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Electrodeposition and characterization of manganese–bismuth system from chloride based acidic bath

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ABSTRACT

In this work, Mn–Bi system has been successfully electrodeposited on Cu/Si substrates from aqueous ammonium chloride containing electrolyte. A thermodynamic study of the electrolysis bath highlights the possible formation of manganese complexes (MnCl⁺, MnCl₂, MnCl₃) and bismuth complexes (BiCl²⁺, BiCl₂, BiCl₃, BiCl₄, BiCl₅²⁻, BiCl₆³⁻). The mechanism process involving Mn and Bi electrodeposition is investigated by cyclic voltammetry. Mn–Bi films can be grown under potentiostatic control. The physico-chemical, morphological and structural characterizations of the deposits were carried out by scanning electron microscopy (SEM) and X-rays analysis (XRD). The results reveal a granular surface quality and a heterogeneous chemical composition of the films. The energy dispersive spectroscopy (EDS) analysis reveals the presence of manganese and bismuth peaks whose relative intensities vary according to the imposed potential and the position on the sample. The X-rays diffraction analysis showed three different crystalline phases: α -manganese (body centred cubic system), γ -manganese (body centred tetragonal system) and bismuth (rhombohedral system).

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1. Introduction

The development of magnetic nanomaterials took a considerable attention in several research tasks in recent years due to their potential applications in high density recording [1–7]. Currently, the efforts made in this field were based primarily on making new materials able to meet increasing power needs. Indeed, many metal systems were studied (FePt, CoPt, MnBi) [8-10]. The development of the MnBi alloy can emerge and make a significant place within the scientific community considering the crossing interest of this type of material in the magneto-optical recording field [11,12]. In fact, it is a hard magnetic material with a strong magnetic anisotropy parallel to the c-axis at low temperature in its hexagonal phase. This makes it a very good candidate for the perpendicular recording [13,14], in particular when the material is fabricated in the nanowires form. Several works related to fabrication of this material by physical techniques exist in the literature [15–18] but in our knowledge, no paper related to the electrodeposition method was reported.

The aim of this work is the electrodeposition of the Mn–Bi system in thin layer. This stage seems important to control the film morphology, composition and structure. In particular, it is impor-

* Corresponding author. E-mail address: baya_pg@yahoo.fr (B. Benfedda). tant to surround conditions to elaborate near stoichiometric MnBi films.

The electrodeposition of the MnBi alloy is a very delicate process, considering the complexity of the manganese deposition kinetic [19–23].

In the present paper, a preliminary study of the conditions of the Mn–Bi system electrodeposited in a chloride bath in the presence of ammonium chloride is described. In this respect, cyclic voltammetry has been used to determine the nature of the various reactional stages occurred during the electrodeposition of Mn as a function of ammonium chloride concentration, and during the electrodeposition of Bi. To identify the electroactive species, a thermodynamic study of the electrolysis bath was discussed. The physico-chemical, morphological and structural characterizations were also performed.

2. Experimental

A vitreous carbon rotating disk electrode (RDE) (0.2 cm^2) and either Cu/Si substrate were used as working electrodes in a classical three electrodes electrochemical cell. The cell was fitted with a thermostatically controlled water jacket. A platinum wire, of 1 cm² area, was used as the counter electrode. All the potentials were measured with respect to a saturated calomel reference electrode (SCE) (*E* = -0.242 V vs SHE). All measurements were made at 25 ± 0.5 °C in a chloride bath under nitrogen gas bubbling. The

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chemical composition of the Mn–Bi electrolysis bath was $MnCl_2$ $4H_2O$ (0.4 mol dm⁻³), BiCl₃ (10⁻³ mol dm⁻³) and different concentrations of NH₄Cl. A preliminary study was conducted as a function of the pH to avoid bismuth precipitation. The adjusted value is 2.26. The solution was prepared immediately prior to each experiment using deionised water and analytical grade reagents (Aldrich).

