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INVENTION REPORT

PULSED CURRENT ELECTROPLATING

by

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February 9, 1966

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DESCRIPTION OF INVENTION

This report of invention concerns improvements to electroplating thin and protective coats for the substrate metal through the application of high current rectangular shaped pulses. It was conceived in the course of a study of various techniques for plating nickel onto uranium metal fuel elements to provide an adherent, non-porous bonding layer between the uranium and an external aluminum jacket.

In one model for the electrodeposition of metals from aqueous solutions, it is suggested that as the ion moves into the electrical double layer it becomes progressively less solvated and, at the same time, associated with the electronic structure of the substrate metal. This species still retains some of its ionic character, and is partially neutralized, at this point. It is often referred to as an "adion". The adion will then migrate, or diffuse, to an active site. The active sites are growth planes, kinks, or corners; but since their number is small as compared to the total surface area, most of the nucleations occur on surface planes. An adion achieves sufficient energy in the double layer to settle on the plane which then becomes a nucleation or active site for further deposition. At very low overvoltages, the metal deposition can often occur at just a few sites, whereas at higher overvoltages the number of nucleation sites may be considerably greater. At very high overvoltages, it might be expected that the entire surface would be active. In this case, protective coverage would be achieved by a thin plate. On the other hand, for the lower overvoltage, coverage may be achieved by lateral growth and bridging; which, if the crystal growth normal to the electrode surface is rapid, would result in a thick plate before protective coverage is achieved.

Often, a special strike solution or high current strike (resulting from a large applied overvoltage) is used to insure good initial coverage. The high current can be maintained just a short time because the diffusion layer is soon depleted of the metal ions; and the subsequent production of hydrogen results in an increase in pH, and possibly the precipitation of the metal as a hydrous oxide or hydroxide. One method to relieve this problem would be to pulse the current, such that the diffusion layer is not seriously depleted. The pulses should be rectangular in shape and as large as possible and their rise time should be as fast as possible so that the maximum useful energy is reached at the electrode in minimal time. Thus the entire surface should be activated and uniformly coated. In general, the pulse length should be kept short to maintain little concentration polarization which is important to good micro throwing power, but the length of the pulse is an important variable to the crystal growth and it may be desirable to lengthen the pulse to obtain certain other plate characteristics. The pulse repetition rate should be slow enough to allow the diffusion layer to return to its initial concentration.

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In this report of invention it is proposed that pulsed current plating, as described above, is a superior technique for electroplating thin protective plates onto metal substrates. This is supported by the following experimental observation. Nickel plates on uranium using current pulses 200 to 400 microsec wide, 750 to 1000 ma/cm², and a repetition rate of 800 to 1200 pulses/sec were inspected by photomicrographs of cross sections. This inspection revealed the nickel deposits (from Watt's chloride or bromide baths) consisted of small crystallites which appeared to be randomly oriented. This is in contrast to plates obtained by d.c. plating from a Watt's bromide bath which were distinctly columnar. Deviations from these pulse conditions lead to deposits which are significantly different; for example, distinctly columnar. The effect of varying pulse conditions is observed for other metals. For example, gold plates from an acid gold bath are rose tinted for pulses of 2.5 amps/cm², 100 microsec wide, and 200 pulses/sec; but by widening the pulse to 200 microsec and reducing the repetition rate to 100 pulses/sec a bright yellow plate results.

Furthermore, the rate of deposition of nickel can be at least five times greater than for d.c. plating (60 ma/cm²) with as good or improved current efficiency. The increase in plating rate also occurs for other metals. For example, gold can be plated from the acid gold bath at a rate of about 10 over that for d. c. plating.

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