Sept. 19, 1972 A. A. DELMOUSOS 3,692,639
MULTIPLICATION OF METAL SURFACE, BY ELECTROPLATING OR ANODIC DISSOLUTION
Filed Sept. 4, 1970 2 Sheets-Sheet 1

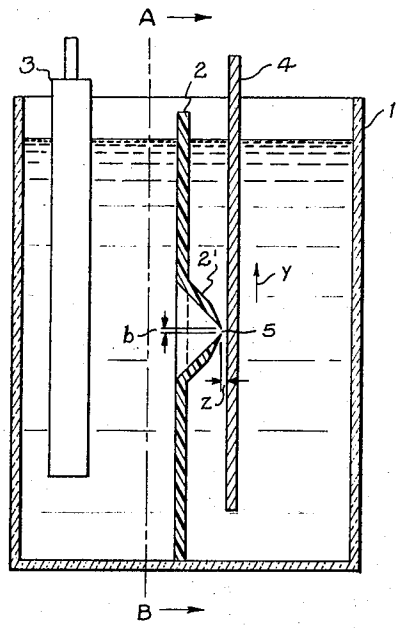


Fig. 1

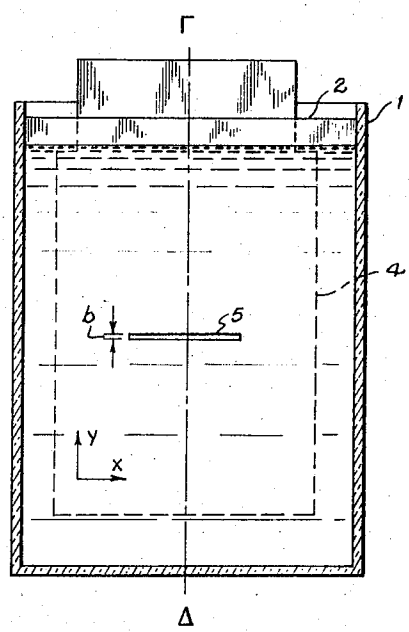


Fig. 1a

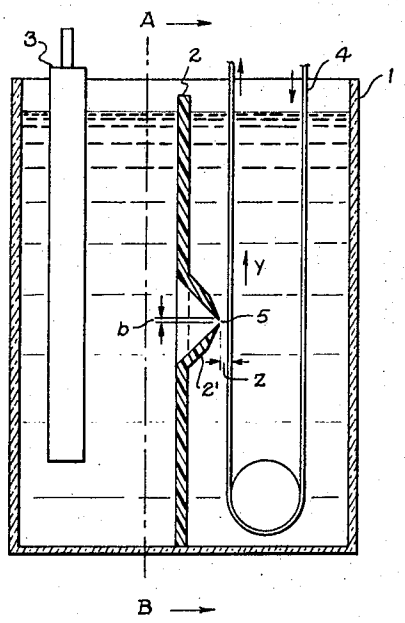


Fig. 2

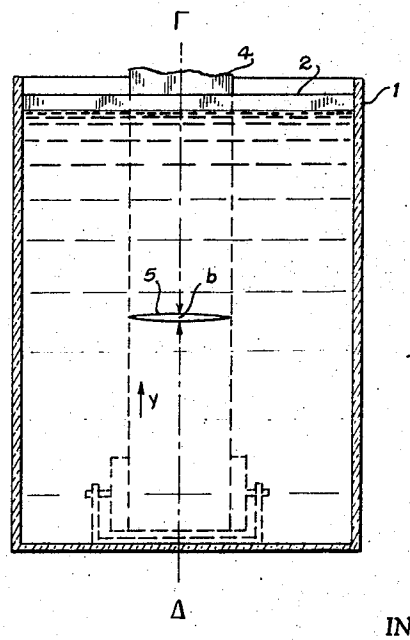


Fig. 2a

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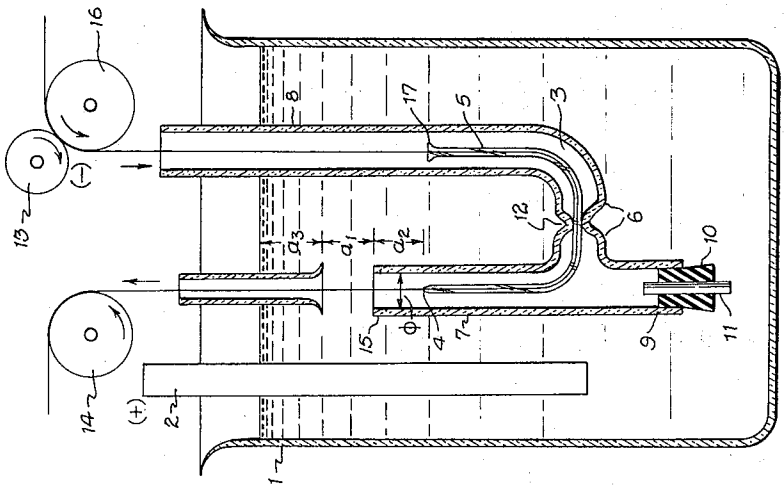


