# THE INVESTIGATIONS AND CHARACTERISATIONS OF COBALT MULTILAYER METAL NANOSTRUCTURES

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Multilayer films of Co, and Co-Cu, in the thickness range of several manometers up to 1 μm, have been electroplated using a single, and a recently developed automated multibath systems. Electroplating bath constituent, pH, temperature, agitation, etc. as well as galvanostatic modes, i.e. direct current versus pulse and/or pulse reverse, were investigated, optimised, and will henceforth be reported. Nanostructures of up to over a thousand layers, with varying thicknesses if desired, were produced in an automated system developed recently in our laboratory. The structures were characterized for composition, texture, magnetic and mechanical properties with optical microscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray fluorescence and diffraction spectroscopies. For cobalt deposition, a combination of direct and pulsating currents under mild air agitation resulted in the best specimens. Compositionally modulated alloys (CMA) of cobalt-copper were obtained employing a combination of alternating current amplitudes and agitation modes. Nanostructures such as those reported herein will have promising applications in a wide area of high tech manufacturing enterprises due to their unique electronic, mechanic, and magnetic properties.

## Introduction

Although the electrodeposition of multilayered metals was introduced in the 20's by Blum [1] employing a manual dual bath system, their optimised manufacturing processes and full potential applications are yet to be realised. This has been in part due to the lack of consistency among the samples for mass device fabrication, and limitations in "nanomizing" the thickness of the deposits. However, the enhancement of tensile strength has been observed for laminated structures in the submicrometer dimension, when compared to the bulk metal of comparable thickness. It was shown[2] that a "supermodulus effect" is observed for such structures, when the thickness of Au-Ni and Cu-Pd laminated structures fall below 10-nm. For instance, a four-fold anisotropic effect of an electrodeposited Co/Cu CMA, in the several nanometer thickness ranges, has been observed[3]. The origin of such changes in magnetic properties is not however established yet[4], mainly due to poor quality of the specimen produced by currently employed processes such as Chemical/Physical Vapour Depositions.

CMAs and multilaminated ultra-thin metal structures, as produced in a single electroplating bath on a rotating disk substrate, have provided high quality alternative deposits with sharp boundaries[5-8]. A rotating disk electrode with a well defined and controllable hydrodynamic mass transport and potential, as it is commonly used, is not, however, an ideal tool in a manufacturing scenario, even though excellent work reported based on such a system was necessary to fully characterise and thus control the bath conditions[9]. We herein describe two complementary methods of generating such structures in a semi-industrial approach: first, employing a single bath containing

optimised constituents for the co-deposition of Cobalt and Copper, by modulation of DC vs. pulse currents and agitation; second, by the use of an automated multibath system recently developed in our laboratory, where multilaminated thin structures of Cobalt-Copper, and Cobalt-Copper-Nickel, in varying thicknesses of nano- to micrometer ranges and of up to several thousand layers, are produced with great precision..

## Experimental Section

*I. Materials*

1. Chemicals: Chemicals used were either reagent grade and/or the manufacturing grade of high purity.
2. Apparatus: The following instruments were used in our investigations: Perkin-Elmer Atomic Absorption spectrometer, Hitachi Scanning Electron Microscope, Siemens D 5000 X-ray diffractometer, and SQUID from Cryogenic Consultants Ltd. Series BP2.

*II. Sample preparation*

1. Single bath: The bath was a modification of an earlier reported system[8]. The concentration of the more noble metal, copper, was maintained in the order of 0.65 %(w/w) to 0.30 % of the less noble metal, cobalt. The bath was composed of reagent grade materials (g/litre) as follows: cobalt sulphate heptahydrate (330), cobalt chloride hexahydrate (40), Boric acid (30), and the equivalent of 0.25 to 0.5 g copper as desired, from a copper sulphate, chloride, or sulphamate salt. The bulk pH was adjusted periodically to 4.50, with sodium hydroxide or hydrogen chloride. The cobalt bath current efficiency was found to be ~90 %. The bath was run at 45 °C under mild aeration, unless otherwise noted. Employing a Computer-Aided Pulse Plating System (CAPP) developed in our laboratory, several galvanostatic programs were executed to supply the total current to an activated steel St. 37 panel of 300 $cm^2$. The most commonly employed applied current programs are depicted in Figure 1: ramp of 0.00 to 4.0 A in 60 seconds to deposit primarily cobalt as an underlayer on an activated steel substrate, followed by a DC current of 0.320 s of 4.0 A, followed by 10.0 s of pulses 0.040 A amplitude for copper deposition (Fig 1A). The other three programs depicted follow the same analogy. A modified version of the above program resulted in micrometer thickness CMAs and/or polylaminated metal structures; in such cases, the agitation was employed during the electrodeposition of copper so as to replenish its concentration in the diffusion layer, whilst the bath remained stagnant during the cobalt electrodeposition.

