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3,734,838

MULTIPLE METAL ELECTRODEPOSITION

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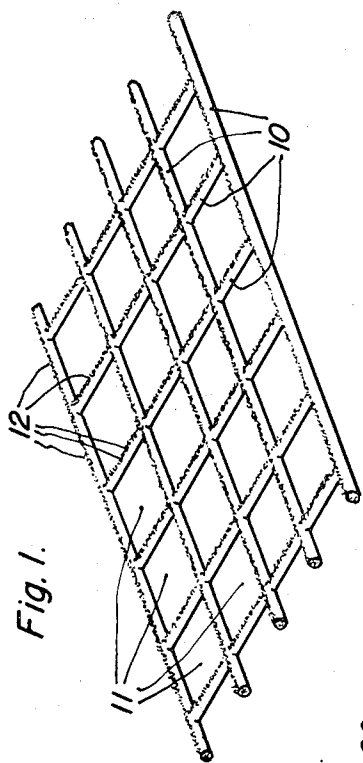


Fig. 1.

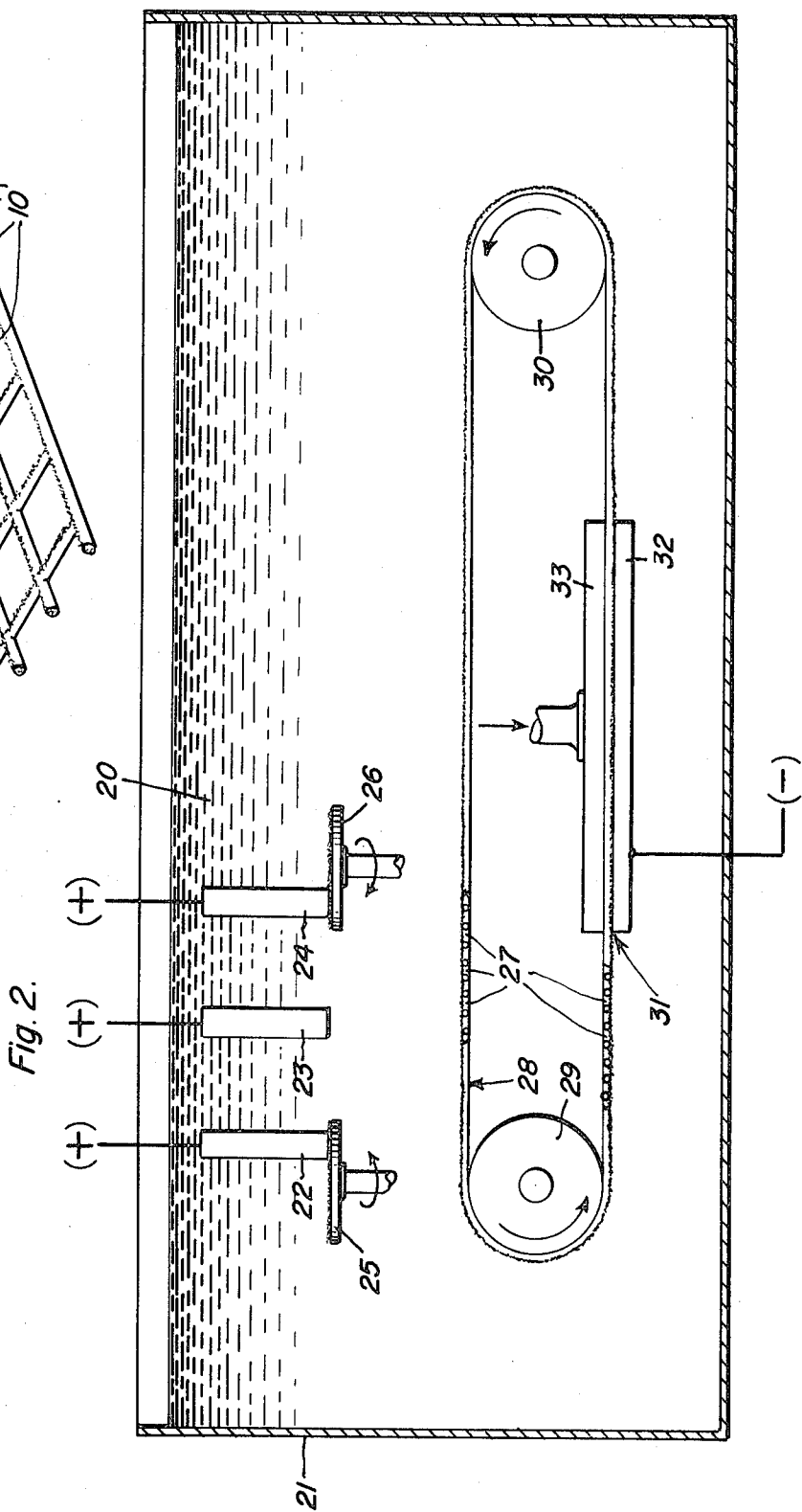


Fig. 2.

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3,734,838
MULTIPLE METAL ELECTRODEPOSITION
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5 Claims

ABSTRACT OF THE DISCLOSURE

A method for deposition of two or more metals simultaneously at high deposition rates by continuously and repetitively contacting the surface of the electrodeposit during its formation with a plurality of small, dynamically hard particles held in spaced, fixed relationship to one another in or on a supporting matrix while simultaneously introducing the electrolyte containing the ions of such metals into the plating zone in the form of small, isolated volumes.

FIELD OF THE INVENTION

While useful in plating essentially any combination of metals capable of electrodeposition separately, the process is also useful for plating equilibrium alloys. Primarily, however, it finds utility in plating combinations or alloys of metals where their deposition potentials are such that normally one would deposit in preference to the other or others.

DESCRIPTION OF THE PRIOR ART

Alloy deposition has generally been restricted to equilibrium alloys, i.e. to combinations of metals having essentially the same deposition potential, e.g. tin-lead from fluoroborate solutions, copper-zinc from cyanide solutions, etc. Some exotic alloy plating systems have been utilized and many of these are described in the reference *Electrodeposition of Alloys* by Abner Brenner, Volumes 1 and 2 (1st Edition, 1963). More recently, Dr. Thomas C. Franklin of Baylor University has reported the plating of dissimilar deposition potential metals at extremely low current densities, e.g. 0.81 to 15 milliamps/cm.², from gels or the like (*Plating*, Volume 58, page 472 (1971)).

SUMMARY

The present invention utilizes the high speed deposition approach of my prior U.S. Pat. No. 3,619,384 wherein mechanical activation of the surface of the electrodeposit by a plurality of small, hard particles is utilized as a technique for removing the depleted ion layer adjacent the electrodeposit surface and also to cause the surface to be much more receptive to the rapid acceptance