Fig. 4

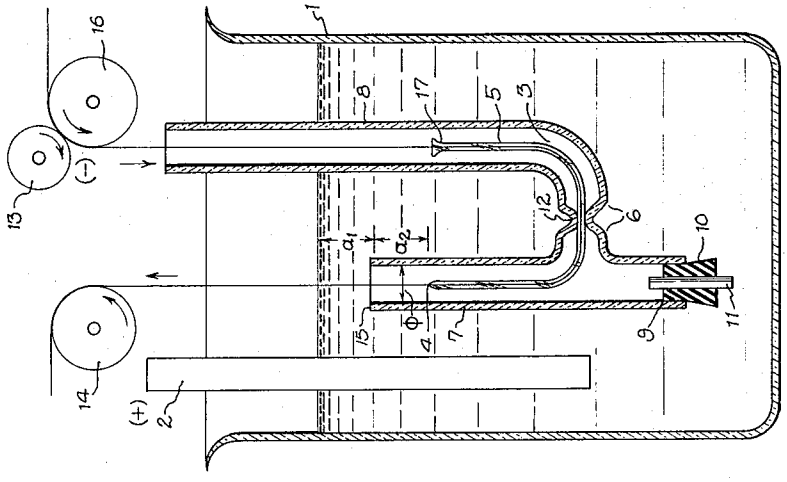


Fig. 3

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MULTIPLICATION OF METAL SURFACE, BY ELECTROPLATING OR ANODIC DISSOLUTION

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Int. Cl. C23b 5/58, 5/68
U.S. Cl. 204—28 11 Claims

ABSTRACT OF THE DISCLOSURE

A method of and an apparatus for multiplying the effective area of a metal surface by electroplating and/or anodic dissolution by using a high density electroplating current while at the same time the current density at the start of the electroplating can be suitable for maintaining the cohesion with the original surface, and simultaneously neutralizing all anomalies which result from a steady strong hydrogen release which cannot be neutralized through the known method of cathode movement, the increased current density at the cathode is achieved and the harmful effect of the released hydrogen is avoided.

This invention provides for the multiplication or increase of the effective area of metal surfaces by means of electroplating and/or anodic dissolution, that is, by metallization or demetallization. A large density current is used on each surface and electrolytes of proper density or concentration are used to assure metallic cohesion.

Metal surfaces having such increased effective surface areas are especially useful in electrolytic condensers, electric accumulators, etc. For increasing the effective areas of metal surfaces, the following two methods are known.

The first, used mainly for making aluminum and tantalum electrolytic condensers, uses chemical means by, for instance, immersing aluminum in hot hydrochloric acid solution. By this means, a multiplication of the surface area of about fifteen times is achieved.

The second is by use of dust of a porous metal under high pressure and subsequent heating (sintering). This method is used in electrolytic tantalum condensers, cadmium-nickeliferous electric accumualtors, etc., but if kept sufficiently porous it no longer has the necessary cohesion and the materials are sensitive to stronger currents. The dust for this use is chemically or electrolytically produced using very dilute electrolytes.

Generally, there are limits to the current density at the anode and cathode to give good electroplate which, if controlled, the grain of the added metallic surface has good cohesion with the original surface, is fine, has good metallic characteristics, and is homogeneous with good physical, chemical and mechanical characteristics.

If the current densities for the anode and cathode are increased beyond the allowable values which fall between 10 and 100 ma./cm.^{2}, the metallization will show irregularities in the above-mentioned characteristics. The grain cohesion will be weak with respect to the original surface, etc. The same also happens during metallization using weak electrolytes. When a slight increase of current density is applied to such electrolytes, the metallization either rests weakly on the surface in the form of dust or falls to the bottom of the plating bath as dust.

Proceeding step by step from the case of ordinary metallization by electroplating to the production of dust by increasing the cathode current and/or by simultaneously diluting the electrolyte, there appears at first a granular surface which, before losing cohesion with the original

surface shows a manifold increase in effective area. This increase is particularly observed at the extremities or edges of the cathode and may exceed by as much as ten times the increase of effective area achieved by chemical methods. The necessary large current density, however, is a limit preventing further increase particularly using the not too dilute electrolyte which is necessary for maintaining the cohesion of the new layer. The high current densities overheat the cathode so much that it is not possible to use them in the methods known prior to this invention. The simultaneous release of hydrogen at the cathode prevents the cohesion of deposited metal and contributes to the decrease of mechanical strength of the layer until it settles in the form of dust, particularly at the extremities of the cathode.