2. Dual bath: The cobalt bath in this deposition mode was the same as above, except that the copper salt was absent. The separate copper bath was composed of 20 g/l Cu ($CuSO_4$), 200 g/l $H_2SO_4$, and commercial brightening agents, typically of less than 1 g/l concentrations. The substrate was activated in a citric acid bath, 20g/L, followed by rinsing in a double distilled, deionised water (18 Ω M-cm), before it was inserted into any of the above two baths.

## Results and Discussions

Figure 2 illustrates the result of a series of Hull cell experiments. The metal distributions were determined with X-ray Fluorescence spectroscopy, and confirmed with in-situ atomic absorption spectroscopy. One notes that percent composition of copper was decreased as a function of increasing current density, whilst the percent cobalt was increased. It is based on such experiments that the current densities to preferentially deposit copper and/or cobalt were pre-selected. Figure 3 illustrates the feature of a cobalt-copper laminated nanostructures obtained with Scanning Electron Microscopy. It is a sample produced in our automated dual bath system. The lighter areas are ~100-nm cobalt layer, followed by three consecutive sub-layers of ~30-nm

cobalt, all interspaced with 100-nm copper layers that have been etched away for SEM preparations. It is admitted that we are still working with various levelling and brightening agents to smooth out the layers. Figure 4 illustrates the x-ray diffraction spectra for laminated 30-100-nanometer structures of cobalt interspaced with 100-nm copper, for a total of 80 sub-layers of each metal present. The substrate was pre-zincated aluminium plate. Figure 4 illustrates a series of x-ray diffraction patterns obtained from direct exposure of the deposits. It is interesting to note that below 50-nm thickness, even though cobalt is still present, it nevertheless takes the crystal structure of copper which is present in higher thickness of 100-nm.

Magnetic characterisation of the specimen based on SQUID techniques to observe the magnetisation as a function of varying applied magnetic field, and temperature are being currently investigated, and will therefore be reported during the presentation; however, preliminary data indicates a change from "in-phase", i.e. negative anisotropy, to an "out-of-Phase", i.e. positive anisotropy when the thickness of cobalt layer is decreased to below ~30-nm. We are currently engaged in further optimising the bath systems and processes in order to generate thinner, more levelled laminated structures. A more thorough characterisation of such specimens is also our other main focus, with emphases on magnetic and electrical properties.

