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Electrodeposition of Mn-Bi rosalike thin films

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ABSTRACT — This work focuses on the electrodeposition of the Mn-Bi system from a mixed sulfate-nitrate bath on a polycrystalline Cu substrate. The electrochemical analyses are carried out by cyclic voltammetry. The effect of some experimental conditions on the deposit morphology and composition are investigated with a scanning electron microscopy (SEM-FEG) and the energy dispersive spectroscopy (EDS) respectively. The Mn-Bi deposits have a rosalike-shaped appearance with a heterogeneous distribution of manganese and bismuth. The EDS analysis shows that the Mn and Bi content in the deposit depend strongly on the pH bath and the applied potential.

***Keywords**: Mn-Bi thin films, electrodeposition, cyclic voltammetry, SEM-FEG, EDS*

I.Introduction

Up to now, due to their potential applications in the recording media, several methods were used for the preparation of hard magnetic nanomaterials and alloys such as CoPt, FePt [1,2] and MnBi [3-5]. The MnBi alloy in its low temperature (LTP) hexagonal phase is a hard magnetic material with a strong magnetic anisotropy along the *c* axis. The most studies reported in the literature for the elaboration of this system are based on the physical methods [6-9]. But the electrochemical way is not sufficiently used for the preparation of this material.

The electrodeposition of metals and alloys from aqueous solution is very delicate as several parameters must be controlled simultaneously: the nature of the electrolytic bath, ions concentration, electrodeposition mode, pH bath, temperature bath, additives, etc ….

In the case of alloys, the problem often encountered is the difficulty in finding the adequate electrolytic bath allowing the simultaneous electrodeposition of the two simultaneous electrodeposition of the two elements with a good efficiency.

In this context the Mn-Bi system is one of these alloys which may not be easily electrodeposited in an aqueous media.

The first difficulty encountered is due to the very low equilibrium potential value of the Mn^{2+}/Mn couple in aqueous solution compared to that of Bi^{3+}/Bi, and also to the complexicity of the manganese electrodeposition kinetics. In fact reduction of Mn^{2+} to Mn is always accompanied by hydrogen evolution, which makes it difficult to clearly detect the manganese reduction process. The manganese deposit is also easily oxidized [10].

In a previous work, our group has explored the chloride bath for the electrodeposition of the Mn-Bi system. The effect of the ammonium chloride on the current efficiency [11] and the annealing process on the deposit properties [12] were studied. In another work [13,14] a mixed sulfate-nitrate bath was used and the initial electrocrystallisation process was studied. The purpose of the present work is to study the effect of some experimental conditions on the composition of thin Mn-Bi films electrodeposited on a copper substrate in a mixed sulfate-nitrate bath.

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II. Experimental details

All the electrochemical experiments were realized in a standard three-electrode glass cell. The working electrode was a gold (99.9985%) rotating disk electrode (RDE) with an area of 0.038 cm^2 and a copper (99.99%) substrate with an exposed area of 0.28 cm^2. The counter electrode was a platinum wire. Saturated calomel electrode (SCE), was used as reference electrode.

Electrochemical experiments were carried out with an EG&G 273A potentiostat/ galvanostat drived with Power-suite software. The electrolytic bath consisted of 0.4 M $MnSO_4$ $1H_2O$, 10^{-3} M Bi $(NO_3)_3$ $5H_2O$, 0.5 M H_3BO_3. $(NH_4)_2SO_4$ (2.5 M) was used as a complexing agent to avoid the Mn and Bi precipitation and as a supporting electrolyte to increase the conductivity of the bath. The electrolytes were freshly prepared with de-ionized water. Before the experiments, solutions were deaerated with nitrogen for 30 min. Deposition was realized at room temperature.

The electrochemical characterization was performed using the cyclic voltammetry (CV). The Mn-Bi deposits were characterized by scanning electron microscopy FEG-SEM, atomic force microscopy (AFM) and energy dispersive spectroscopy (EDS).

III. Results and discussions

III.1. Electrochemical characterization

Cyclic voltammetry measurement was used to determine the deposition and dissolution potential of bismuth, manganese and manganese-bismuth system.

Fig.1 (a and b) show the cyclic voltammogram recorded on a gold rotating disk electrode (RDE) in a manganese, bismuth and Mn-Bi electrolytic bath respectively.