of metal ions. However, in the approach of my prior process, the preferred embodiments utilized porous activators or particle-carrying media wherein the pores were intercommunicating. This provided an extremely efficient electrolyte-transport mechanism as well, insuring an adequate flow of electrolyte to bring in fresh metal ion supplies to replace those deposited at the high current densities employed. In the present invention, the supporting media for the particles is designed with regular pores or electrolyte-transport cells which either are non-communicating at all times or are designed to so become when pressure is applied to the activator material during its passage through the plating zone. The supporting media still performs its function as an electrolyte pump but now presents the electrolyte within the plating zone in the form

of a multitude of small, isolated volumes of liquid. When these isolated volumes or cells are exposed to very high current densities, all of the metal values within the individual electrolyte cell are driven out despite differences in the deposition potentials of the metals involved. The resulting deposits may be either a co-deposition or a true alloy depending upon the particular metals utilized. It is particularly important that the isolation of the volumes of electrolyte contained within the cells or pores of the activating media be from the bulk quantity of the electrolyte external of the plating zone.

Control of the metal ion composition in the main body of electrolyte may be accomplished by conventional techniques, e.g. supply of metal salt solutions in the same ratio as the metals are depositing out in the plating zone, or by controlling dissolution rates of soluble metal anodes through controlled activation of one or more of such anodes. As described in my prior patent, U.S. No. 3,619,389, anode dissolution may be varied by activation similar to that used to increase deposition rates through cathode activation. Incorporation by reference of the process descriptions of separate or simultaneous anode and cathode activation as described and claimed in my prior U.S. Patents Nos. 3,619,384 and 3,619,389 is made in the present case to avoid making the specification unduly long.

DRAWINGS

FIG. 1 illustrates an enlarged section of one type of activator material which can be utilized in the present invention.

