

Electrochemical Synthesis of Fe/Ag and Co/Ag Granular Thin Films

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Abstract: A voltammetric analysis has been employed as a means for investigating behaviour of the electrochemical deposit of silver-cobalt and silver-iron granular thin films. In this paper, we report that by controlling some electrochemical variables such as the concentration of complexing additives, the silver deposition will be controlled diffusionally. Based on these considerations, periodic perturbations have been used as electrodeposition technique, because with pulsed current we can control several variables to change the kind of deposition, which produce considerable modifications on electrodeposits as far as the morphology, roughness, structure of electrodeposits, alloy ratio and consequently the magnetic behaviour. We have focused on how the pulsed parameters can change the alloy composition.

INTRODUCTION:

In recent years interest has been focused on the properties of magnetic multilayers[1], and in granular materials[2, 3] due, basically, to the giant magnetoresistance (GMR) effect. In order to optimise the parameters that control GMR, it is essential to have a basic understanding of the kind of technique employed, or the way to build the magnetic structures. More recently, there have been a number of experiments reported on thin films prepared by such techniques[4] as sputtering[5], melt spinning[6], laser ablation[7] or various types of deposition involving high-vacuum conditions. However, all of these methods are relatively complicated or expensive. On the other hand, electrodeposition technique[8] gives a suitable and relatively cheap technique for the preparation of thin films of granular alloys. The use of pulsating current[9] for metal plating has been proposed to facilitate the deposition control. In case of alloy plating it is to be expected that the choice of pulse parameters influence, among other things, the composition of the deposit.

EXPERIMENTAL:

A Scanning Potentiostat Model 326 EG&G as potential controller, connected to a Gould 20 MHz Digital Storage Type 1425 oscilloscope was used and the whole set was controlled by a computer. For the pulse deposition experiments 20 Hz Pulse generator HM 8035 HAMEG was employed. Fig. 1 shows a schematic picture of the equipment. For pulsed deposition we use a Al rotating disk electrode as working electrode and Ag/AgCl saturated electrode as reference electrode. All pulsed experiments were carried out at 600 r.p.m, to avoid the H₂ bubbles generated.

Table 1 shows the electrolyte composition. We choose those conditions in order to obtain an optimal homogeneous deposition. We introduce Coumarine (for Ag/Co system) and Saccharin (for Fe/Ag system) in order to avoid dendritic deposition.

REACTIVE	Ag-Fe SYSTEM	Ag-Co SYSTEM
H ₃ BO ₃	0.5 M	6 gr/L
Ammonium citrate (dibasic)	-	10-40 gr/L
Magnesium sulphate	-	25 gr/L
Silver sulphate	0.0500 gr/L	0.0528 gr/L
Cobalt sulphate (heptahydrate)	-	40 gr/L
Ammonium iron (II) sulphate (hexahidrate)	7.8-26 gr/L	-
Coumarin	-	1 gr/L
Saccharin	4 gr/L	-

Table 1: Bath composition

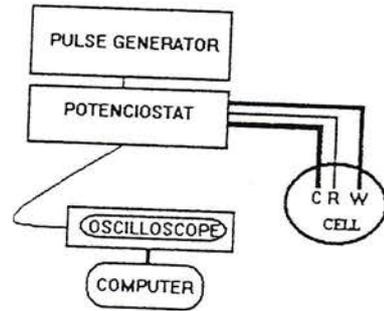


Fig. 1 Schematic diagram of the instrument employed for pulsed deposition.

RESULTS AND DISCUSSIONS:

VOLTAMMETRIC STUDY:

Cyclic Voltammeteries (CV) for the electroreduction of Ag⁺, Co⁺² and Fe⁺² in H₂O solutions are shown in figures 2-7. A significant separation (ΔE_p) between the cathodic and anodic peaks was obtained in all solutions investigated (Fig 2,4,6), showing that in all systems we have an irreversible behaviour. This may be due to hindrance of the reaction by molecules adsorbed on the electrode surface. In case of Ag (Fig 2), the separation is the biggest, showing that it is more complexed, than Co or Fe.