Starting from the rest potential (0.2 V/SCE) and sweeping towards the cathodic direction a weak current which corresponds to reduction of Bi^{3+} ions is observed at -0.17 V/SCE. In the reverse scan, a dissolution peak of bismuth starts at -0.01 V/SCE, it reaches a maximum at around 0 V/SCE (Fig.a). In the case of the manganese bath (0.4M $MnSO_4$, 0.5M H_3BO_3, 2.5M $(NH_4)_2SO_4$), a reduction plateau corresponding to the hydrogen evolution and water reduction appears between -0.6 V/SCE and -1.65 V/SCE, at -1.65 V/SCE a signified current is observed, it is attributed to both Mn(II), H_2O and H^+ reduction. On the reverse scan, a dissolution peak of manganese was observed at -1.42V/SCE. We can notice here that the current density in this case still remains negative; this is related to the additional reduction current of H^+ and H_2O.

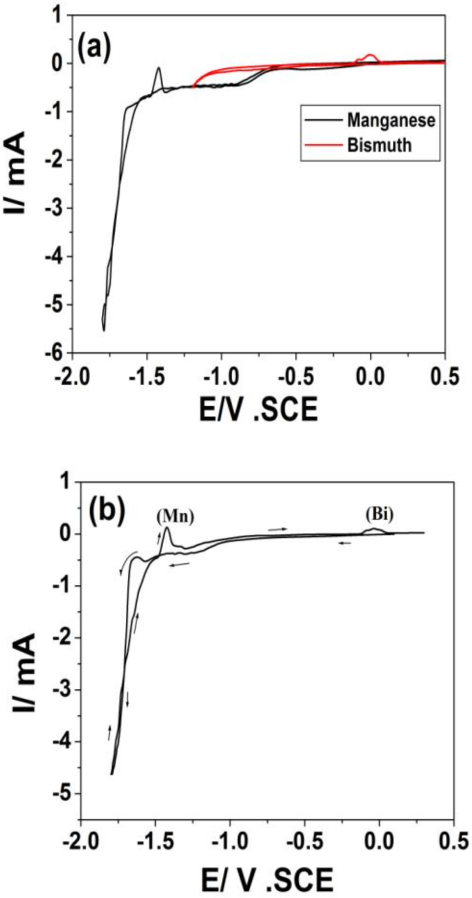

Fig 1. Cyclic voltammety study of a manganese and bismuth bath **(a)** and a complete Mn-Bi bath **(b)** 0.4 M $MnSO_4$, 10^{-3} M $Bi(NO_3)_3$ 0.5 M H_3BO_3, 2.5 M $(NH_4)_2SO_4$, E= -1.8V.vs.SCE. V_b=20mV.S^{-1}, ω=250rpm

In the other hand, we can note clearly the difference between the dissolution potentials of two ions Mn(II) and Bi(III) in the complete solutions (Fig 1.b) which is around 1.43 V : this high value make the codeposition of a MnBi alloy extremely difficult.

The study of the electrodeposition kinetics of Mn, Bi and Mn-Bi system as a function of the pH by cyclic vollammetry was used to estimate the current efficiency during the electrodeposition.

In this method the current efficiency of the each element has been estimated by calculating the total charge from different voltammograms recorded at different pH, assuming that the anodic peak correspond to the amount of the deposited Mn-Bi and the cathodic current to both Mn, Bi and hydrogen evolution.

The Table1 presents the current efficiency calculated. We can note that the current efficiency of Mn-Bi electrodeposition is very low.

Table 1.Current efficiency (%) of Mn, Bi and Mn-Bi as function of pH bath at E=-1.8V/SCE

pH	*Manganese*	*Bismuth*	*Mn-Bi*
1.8	0.56	4.28	3.19
2	1.15	3.42	4.40
2.3	4.15	2.50	6.92
2.5	4.60	1.82	6.90
2.9	5.33	0.73	7.00

III.2. Morphological characterization

According to the electrochemical study, Mn-Bi thin films were electrodeposited on copper substrates at different deposition times and a fixed potential of -1.8 V/SCE (Fig.2).

As we can see, the surface morphology of the deposit changes according to the deposition time. At a short deposition time, the deposit consists of dispersed 3D grains with various sizes less than 100 nm, this behavior is characteristic of a progressive nucleation mode as already reported before [14]. No distinction can be done between bismuth and manganese at this stage of deposition and the surface substrate is not completely covered (Fig.2a). The 3D character of this early stage deposited films at two different applied potentials is well highlighted by the AFM observations and their corresponding extracted profiles displayed on Fig 4a and 4b. As the deposition time increases the form of the deposit changes. As displayed in the BSE SEM-FEG images (Fig.2c) the deposit has now a rosalike aspect consisted of a fine and dispersed grain of bismuth (white area) imbedded in large platelets of manganese deposit (grey area), as confirmed by the EDS analysis (Fig. 3). Another heterogeneous Mn-Bi deposit with a different appearance has already been observed in a previous work [11] using a chloride bath under direct and double pulse electrodeposition mode [11,12]. This was related to the difference between the equilibrium potential of the two redox couple and to the strong immiscibility of the two elements.

