. Further, the upper rectilinear section 24 of belt 13 is held in moving contact with the lower rectilinear section 25 of the endless belt 17 by the anode 11. The operation of the apparatus of FIG. 3 is very similar to the operation of the apparatus of FIG. 1. The endless belt 17 travels in a counterclockwise direction being driven by one of the drums 16 which in turn is driven by a suitable means (not shown). The activating belt 13 can travel in either clockwise or counterclockwise direction. However, if belt 13 travels in the same direction as the endless belt 17, it must also travel at a rate at least some 15 percent slower or faster than the rate of travel of belt 17. In addition to the clockwise or counterclockwise travel, the belt 13, can if desired be oscillated in a perpendicular direction with respect to its linear travel. As a section of the endless belt 17 travels between points C and D as shown in FIG. 3, a thin film of metal is electroplated on its uncoated surface by normal electrolytic technique. When this section of endless belt 17 travels between points D and F as shown in FIG. 3, the thin film of electroplated metal on its uncoated surface is brought into sufficient contact with the dynamically hard particle of the activating belt 13 to activate the surface of the thin metal film. Due to the increased plating rates obtained by this activation, a thick metal sheet is formed on the outer surface of the endless belt 17 reached point F. The metal sheet 15 is then stripped from the endless belt and collected. As in FIG. 1, an auxiliary anode 11a can be used as shown in FIG. 3 to induce formation of the thin film of metal on endless belt 17.

FIG. 4 shows a highly enlarged and idealized portion of a typical activating media suitable for use in the present inven-
tion and illustrates the hard particle-connecting matrix relationship. Reference numeral 85 represents fibers of a nonwoven web (nonconductive fibers such as polyethylene terephthalate or the like) which are anchored one to the other at their points of intersection by an adhesive binder 86. A plurality of small, hard, discrete particles 87 are positioned on the fibers 85 and in the present illustration are held to such fibers by the adhesive 86. At least some of the fibers 85 extend relatively parallel to the cathode face 89 as shown at 88 to form the thin-walled cells or electrolyte sweeping members which, as explained in my copending application, Ser. No. 718,468, mentioned earlier, provides fresh electrolyte constantly to the activated plating surface of the cathode. (For purposes of illustration, the activating particles 87 are here shown at some distance from the cathode face 89 and associated electrodeposit 90 although in operation of the present apparatus they would be in contact therewith.)

FIG. 5 shows an edge view of a curved surface drum 12a which can be substituted for the drum 12 in FIG. 1 to produce a curved sheet metal structure having the radius of the curved surface of the drum.

FIG. 6 illustrates another variation in the apparatus of FIG. 1. The cathodic drum 12 of FIG. 1 is replaced by the cathode strip 61 which is a fixed length of stainless steel or other suitable metal strip. At the start of the process, strip 61 is coiled on feed roll 62 and is fed through a pretreating means 63 where the strip 61 has a thin deposit electroplated on its surface whereby the electroplated deposit adheres very weakly to the strip 61 itself. The strip is then introduced into the electrolyte bath 64 and around guide element 65. The guide element 65 can be of several shapes such as shown in FIG. 7. The strip is then brought into contact with the activating belt 66 at the nip formed between the anode element 67 and guide element 65. A deposit is electroplated on the strip while being activated by the belt 66. The belt 66 is identical to the belt 13 of FIG. 1 both in structure and operation. The anode element 67 is moveable laterally towards the guide element 65, and thereby a predetermined pressure between the electroplated strip and the activating belt can be obtained. The electroplated strip 61 is then wrapped around pulley 68 and emerges from the electrolyte solution. The electrodensitized sheet 69 is then separated from strip 61 and both the sheet 69 and strip 61 are collected on rolls 70 and 71 respectively.

If the strip 61 of FIG. 6 is made continuous instead of a definite length (this variation is not shown in the drawings), the apparatus becomes very similar to that shown in FIG. 3, and disc adapted to be driven in a rotary motion and held in contact with the metal film forming on the surface of the endless belt 17.