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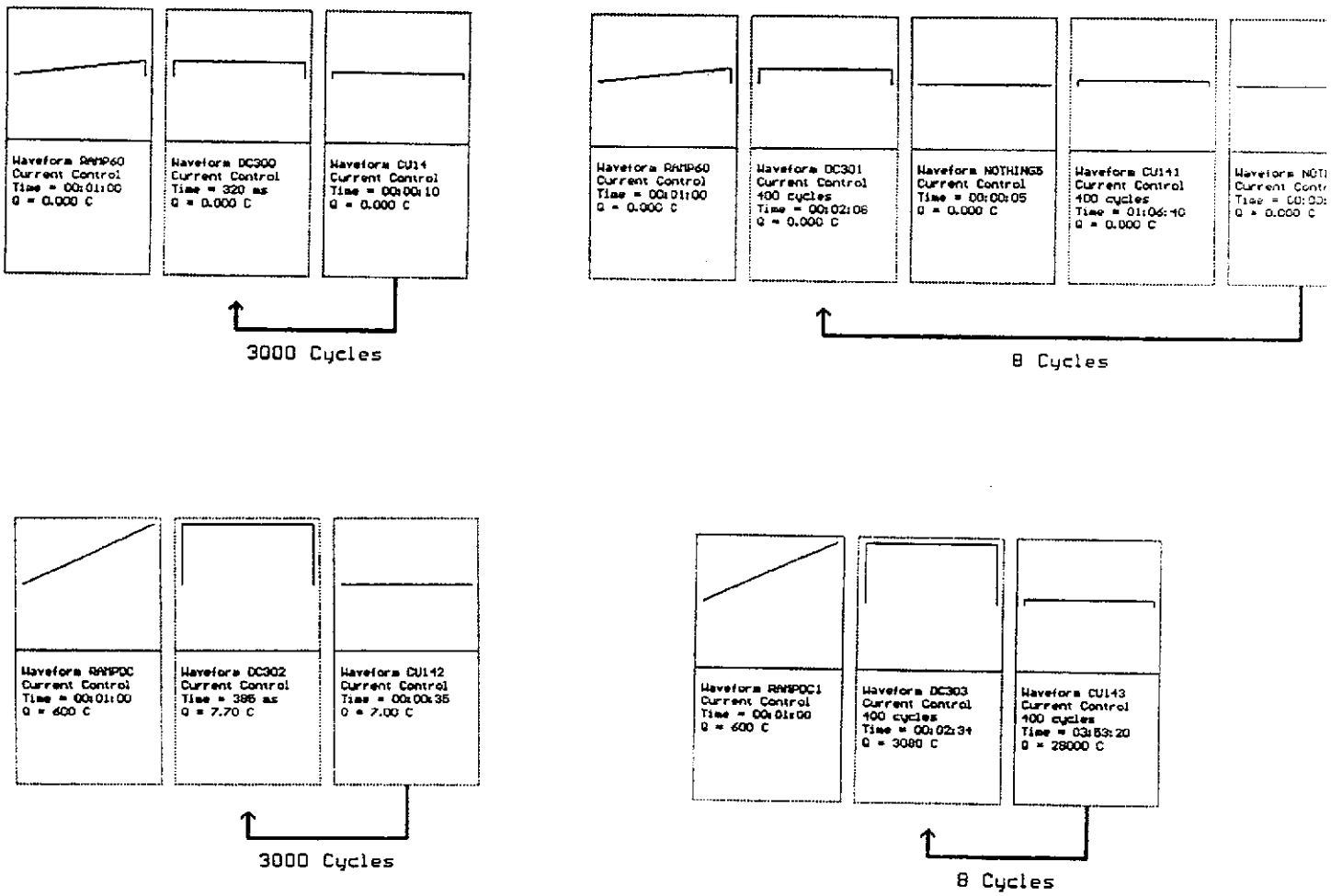


Figure 1: Typical applied current programs based on computer assisted pulse plating software.