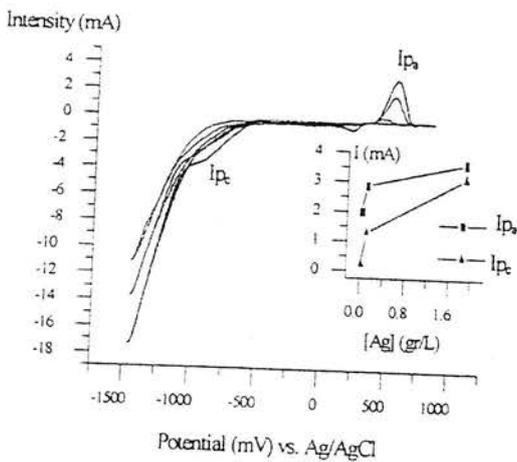


Fig. 2: Ag CV at different silver concentrations. ($v_p = 100 \text{ mV S}^{-1}$; [CITRATE]=10 gr/L ;)

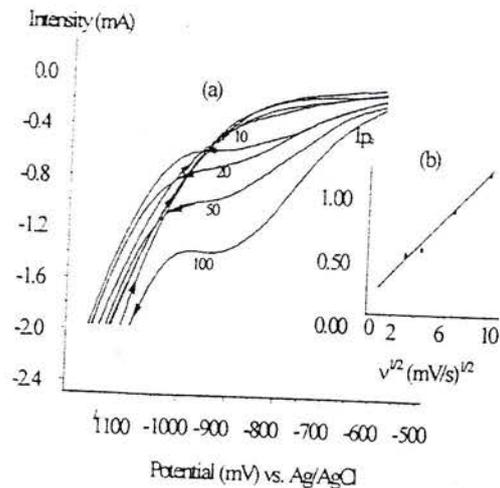


Fig. 3: Cathodic Ag peaks at various v_p (mV S^{-1}) ([Ag]=0.014 gr/L; [CITRATE]=40 gr/L).

In Ag system, an increase in the scan rate (v_p) leads to a shift in the cathodic potential (E_{pc}) towards more negative values. This also confirms that in the solutions investigated, silver

reduction is irreversible. Moreover a linear relationship between cathodic intensity (I_{pc}) and ($v_p^{1/2}$) was found (Fig. 3b), which is often taken as evidence of diffusion control[10]. There is no significant variation on I_p with v_p in cobalt system (Fig 7). This result suggests that cobalt deposition is not controlled by diffusion, which could be expected because cobalt is in high concentration and is not complexed.

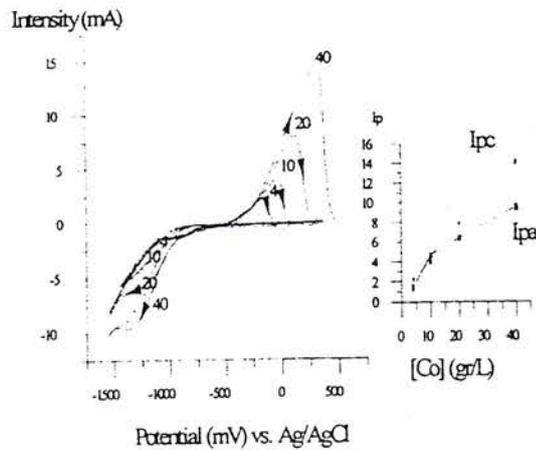


Fig. 4: CV Co measurements depending on the cobalt concentration ($v_p=100$ mV/s; [CITRATE]=40 gr/L)

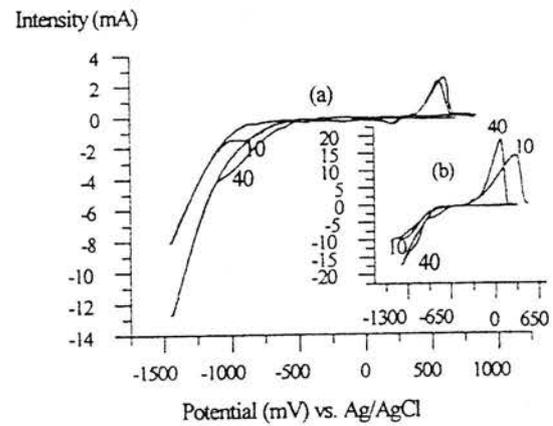


Fig. 5: Ag(a) and Co (b) CV depending on citrate concentration ($v_p=100$ mV/s; [Ag]=0.1 gr/L; [Co]=40 gr/L)

The electrodeposits can also be guessed from the voltammetric curves. For silver deposition, the hysteresis loop (cross-over potential) disappears for $v_p > 0.1$ V s⁻¹, (Fig 3a) indicating that no nucleation occurred and hence there was no increase in the electrode surface as a result of silver deposition[11], forcing a dendritic silver deposition growth. The features of the silver anodic peaks (smooth gaussian curves) are characteristic of an instantaneous nucleation[12]. In contrast, cobalt and iron deposition can be described with progressive nucleation as the features of anodic peaks show (there is a shift on the anodic peak maximum) (Fig. 4,6).