The metal sheet 15, produced by either the apparatus of FIG. 1 or FIG. 3 and sheet 69 produced by the apparatus of FIG. 6, has a smooth, hard, dense and bright surface on the face of the sheet away from the drum or belt and has a hard, dense surface on the face of the sheet in contact with the drum or belt which assumes the smoothness and brightness of the surface of the drum or belt. There is no special need for using prior art agents and additives to obtain the bright, smooth, hard and dense surface on the face of the sheet away from the drum or belt. However, such agents and additives can be incorporated, if desired, in the electrolyte baths to enhance brightness or other characteristics of the deposited metal where appropriate.

EXAMPLE

Using the equipment arrangement as is illustrated in FIG. 1, a 15-mil strip of copper foil was prepared as follows:

The plating cell 10 was filled with a solution of copper sulfate containing 45 grams of copper sulfate per liter. Cathodic drum 12, 4 inches wide and 12 inches in diameter, was fabricated from steel. The plating surface of drum 12 was chromium plated and highly polished. The electrolyte level was maintained approximately 1 inch below the top of the drum 12. The drum 12 was rotated at a linear surface speed of 4 feet per minute. The linear distance from point A to point B as represented in FIG. 1 was approximately 19 inches, the linear distance from point B to point 18 as represented in FIG. 1 was approximately 12 inches and the linear distance from point 18 to point A as represented in FIG. 1 was approximately 6 inches.

The activating belt 13 was made, in this instance, from a nonwoven web of polyester fibers bonded with an acrylonitrilemelamine resin adhesive and roll coated with a phenolic adhesive and abrasive grain as described in my copending application, Ser. No. 718,468, mentioned earlier.

The belt was 3 inches wide and approximately 5 feet in circumference. The belt was operated at a linear speed of 1050 feet per minute.

In starting the apparatus, drum 12 and belt 13 was held stationary until a metallic deposit of sufficient thickness was formed on the submerged portion of the surface of drum 12 which could easily be stripped therefrom. The drum 12 and belt 13 were then set in motion and the strip metal sheet was stripped from the drum or belt selected on a takeup roll.

The cathode current density was maintained at 7500 amps per square foot and the electrolyte bath temperature was held at approximately 70° F. A 3-inch wide by 12-mil thick strip of copper foil having a dense, smooth, hard and semi-bright surface was produced at the rate of 4 linear feet per minute. This compares to a production rate of 1 linear foot per minute for a 1.4 mil thick copper foil as disclosed in U.S. Pat. No. 3,151,048.

It is also possible, within the present invention, to produce continuous belts of electrodensitized metal by initiating the plating process, but omitting the step of stripping the sheet metal from the drum or belt thereby continuously plating on the drum or belt until the desired thickness of electrodensitization is formed. It should be noted that the current being supplied to the auxiliary (or initial) anode should be discontinued as soon as a continuous electrodensitized metal of have been formed on the drum or belt. While the invention has been described as to electrodensitizing a copper foil, the invention is applicable to all metals that can be electrodensitized in sheet form including such examples as iron, nickel, zinc, tin and copper.

While preferred embodiments of the invention have been disclosed, other embodiments and variations thereof are undoubtedly possible, and the scope of the invention is defined by the appended claims.

I Claim:

1. A process for producing sheet metal by electrodensitization from an electrolyte solution comprising:
   a. electrodensitizing an initial thin layer of metal on a cathode surface, said cathode surface being of such a nature that the thin electrodensitization has only a very weak adhesion thereto;
   b. mechanically activating the surface of the initial thin layer of electrodensitization by moving contact between such surface and a plurality of small, spaced activating particles supported on and affixed to a matrix to increase the rate of electrodensitization thereof;
   c. continuing said mechanical activation of the electrodensitized surface during the remaining period of electrodensitization to build up the thickness of said electrodensitization; and
   d. stripping the sheet of electrodensitization so formed from the cathode surface.