The electrolytic surface multiplication of the present invention uses large current density while at the commencement of the metallization or plating the current density is suitable for cohesion of the deposited metal with the original surface. At the same time, there is a neutralization of all anomalies which result from the steady strong release of hydrogen which cannot be neutralized by use of the known method of cathode movement. The increased current density at the cathode and the avoidance of the harmful effect of hydrogen release is achieved through the use of two methods, or the combination of the two methods.

The first method calls for the provision of pulsating current. The heat developed at the cathode is:

$$\theta = af\int_0^T i^2 dt$$

which a is a constant, f is the frequency of the pulses, i the instantaneous current valve, and T the period of each pulse. We can, therefore, increase the allowable cathode current density at will by decreasing the period of the pulses and by reducing their frequency. The period and frequency of oscillations can be reduced to a degree such that current densities much greater than needed for surface multiplication can be used. Through this method, current densities exceeding 150 a./cm.^{2} were achieved. At the same time, by providing the current in the form of pulses, we avoid the disadvantages caused by steady hydrogen release. On the contrary, though, the instantaneous hydrogen release during the period of the pulsation contributes to the porosity of the surface and therefore to its increase in effective areas, or area multiplication.

The second method provides for exposing successive small areas of a moving cathode surface to the current flow. This method permits a large current density per small area of surface and also allows a gradual increase of current density at will as well as gradual current density drop toward the end of metallization; and at the same time, it provides partial neutralization of the harmful effect of the released hydrogen.

The method described above may be practiced by use of the apparatus illustrated in the attached drawings in which:

FIGS. 1 and 1*a* illustrate by a front and side view a means for performing the method on a plate of material;

FIGS. 2 and 2*a* illustrate by a front and side view a means for performing the method on a continuous band of sheet material; and

FIGS. 3 and 4 illustrate by side views means to perform the method on a wire.

FIGS. 1, 1*a* and 2, 2*a* represent two simple systems for the second method. In these figures, container **1** with the electrolyte is divided by insulated diaphragm **2** into two sections. One section contains the positive electrode (anode) **3** and the second contains the negative electrode (cathode) **4** whose effective surface area is to be multi-

plied. The diaphragm has a slit or opening **5** which should preferably be bounded by lips such as **2'** extending toward the cathode in order to facilitate the hydrogen escape. The cathode is positioned at a very small distance from the slit and, preferably, at a distance Z smaller than the width *b* of the slit **5**. The distance of the lips of the slit from the cathode and the slit width are functions of the desired current density and density increase and decrease during metallization. The greater the distance the smoother the current density increase. In FIGS. 1 and 1*a*, the slit is sufficiently smaller than the cathode width and the cathode moves in the directions *x* and *y* so that, during metallization, all the surface of the cathode passes successively before the slit. In FIGS. 2 and 2*a*, the width of opening or slit **5** is about the same as the width of the cathode which moves only vertically in reference to the slit. In this case (FIGS. 2, 2*a*), the cathode may have the form of a band as shown and metallization may be continuous. A change of the slit shape to that shown in FIG. 2*a* helps avoid the development of greater current density at the extremities of the cathode, thus avoiding development of thicker layers at these points.

The best results for a large multiplication of effective area with good mechanical strength are attained through a combination of the first and second methods. This combination can be achieved by feeding pulsatory current to the system of FIG. 2. For a slit 0.5×20 mm. and for a current density of 100 a./cm.^{2}, current pulsations of 10 a. are required which can be given, for example, at a frequency of three pulses per second and a pulse period of 40 ms.

Use of a thin wire as the cathode gives, for the same metal weight, a still greater surface multiplication. An apparatus is shown in FIG. 3 that combines the first and second methods of increasing or multiplying the effective area of the surface of a wire.

The apparatus in FIG. 3 consists of container **1** which contains the electrolyte, anode **2** connected to the appropriate source of electricity, a thin glass U-shaped tube **3** with a small aperture at one end **4** and a flared opening **17** at the other end. Tube **3** is placed in another thicker U-shaped tube **6** of insulating material with uneven legs **7** and **8**. The shorter of the legs **7** has at its lower part an open extension **9** which is stopped by plug **10** having a thin tube or hole **11**. The upper end of outer tube **6**, ending below the level of the electrolyte, provides an annular opening to compare with slit **5** in FIG. 2*a*. At the lower part **12**, tubes **3** and **6** are fused together so that the electrolyte in legs **7** and **8** will be isolated. The wire used as a cathode passes over pulley **16**, and through tubes **3** and **6** to pulley **14**. A section of the wire of length a_2 is located in the thicker tube **6** of diameter ϕ while another section of length a_1 is free in the electrolyte. The current is provided to the cathode in the form of pulsations through pulleys **16** and **13**. Diameter ϕ of tube **6** and height a_2 determine the desired curve of current density. The least current density is at the opening **4** of the thin tube **3** while most of the density is located after the wire leaves the edge **15** of tube **7**. The biggest density value is given with small variations along course a_1. Tube **11** is used to facilitate the electrolyte's motion due to hydrogen developed during course a_2 without, however, creating any current density increase at **4**.