The electrochemical measurements were performed using an EG&G 273A potentiostat/galvanostat controlled by a microcomputer via GPIB interface operated by M352 EG&G software. The deposited Mn–Bi layers were characterized by energy dispersive X-ray spectroscopy (EDS), X-ray Diffraction (XRD), and scanning electron microscopy SEM (secondary electron (SE) and backscattered secondary electron (BSE) imaging).

3. Results and discussions

3.1. Thermodynamic study

Manganese is the least noble metal obtained by electrolysis in aqueous solution. Its electrodeposition is very delicate and requires some precautions. Moreover, Mn can exist under several states of oxidation. So, to maintain the Mn^{2+} ions in suspension in the solution their complexation using Cl^- as ligand proves to be essential.

The thermodynamic study presented below was carried out for a solution containing the metal ions Mn²⁺. In the presence of Cl⁻, several manganese complexes such as MnCl⁺, MnCl₂ and MnCl₃⁻ are susceptible to be formed. These last are respectively characterized by their formation cumulative constants $\beta_1 = 10^{0.6}$, $\beta_2 = 10^{0.8}$, $\beta_3 = 10^{0.4}$ [24]. The distribution diagram of the various complexes and not complexed species is illustrated in Fig. 1.

It can be seen that Mn may exist in several complexes form as a function of *p*Cl. Indeed, for pCl ≤ -2 , Mn²⁺ is mainly in the MnCl₃⁻ form. For weak chloride concentrations pCl ≤ -2 , Mn²⁺ is the dominating species. In the range of (-2 < pCl < 2), the intermediate species MnCl⁺ and MnCl₂ are also present with MnCl₃⁻. The *p*Cl relating to the present study is located in the range $-0.25 \leq p$ Cl ≤ -0.76 . These values were obtained by taking into account the chloride concentration in the different electrolysis baths. In this case MnCl₃⁻ is the dominating species in the bath (Table 1). Thus, we can assume that the manganese reduction may occur as follow:

$$MnCl_{3}^{-} + 2e^{-} \leftrightarrow Mn + 3Cl^{-} \quad (E_{MnCl_{3}^{-}/Mn}^{0} = -1.197 \quad V \quad vs \quad SHE)$$



Fig. 1. Distribution of the Mn (II) complexes in a chloride bath.

Table 1

Repartition of Mn (II) and Bi (III) complexes in the MnBi used bath (pCl = -0.58).

(a) Manganese chlorocomplexes repartition (mol %)	
Mn ²⁺	0.4
MnCl ⁺	6.16
MnCl ₂	37.16
MnCl ₃ ⁻	56.252
(b) Bismuth chlorocomplexes repartition (mol %)	
Bi ³⁺	414.22×10^{-1}
BiCl ²⁺	$5.86 imes 10^{-6}$
BiCl ₂ ⁺	$2.8 imes 10^{-4}$
BiCl ₃	8.47×10^{-2}
BiCl ₄ -	1.615
BiCl ₅ ^{2–}	24.4529
BiCl ₆ ³⁻	73.8465

The equilibrium potential calculated, by the Nernst equation, for each chloride concentration (taking into account the ionic force of the solution) is in the range:

-1.468 V vs SCE $\leq E_{eq} \leq -1.495$ V vs SCE

Several bismuth complexes are also susceptible to be formed in a chloride bath: BiCl²⁺, BiCl₂⁺, BiCl₃, BiCl₄⁻, BiCl₅²⁻, and BiCl₆³⁻ (Fig. 2). These complexes have been respectively characterized by their formation cumulative constants $\beta_1 = 10^{2.4}$, $\beta_2 = 10^{3.5}$, $\beta_3 = 10^{5.4}$, $\beta_4 = 10^{6.1}$, $\beta_5 = 10^{6.7}$, $\beta_6 = 10^{6.6}$ according to [24].

For weak values of *pCl*, bismuth is essentially present as $BiCl_6^{3-}$ complex species whereas for higher values it is rather stable in the form of metallic ion Bi^{3+} . For intermediate *pCl*, several complexes species of bismuth are present such as $BiCl_{2^+}^{2^+}$, $BiCl_3$, $BiCl_4^-$, and $BiCl_{2^-}^{2^-}$.