2. The method of continuously making metal sheet or foil which comprises:
   a. providing a cathode which moves into, through and out of an electrolyte solution;
   b. plating on the surface of the cathode an initial layer of poorly adherent electrodensitization during the initial movement of the cathode in the electrolyte solution;
3,619,400

c. at a point intermediate in the cathode’s movement through said electrolyte solution, mechanically activating the surface of the electrodeposit by moving contact of such surface with a plurality of small, spaced activating particles supported on and affixed to a matrix and continuing said activation during the remaining movement of the cathode through the electrolyte; and
d. stripping the electrodeposit from the surface of the drum as it emerges from the electrolyte solution.

3. An apparatus for producing sheet metal by electrodeposition from an electrolyte solution comprising:
a. a movable cathode having a surface of such a nature that an electrodeposit has only a weak adhesion thereto;
b. means to electrodeposit a thin initial plate on the surface of such cathode;
c. means comprising a plurality of small activating particles affixed in spaced relationship to a supporting matrix to mechanically activate the surface of the electrodeposit to rapidly build up a desired thickness of electrodeposit; and
d. means to strip said electrodeposit from said movable cathode surface.

4. An apparatus for producing sheet metal by electrodeposition from an electrolyte solution onto a cathode surface comprising:
a. a first anode and a second anode spaced from said first anode;
b. a cathode, having a surface of such a nature that an electrodeposit has only a weak adhesion thereto, said cathode being movable successively adjacent said first anode and then adjacent said second anode;
c. means to supply electrical current flow between said cathode and said first and second anodes;
d. means to supply electrolyte between said cathode and said first anode whereby an initial thin electrodeposit is formed on the surface of said cathode when it is adjacent said first anode;
e. means to move said cathode with the initial thin electrodeposited on its surface from adjacent said first anode to adjacent said second anode;
f. activating means comprising a plurality of small spaced activating particles supported in fixed, spaced relationship to each other on a matrix so positioned as to contact the surface of the said initial thin electrodeposited at a point adjacent said second anode;
g. means for establishing relative motion between said initial thin electrodeposited and the activating means, thereby mechanically activating the surface of said initial thin electrodeposited;
h. means for continuing said relative motion and contact between the entire surface of said electrodeposited and the activating means during the remaining period of electrodeposition, thereby rapidly increasing the thickness of said electrodeposited; and
i. means to separate said thick electrodeposited from said cathode surface and from said electrolyte.

5. An apparatus as in claim 3 wherein said cathode is a rotatable drum.
6. An apparatus as in claim 3 wherein said cathode is an endless movable belt.
7. Apparatus as in claim 3 wherein said activating means comprises an electrolyte-permeable matrix having a plurality of small particles adhered thereto in fixed spaced relationship one to the other.
8. Apparatus as in claim 7 wherein said matrix comprises a porous nonwoven web.
9. Apparatus as in claim 7 wherein said matrix comprises an open-weave fabric.
10. Apparatus as in claim 7 wherein said particles comprise abrasive grains.
11. In an apparatus for producing sheet metal by electrodeposition from an electrolyte solution wherein an electrodeposited of metal is deposited on a cathode surface, the cathode surface being of such a nature that the electrodeposited has only a very weak adhesion thereto, the improvement which comprises:
a. a plurality of small activating particles supported in fixed, spaced relationship on a matrix and disposed adjacent to said cathode;
b. means to move said activating particles and supporting matrix relative to the surface of said cathode and in contact with said electrodeposited on the surface thereof whereby the entire surface of the electrodeposited formed on said cathode is mechanically activated resulting in a rapid build up of a thickness of electrodeposited on said cathode; and
c. means to remove said electrodeposited from the surface of said cathode.

* * * * *
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,619,400 Dated November 9, 1971

Inventor(s) Steve Eisner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 6, line 25, change "7500 amps" to read --5700 amps--.

Signed and sealed this 25th day of April 1972.

(SEAL)
Attest:

EDUARD M.FLETCHER, JR. ROBERT GOTTSCHALK
Attesting Officer Commissioner of Patents