FIG. 2 is a schematic illustration of the process.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of the present invention requires the incorporation into an electrolyte of the ions of two or more metals in a predetermined ratio. This electrolyte containing the multiple metal ions is then incorporated into individual cells of a moving porous structure which carries on its surface a plurality of small, hard particles affixed thereto in spaced relationship to one another. The moving porous structure then transports the electrolyte within such cells into a plating zone wherein the cells are made into closed, non-communicating cells by contact under pressure between the porous structure on one side with the surface of the electrodeposit or cathode and on the other side with an imperforate pressure plate (which in some instances may be anodic and in other instances may be electrically insulated from any potential). A high current density is imposed on the electrolyte in the closed cells with the potential exceeding the deposition potential of all of the metals present in such electrolyte. This drives essentially all of the metal ions within the closed cell out, causing them to deposit on the cathode surface. The porous structure continues to move throughout causing the particles on its surface to activate the electrodeposit or cathodic surface, permitting deposition of the metal ion at these high rates in the form of coherent, dense plate instead of powder. As the cells from which the metal values have essentially all been stripped pass out from the plating zone, the cells are re-opened to the main body of electrolyte which flushes out the spent electrolyte, replacing it with fresh, metal ion containing solution and the process is repeated. Preferably, the moving porous structure is in the form of an endless belt although obviously a disc or other physical form could be used if desired.

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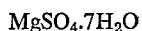
Referring now to the drawings, FIG. 1 illustrates a section of porous activator material wherein the structure consists of a screen-like fabric made up of fibers 10 interconnected with each other to produce regularly spaced, equal-dimension cells 11. Supported by the fibers 10 are a plurality of hard, spaced small particles 12 held to such fibers by a suitable adhesive (not shown). The fibers are formed of a material resistant to the electrolyte with which the activator is to be used (or coated with a resin resistant to such electrolyte), and the small, hard particles and anchoring adhesive are also preferably inert with respect to the electrolyte to be used. For most electrolytes, fibers such as Dacron and adhesive such as commercially-available urethane or imide type adhesives are satisfactory. The small particles are described in my aforementioned prior U.S. patents and preferably are abrasive grains, these being inert and of adequate hardness for all applications of the process.

FIG. 2 is a schematic illustration of the process showing the main body of electrolyte 20 in an enclosure or tank 21. A plurality of anodes 22-23-24 are shown—these being soluble anodes of different metals whose ions are desired in the electrolyte and in the electrodeposit to be obtained therefrom. To indicate the control of metal ion concentration in the solution, anodes 22 and 24 are shown being mechanically activated by activator discs 25 and 26 respectively. Assuming anode 22 is more difficultly soluble than anode 24, the activator structure 25 and activating conditions of such structure will be more aggressive than those of activator 26. Anode 23 is shown without activation, indicating that it will corrode at the desired rate by itself. The electrolyte 20, with the ion concentration therein controlled by the anode dissolution rates is then picked up by the individual electrolyte transport cells 27 of the porous activating belt 28. This belt 28, driven by any suitable means over rolls 29 and 30, carries the electrolyte 20 within cells 27 into the plating zone 31 where the belt 28 passes between the cathode 32 and an imperforate pressure plate 33. The gap between the cathode 32 and plate 33 is such that an essentially liquid-tight seal is made with the fibers of the belt 28 resulting in closing and preventing inter-communication between the cells 27 of belt 28 while such cells are between the cathode 32 and plate 33. A high potential difference is maintained on the cathode 32 so that essentially all of the metal ions in each closed cell 27 deposit out. As the cells 27 emerge from the plating zone they again open up and receive fresh electrolyte 20 as a result of the motion of the belt 28.

The following examples are illustrative of the process of the present invention and are furnished for such purpose:

EXAMPLE I

Utilizing a belt machine of the general type illustrated in FIG. 1 of U.S. Letters Pat. No. 3,619,401, an 80-20 brass was electrodeposited from a copper and zinc sulfate mixture. The electrolyte consisted of 250 grams/liter $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 110 grams/liter H_2SO_4 , 372 grams/liter ZnSO_4 , 71 grams/liter Na_2SO_4 , and 60 grams/liter



This was a mixture of an acid copper electrolyte with a zinc sulfate electrolyte. The approximate ratio by weight of Cu to Zn in the mixed electrolyte was 3:1. In this particular run, the belt was not submerged in the electrolyte but instead the electrolyte was introduced onto both surfaces of the vertically-oriented belt just prior to its entry between the inner anode (lead) and the steel cathode plate upon which the deposit was to be formed. The porous belt used in this run was a compressed non-woven having a plurality of small, hard particles secured to its surface by a phenolic adhesive.