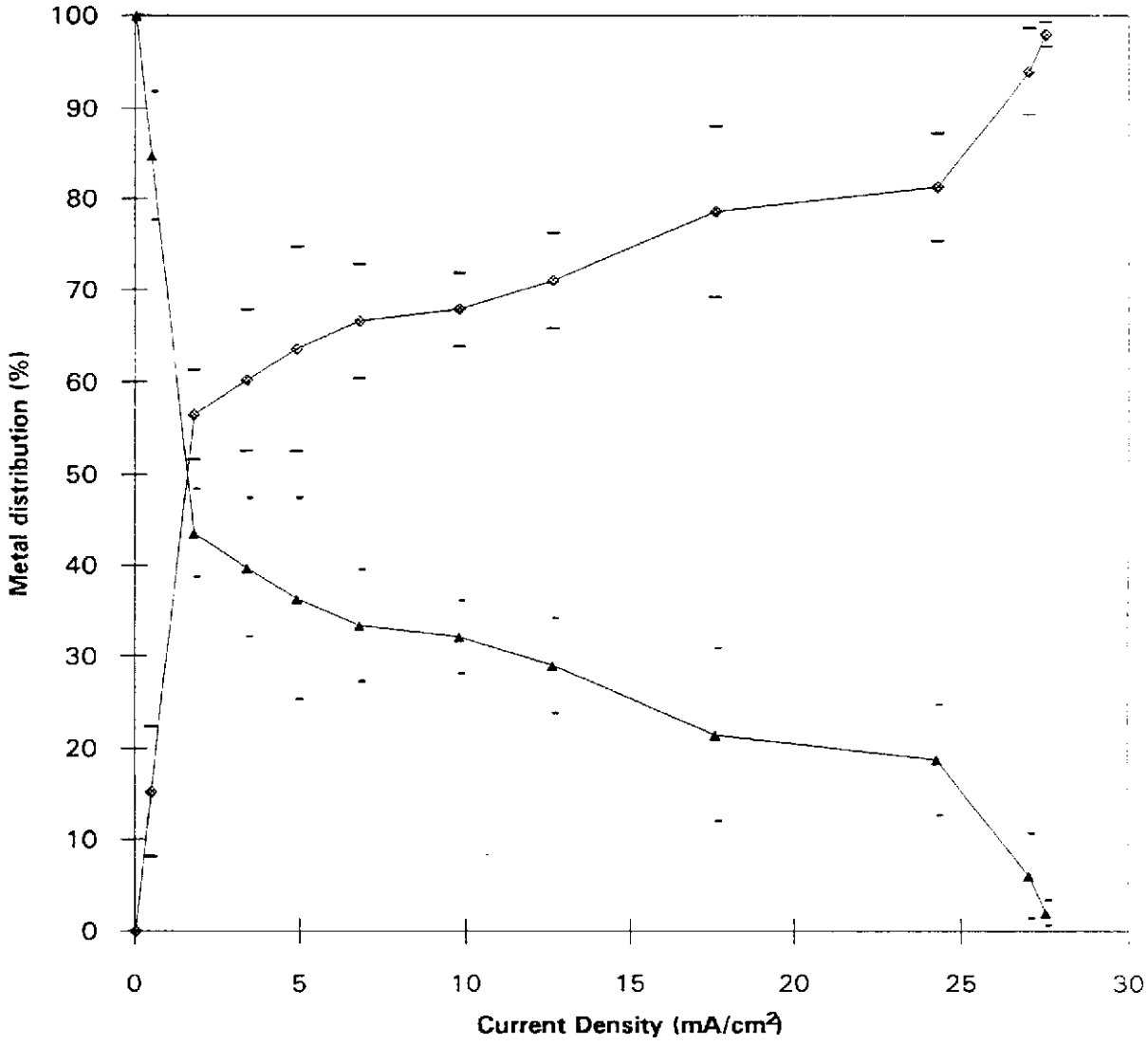


Figure 2: Cobalt-copper distribution as a function of current density (▲ copper; ◆ cobalt), each an average of five measurements, where horizontal bars indicate the standard derivations.

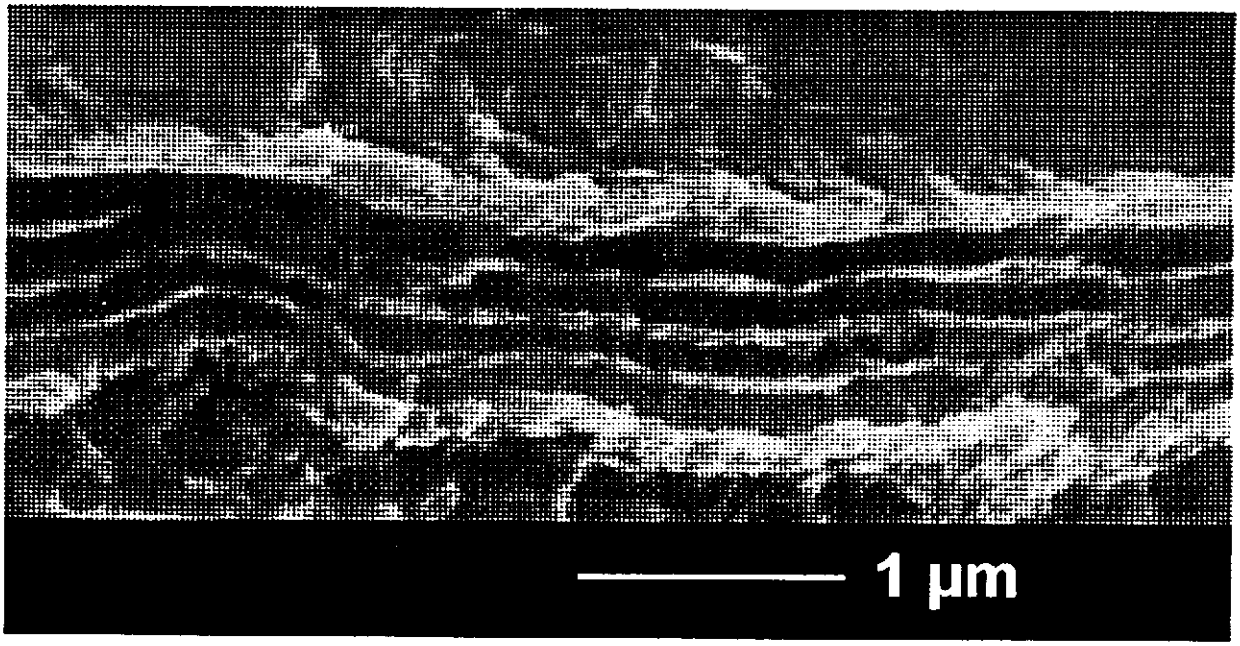


Figure 3: Scanning electron microscopic image of a cobalt-copper laminated structure, in nanometer dimension.