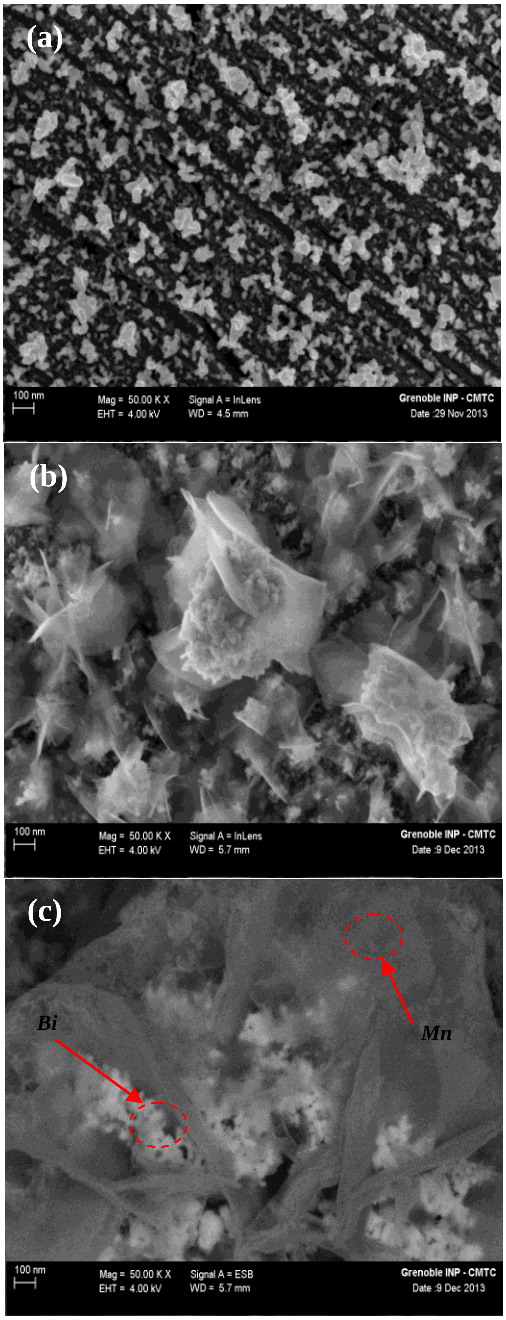

Fig.2 SEM-FEG images of manganese-bismuth system electrodeposited on Cu substrate at different times. (a) 25s, (b) 75s, (c) 300s. E=-1.8V/SCE.

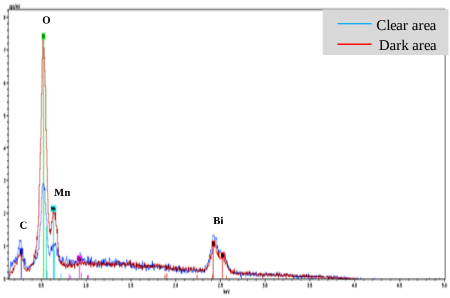

Fig.3 The corresponding EDS spectrum of manganese-bismuth system electrodeposited during 300s. E=-1.8V/SCE

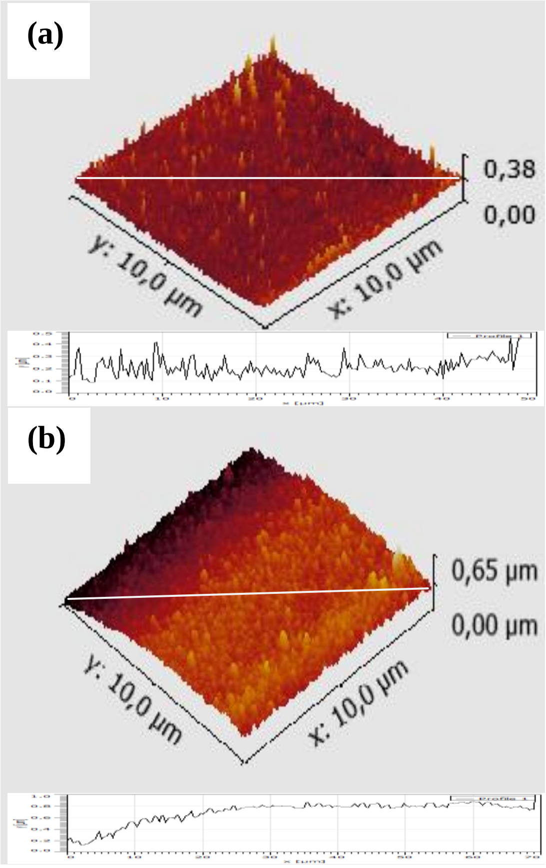

Fig.4 AFM images of manganese-bismuth system electrodeposited during 25s. (a) E=-1.7V/SCE (b) E=-1.8V/SCE.