The electrolyte at room temperature was sprayed onto both surfaces of the belt and carried in the pores of the

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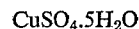
belt into the constricted zone between the cathode and anode. In this instance, the anode acted as the pressure plate and applied approximately 1.25 pounds/inch² pressure, sealing off the pores of the belt against intercommunication with each other. The belt was driven through this narrow gap at a speed of 1,000 surface feet per minute. The current density applied was 2,400 amps/ft.².

The deposit was compact, brass colored metal having the specific composition of 78.8% copper and 21.2% zinc. The deposition rate was 2 mils/minute.

EXAMPLE II

Utilizing a disc machine of the type illustrated in FIG. 3 of U.S. Letters Pat. No. 3,619,401, a copper-nickel composition was deposited in essentially equal proportions at high deposition rates. The 7 inch diameter porous disc was similar in construction to the belt of Example I and was rotated against a 1/2 inch diameter cathode rod under a pressure of approximately 3 pounds/inch.² Speed of rotation at the center of the cathode was approximately 1,000 surface feet per minute.

The electrolyte, consisting of 19.6 grams/liter



292 grams/liter $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 80 grams/liter NH_4OH and 150 grams/liter $(\text{NH}_4)_2\text{SO}_4$, was supplied to the surface of the porous disc at room temperature. Again, as each portion of the disc passed into contact with the end of the cathode rod, it was compressed and the communication between pores of the disc was broken. The isolated cells of electrolyte were subjected to a current density of 1,850 amps/ft.² and the metal was deposited on the cathode. The run was continued for 5 minutes, producing a compact, dense metal deposit 7 mils thick which analyzed as 47% Cu and 53% Ni.

The pressure in the plating zone may vary within wide limits, depending primarily on the structure of the porous media used to transport the electrolyte and particles. It should be sufficient to effectively cause the cessation of communication between the cells in the media within the plating zone to minimize or eliminate electrolyte flow from cell to cell. Generally, pressure will range from a few tenths of a pound per square inch up to as much as 25 p.s.i. Usual pressures for most activators will fall between about 0.8 p.s.i. and 3 p.s.i. Speeds of the media through the plating zone will be dependent to a considerable degree upon the deposition rates employed. However, in general, rates of 200 to 1,000 feet per minute have been found adequate.

The activator material used is preferably designed with regular, uniformly-shaped cells. However, cells or pores of irregular size and shape may be used where extremely careful control is not required.

What is claimed is:

1. A process for the simultaneous electrodeposition of multiple metals from a liquid electrolyte which comprises:

- (a) supplying a bulk quantity of electrolyte containing ions of multiple metals;
- (b) subdividing a portion of such electrolyte into multiple small volumes;
- (c) introducing said multiple small volumes into a plating zone wherein a cathode is undergoing mechanical activation;
- (d) preventing any major interflow of electrolyte within said plating zone from said bulk quantity of electrolyte into said multiple small volumes and preventing any major interflow between said multiple small volumes; and
- (e) imposing within said plating zone an electrodeposition potential in excess of the deposition potential of any metal in said electrolyte

whereby essentially all of the multiple metal ions within said small volumes of electrolyte are electrodeposited on said cathode within said plating zone.

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2. A process as in claim 1 wherein a porous, particle-supporting media is used to carry said electrolyte volumes and to provide said mechanical activation of the cathode.

3. A process as in claim 2 wherein said porous media has uniform pore sizes.

4. A process as in claim 1 wherein a plurality of soluble anodes are provided to furnish the multiple metal ions to said electrolyte.

5. A process as in claim 4 wherein at least one of said anodes is mechanically activated to control its rate of supply of metal ion to said electrolyte.

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5 JOHN H. MACK, Primary Examiner

W. I. SOLOMON, Assistant Examiner

U.S. Cl. X.R.

10 204—35 R, 36, 44, 45 R, DIG 10