According to pCl = -0.58 (used value for the Mn–Bi bath), BiCl₆^{3–} is the dominating species (Table 1). So the deposition process may be presented by the following reaction:

$$\operatorname{BiCl}_6^{3-} + 3e^- \Leftrightarrow \operatorname{Bi} + 6\operatorname{Cl}^- \quad E^0_{\operatorname{BiCl}_6^{3-}/\operatorname{Bi}} = 0.176 \quad \text{V} \quad \text{vs SHE}$$

The equilibrium potential calculated by the Nernst equation, taking into account the ionic force of the bath is then:

$$Eeq_{BiCl_6^{3-}/Bi} = -0.202$$
 V vs SCE

It should be noted that for the pH 2.26 (the used bath), the equilibrium potential of hydrogen evolution according to the following



Fig. 2. Distribution of the Bi (III) complexes in a chloride bath.



Fig. 3. (A) Cyclic voltammograms for Mn electrodeposition onto vitreous carbon RDE in 0.4 mol dm⁻³ MnCl₂; 0 mol dm⁻³ of NH₄Cl; pH 2.26; $V_b = 20$ mV/s; $\omega = 250$ rpm. Effect of the cathodic limit potential (a) E = -1.65 V vs SCE, (b) E = -1.70 V vs SCE, (c) E = -1.75 V vs SCE, (d) E = -1.80 V vs SCE. Insert: Blank electrolyte. (B) Cyclic voltammograms for Mn deposition onto vitreous carbon RDE in 0.4 mol dm⁻³ MnCl₂; pH 2.26; $V_b = 20$ mV/s; $\omega = 250$ rpm. Effect of NH₄Cl concentration (a) 0 mol dm⁻³, (b) 1 mol dm⁻³, (c) 2 mol dm⁻³, (d) 3 mol dm⁻³, (e) 4 mol dm⁻³, (f) 5 mol dm⁻³. Insert: Blank electrolyte. (C) Manganese current efficiency vs



Fig. 4. Cyclic voltammograms for Bi deposition onto vitreous carbon RDE in 10^{-3} moldm⁻³ BiCl₃⁺³; 3 moldm⁻³ NH₄Cl; pH 2, 26; V_b = 20 mV/s; ω = 250 rpm. Effect of the cathodic limit potential (a) E = -0.5 V vs SCE: (b) E = -1 V vs SCE, (c) E = -1.2 V vs SCE.

reaction:

 $\mathrm{H^+} + e^- \leftrightarrow (1/2)\mathrm{H_2}$ is $E_{\mathrm{eq}} = -0.377$ V vs SCE

In the light of this thermodynamic study, the evolution of hydrogen from the acidic bath and water decomposition which occurs around -1 V vs SCE will take place before the manganese reduction; this may reduce the current efficiency of the manganese deposit.

3.2. Electrochemical study

3.2.1. Electrodeposition of manganese

In order to control the manganese electrodeposition kinetic, the effect of two factors on the evolution of the shape of the voltammograms is considered, namely the cathodic limit potential and the NH₄Cl concentration.

3.2.1.1. Effect of the cathodic limit potential. The electrochemical reactions taking place at the vitreous carbon RDE in the chloride based bath were first analysed in the absence of ammonium chloride.