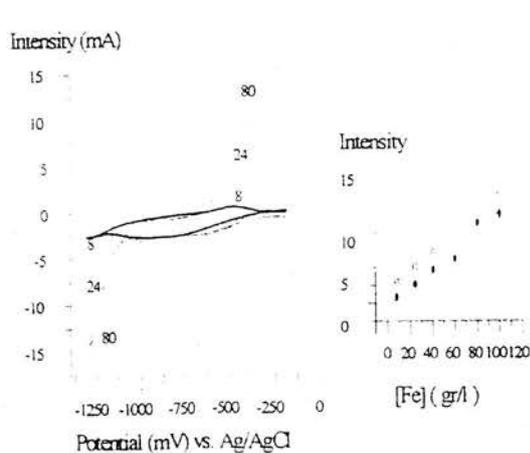


Fig. 6: Fe CV at different Fe concentrations. ($v_p=50$ mV/s)

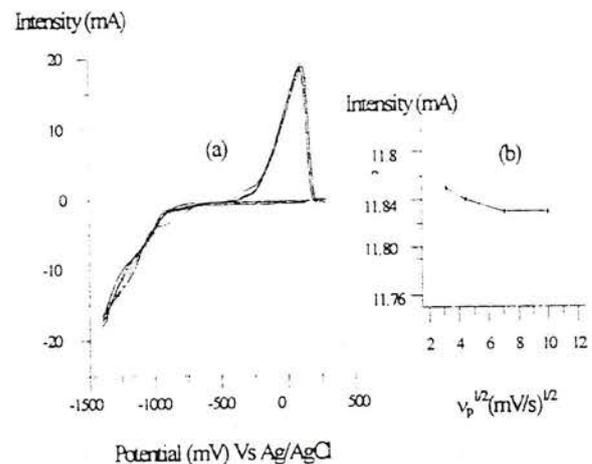


Fig. 7: Co CV measurements varying the v_p . ([CITRATE]=40gr/L; [CUMARINA]=1 gr/L; [H₃BO₃]=25 gr/L)

The influence of citrate concentration as a complexing agent was investigated. In Fig 5, we can see that increasing citrate concentration increases the intensity of cathodic peak (I_{pc}), as for Co or for Ag. This can be explained because the H^+ activity (a_{H^+}) at the electrode interface increases. In fact a rise in the H_2 evolution was observed. It was also found a shift towards more negative potentials on silver E_{pc} (Fig 5 (a)) but not on Co (Fig 5 (a)), showing that silver is only significantly complexed by citrate molecules.

PULSED ELECTRODEPOSITION:

We have employed pulsed current instead of DC deposition in order to avoid the silver dendritic deposition above mentioned also to obtain smooth deposits. To make a systematic study of how the pulse parameters affect alloy compositions, we based our study on frequency, width, intensity and pulse voltage.

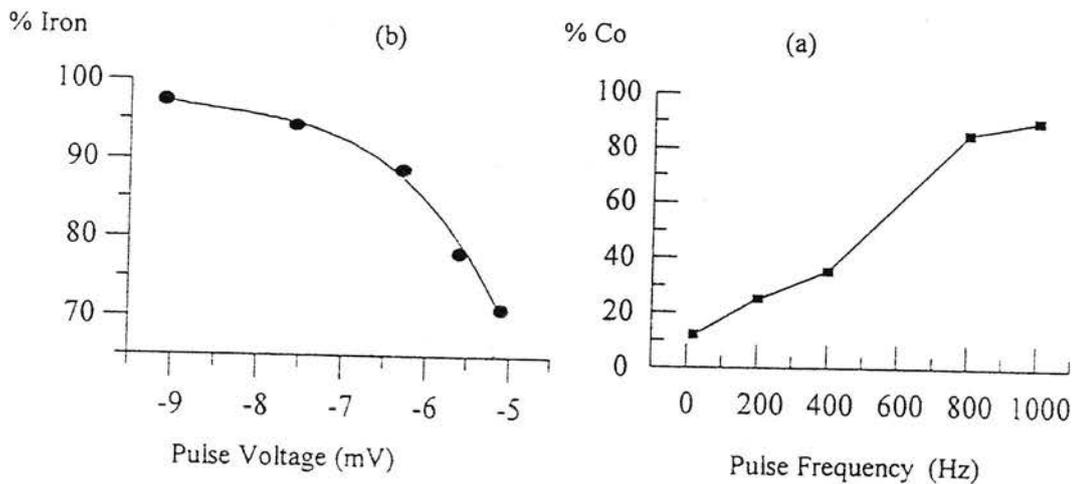


Fig. 8: Pulse analysis. (a) Voltage and (b) Width influence on alloy ratio.