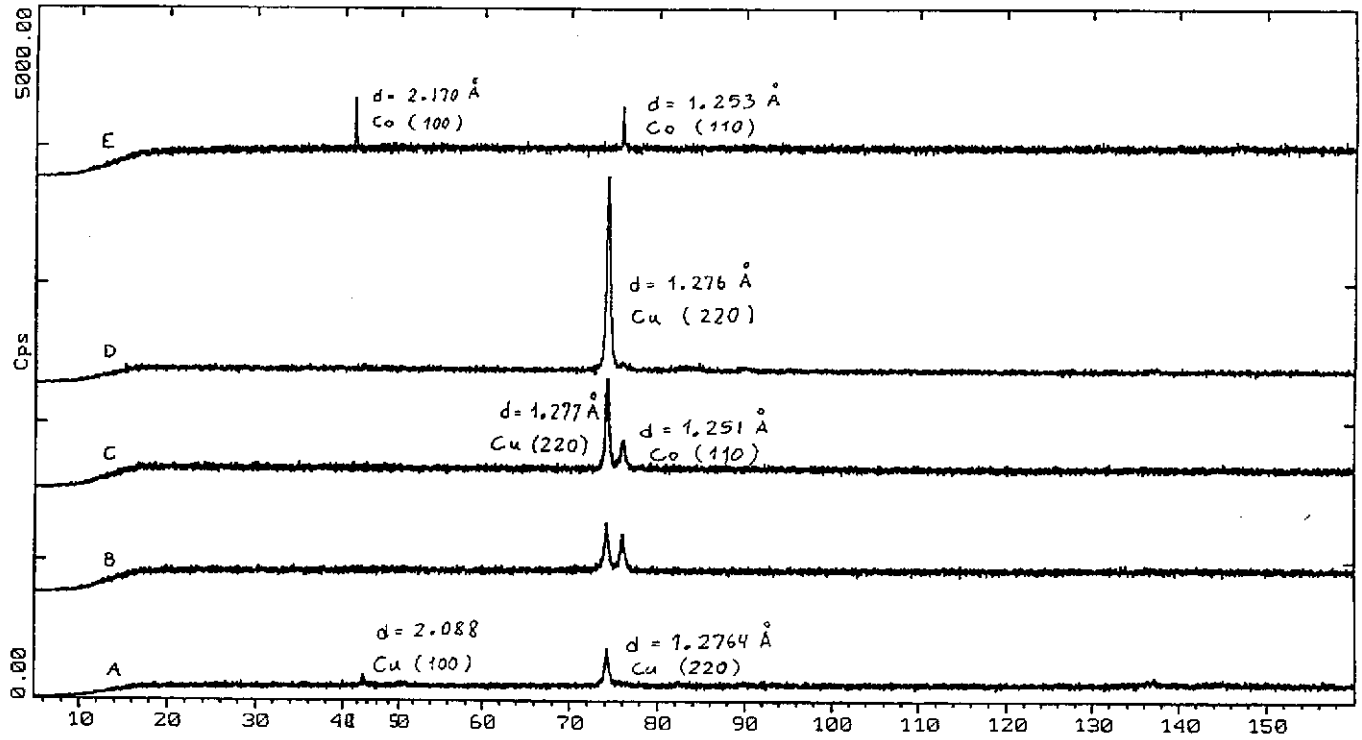


Figure 4: Examples of X-ray diffraction patterns for cobalt-copper laminated deposits; A) Cobalt below 30 nm, copper 100 nm; B) 100 nm of each with a levelling agent normaly used for nickel plating (OXY 0.5 ml/l); C) Cobalt 50 nm, copper 100 nm; D) 100 nm of each; E) ~8 µm cobalt deposited under pulse mode and agitation.



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