Different voltammograms are reported for various cathodic limit potential (Fig. 3a). Starting from the rest potential (open circuit potential: $E_{OCP} = -0.8$ V vs SCE) in the negative direction scan, all the voltammograms exhibit a current onset between 0.8 V vs SCE and -1.3 V vs SCE. This may be explained in terms of proton discharge reaction, as can be seen on the insert of Fig. 3a recorded in the blank electrolyte. From -1.3 V vs SCE, a weak deposition plateau followed by a strong increase in the cathodic current at -1.58 V vs SCE is observed, this is due to both manganese deposition and water decomposition which is important in this range of potential as predicted in the thermodynamic studies.

different cathodic limit potentials: E = -1.65 V vs SCE, E = -1.70 V vs SCE, E = -1.75 V vs SCE, E = -1.80 V vs SCE and vs different NH₄Cl concentrations: (a) 1 mol dm⁻³, (b) 3 mol dm⁻³, (c) 4 mol dm⁻³, (d) 5 mol dm⁻³. Blank electrolyte voltammograms vs cathodic limit potential, $V_b = 20$ mV/s, $\omega = 250$ rpm, pH 2.26, 0 mol dm⁻³ NH₄Cl, (a) E = -1.65 V vs SCE, (b) -1.7 V vs SCE, (c) E = -1.75 V vs SCE, (d) E = -1.8 V vs SCE. Blank electrolyte voltammograms vs NH₄Cl concentration: $V_b = 20$ mV/s, vitreous carbon RDE, $\omega = 250$ rpm, pH 2.26, E = -1.7 V vs SCE. (a) 0 mol dm⁻³, (b) 3 mol dm⁻³, (c) 5 mol dm⁻³.



Fig. 5. (a) Linear potential sweep curves for Bi³⁺ reduction on vitreous carbon RDE in a chloride bath (10⁻³ mol dm⁻³ BiCl₃, 3 mol dm⁻³ NH₄Cl, pH 2.26, $V_b = 5$ mV/s,(a) 400 rpm,(b) 600 rpm, (c) 800 rpm,(d) 1200 rpm, (e) 1400 rpm. (b) Linear potential sweep curves for Bi³⁺ reduction on vitreous carbon RDE in a chloride bath (10⁻³ mol dm⁻³ BiCl₃, 3 mol dm⁻³ NH₄Cl, pH 2.26, $V_b = 20$ mV/s, (a) 400 rpm, (b) 600 rpm, (c) 800 rpm, (e) 1400 rpm. (c) $i_{\rm lim}$ vs ($\omega^{1/2}$).

In the reverse scan, the current loop noticed between the forward and the reverse scan results from the nucleation process on vitreous carbon RDE. In fact, an over potential is required to cause the nucleation of Mn on vitreous carbon [25]. Anodic current peak appears at -1.44 V vs SCE. It presents two principal structures, the peak A₁ located at -1.35 V vs SCE and the peak A₂ at -1.1V vs SCE, their intensities and positions evolve according to the cathodic limit potential. These are attributed to the dissolution of manganese (peak A₁) and probably its oxides and/or hydroxides (peak A₂) especially in this range of cathodic potential. The formation of manganese hydroxide has already been reported in other works [19–21].

3.2.1.2. Effect of NH₄Cl concentration. Series of experimentation are carried out to highlight the contribution of NH₄Cl in the kinetic process of Mn deposition. For this purpose, the experimental procedure consists of a 0.5 mol dm^{-3} addition of this additive. The Fig. 3b shows only the voltammograms obtained for 0, 1, 2, 3, 4 and 5 mol dm⁻³ of NH₄Cl.



Fig. 6. (a) Cyclic voltammograms for Mn–Bi system deposition on vitreous carbon RDE in 0.4 mol dm⁻³ MnCl₂ 4H₂O, 10⁻³ mol dm⁻³ BiCl₃, 3 mol dm⁻³ NH₄Cl; pH 2.26; $V_b = 20 \text{ mV}/\text{s}; \omega = 250 \text{ rpm}$ at different cathodic limit potentials: (a) E = -1.65 V vs SCE, (b) -1.7 V vs SCE, (c) E = -1.75 V vs SCE, (d) E = -1.8 V vs SCE. (b) Current-time transients for Mn–Bi films deposited on copper substrate in 0.4 mol dm⁻³ MnCl₂ 4H₂O, 10⁻³ mol dm⁻³ BiCl₃, 3 mol dm⁻³ NH₄Cl; pH 2.26; (a) E = -1.65 V vs SCE, (b) -1.65 V vs SCE, (c) E = -1.75 V vs SCE, (d) E = -1.8 V vs SCE.