Our results show that there is an increase of Co/Ag or Fe/Ag ratio in the binary alloy, when voltage, intensity, width or pulse frequency is increased. This is consistent because we use Citrate (for Ag/Co system) or Ascorbic acid (for Fe/Ag system) to minimise the silver activity at the electric interface, i. e. we complex the silver in both systems, and the silver deposition is controlled by diffusion. Therefore, by diminishing diffusion layer width, we will have an increase of Ag/Fe or

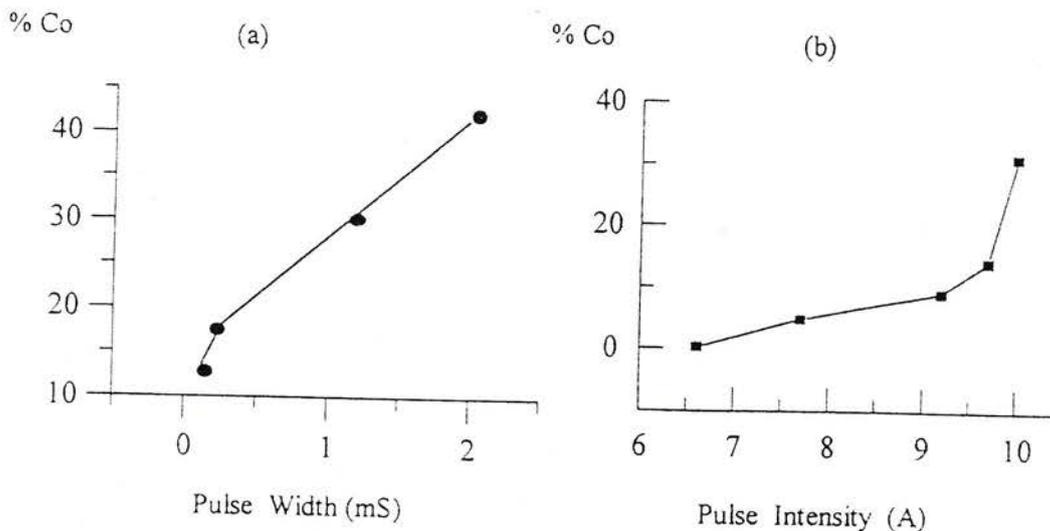


Fig. 9: Pulse analysis: Influence of (a) width and pulse (b) intensity on alloy ratio.

Ag/Co ratio. Increasing voltage, intensity, width or frequency we also increase the rate of the electrodeposition, enlarging the width of the diffusion layer. As some examples we show in Figs. 8,9 the alloy composition in different systems.

CONCLUSIONS:

Controlling pulsed parameters, we can control the alloy composition. We have obtained a wide range of binary alloys. The next step is to study how the pulse parameters can influence the magnetic parameters. As an example we can see in the Fig 10, how influences the pulse frequency in the VSM measurements (keeping constant the Ag/Co ratio).

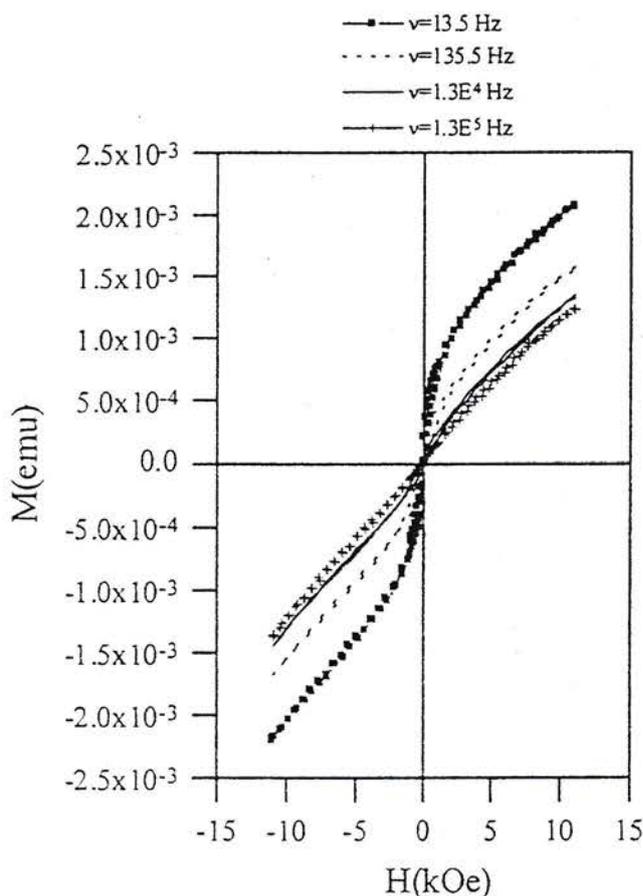


Fig. 10: Influence of the pulse frequency on the magnetic properties. (%Co=25; 400°C annealed samples)

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