With the above apparatus which is simply an example for the application of the two methods, we can achieve in a wire of 0.1 mm. diameter a density between 80 and 140 a./cm.^{2} depending on the frequency and the period of oscillations which (period) in a nickel wire, for instance, gives a surface multiplication of over 2,000. The speed of the wire's motion in conjunction with the form and the strength of the pulsations gives the desired thickness of surface increase.

FIG. 4 shows an apparatus similar to that of FIG. 3 with the addition of a glass tube or cone which at height a_3 allows a steadier metallization of the already multiplied

surface through a decrease of current density after the surface multiplication. This is, in effect, a change in the opening or slit between the anode and the cathode.

The above additional regular metallization of the already multiplied surface in the area above slit or opening *a*, in FIG. 4, due to the reduced current density in distance a_3, can also be achieved separately in another apparatus after use of the FIG. 3 device. But, for determining the current density in such other apparatus which must be somewhat less than for the regular metallization in a usual electrolyte, the already multiplied surface must be taken into consideration and not the original surface.

For improving the layer during the process of surface multiplication, it is, naturally, possible to use all the known means, such as heating, stirring, constant watching of the density and of pH which for surface multiplication should particularly be observed with great attention. Also, for determining the size of the anode, the increased surface should be taken into consideration and not the original surface.

Satisfactory results of surface multiplication can also be achieved through demetallization. If the surface to be multiplied is used as cathode in the above two methods and if the anode current density is increased then we can accomplish surface multiplication through demetallization. There can also be periodic placement of the surface to be multiplied as anode and cathode alternately. In such a case, the anode and cathode poles will change periodically.

I claim:

1. A method of forming a porous metallic coating on a substrate including the steps of providing a plating bath separated into two volumes by an insulating partition, said partition provided with a small opening therethrough, positioning an anode on one side of said partition and said substrate material used as a cathode on the other side of said partition adjacent said small opening, impressing a plating current of from 40–80 a./cm.^{2} between said anode and said substrate while moving said substrate opposite said small opening to expose only a small area of said substrate to said plating current flowing through said small opening at any instant.

2. The method of claim **1** in which said substrate is a band of foil like material of indefinite length and said small opening is a narrow slot of a length corresponding to the width of the band of material extending across the width of said band, said band of material being moved lengthwise past said small opening at a uniform speed and closely adjacent thereto, whereby the current density will vary from a low value as the substrate approaches the small opening, increases to a maximum as the substrate passes in front of the opening, and reduce as the substrate passes the opening.

3. The method of claim **2** in which said small opening is located in a boss formed in said partition extending toward said substrate so that said substrate moves past said opening at a distance from said opening less than the width of said opening.

4. A method of forming a porous metallic coating by electroplating a metallic substrate, as in claim **1**, by applying a pulsating direct current, having a duration t=20–80 msec. and a period T=550 msec., so that during the time of the zero current amplitude, that is $T-t$, the cathode will be cooled and so any destruction by overheating to the cathode, due to the applied high current density, will be avoided.

5. A method of forming a porous metallic coating, as in claim **1**, having a good adhesion to the metallic substrate that is achieved by a first plating, which starts at a low current density that increases continuously up to a maximum value reaching the 80–140 a./cm.^{2}, so that the main plating will take place at this maximum current density to give the desired porous coating.

6. The method of claim **1** in which the cathode is a strip of material of indefinite length moving lengthwise opposite said opening.

7. The method of claim 6 in which the opening is an elongated slit having its length at right angles to the direction of movement of said material and of a length approximating but less than the width of said strip of material, said slit being of reduced width at its ends adjacent the edges of said strip.

8. The method of claim 7 in which the current is supplied in pulses.

9. The method of claim 8 in which the current pulses are at a frequency of three pulses per second and at a pulse period of 40 ms.

10. The method of claim 1 in which the movable cathode is a wire and the opening is provided as an annular opening surrounding the wire.

11. The method of claim 10 in which the current is supplied in pulses.

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F. C. EDMUNDSON, Primary Examiner

U.S. Cl. X.R.

204—206, 228, 242, 279, Dig 7, 49