III.3. composition analysis

The Mn and Bi contents in the deposit was studied at different experimental conditions such as the pH bath, potential and the deposition time using the EDS spectroscopy (Fig.5a,b,c respectively).

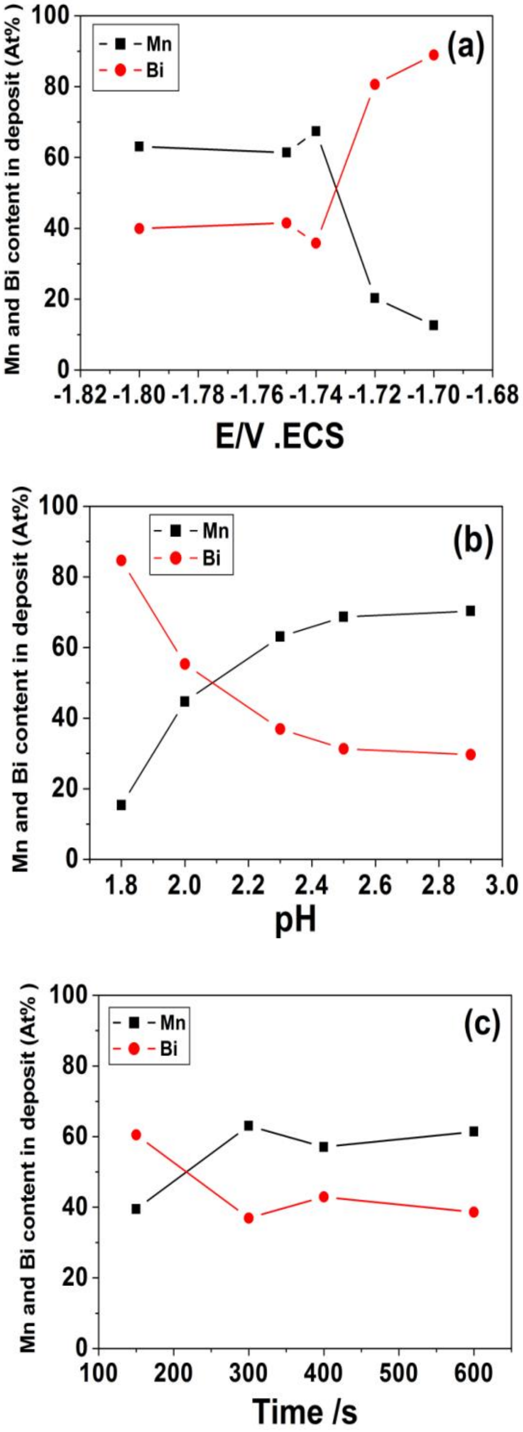

Fig.5 Variation of Mn and Bi content in the deposit at different experimental conditions, (a) potential, (b) pH, (c) time

The global composition analysis obtained at different deposition potential (Fig.5a) indicates that Bi predominate at lower potential (-1.7V/SCE). As the deposition potential increases the Bi content decreases while the Mn content increases up to a deposition potential of -1.75V/SCE where the film composition becomes relatively constant (63% Mn and 37% Bi).

On the other hand the contents of Mn and Bi in the deposited films depends strongly on the pH bath (Fig.5b), indeed bismuth predominate at lower pH value, while the manganese content increases with increasing the pH bath. This observation presents a good agreement with the current efficiency estimation in function of the pH bath (Table.1) where the current efficiency of Mn^{2+} reduction increases with increasing the pH, whereas the current efficiency of Bi^{3+} decreases.

The effect of the deposition time is displayed on (Fig.5c), as can be seen, there is no appreciable variation in the Mn and Bi content, however the deposits became dark and poor quality at a high deposition time.

IV. Conclusions

In summary, the electrochemical study shows that the potential region for the deposition and dissolution of bismuth is very distant compared to that of manganese.

The morphological characterization of the deposit shows a heterogeneous surface with dispersed bismuth grains embedded in large platelets of manganese, giving then a rosalike appearance for the deposit.

The AFM image highlights the 3D character of the electrodeposed Mn-Bi films.

The EDS analysis indicates that the Mn and Bi content in the deposit depends strongly on the pH bath and the applied potential.

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