It can be noticed that the shape of the voltammograms is strongly dependent upon NH₄Cl concentration. Indeed, as in Fig. 3a plots, in the negative scan a weak deposition plateau appears in the vicinity of -1.3 V vs SCE followed by a strong cathodic current up to -1.58 V vs SCE. It can also be noticed that the current density increases with increasing the NH₄Cl concentration, this is attributed to improvement of bath conductivity and also probably to the discharge of the ammonium proton ions according to the following reaction:

$$NH_4Cl \leftrightarrow NH_4^+ + Cl^-$$

 $\mathrm{NH_4^+} + \mathrm{H_2O} \rightarrow \mathrm{H^+} + \mathrm{NH_3} + \mathrm{H_2O}$

$H^+ + 1e^- \rightarrow (1/2)H_2$

This is confirmed by the blank electrolyte voltammograms displayed on the insert of Fig. 3b. We note also in this figure a displacement of the hydrogen current density to less cathodic potential with increasing the NH_4Cl concentration, this effect is more pronounced for 5 mol dm⁻³ value.

In the reverse scan, towards the anodic direction, one observe a strong over potential from -1.57 V vs SCE up to -1.40 V vs SCE, this is allotted, as in the Fig. 3a to the typical nucleation process on the working electrode. Further, in the anodic part of the voltammograms, a high anodic peak is observed at -1.44 V vs SCE, its intensity changes with the NH₄Cl concentration, indeed it increases up to 4 mol dm⁻³, and decreases for higher concentration.

It is important to note that the shape of this peak is quite different from the one observed in Fig. 3a for the same cathodic limit potential, where different structures were observed. In the presence of NH₄Cl, the anodic peak has just one structure located at -1.35 V vs SCE. This peak is then attributed to the dissolution of manganese deposit in the ammonium chloride bath without the presence of other species (hydroxides, etc.).

If the role of NH₄Cl was only to complex with chlorides, a modification of the interfacial pH could occur, thus it will not contribute to the deposit improvement, so then NH_4Cl must play in more the role of a pH buffer.

The use of ammonium salts, as a buffering agent on the pH, in the electrodeposition of manganese has been reported earlier in the literature [26–28]. It was reported that this additive can prevent precipitation of manganese hydroxides during electrodeposition as the pH increases. But when added with small quantities the pH decreases (the buffering effect is not efficient) and when added in excess the current efficiency decreases.

According to our experimental results, it is confirmed that the NH_4Cl improves the Mn deposition but at higher concentration (up to 4 mol dm⁻³) hydrogen evolution is dominating.

The current efficiency of manganese reduction has been estimated by calculating the total charge from different voltammograms recorded at different cathodic limit potentials and different NH₄Cl concentrations, assuming that the anodic peak correspond to the amount of the deposited manganese and the cathodic current to both manganese and hydrogen evolution. It is found that the best current efficiency (22%) is obtained for 3 mol dm⁻³, while for 5 mol dm⁻³ the current efficiency decreases (14%) (Fig. 3c). This is foreseeable as the hydrogen evolution became very important (insert Fig. 3b). It must be noted that the current efficiency calculated with this method is very low compared to that calculated by other authors using the weight gain of the sample [19]. In this method, we under estimate the real efficiency as the manganese deposit is not completely dissolved at the end of the cyclic voltammetry [20].

The intermediate concentration $(3 \text{ mol } dm^{-3})$ seems then to be a good compromise to enhance the Mn deposits in our experimental conditions.

The experimental equilibrium potential, as measured from the voltammograms does not have a significant variation with the NH₄Cl concentration. The values are located in the range (-1.44 V vs SCE to -1.45 V vs SCE). It is very close to the one calculated in the thermodynamic study ($E_{eq} \sim -1.47$ V vs SCE). The light shift observed in the experimental value may be due to additional current like hydrogen evolution.



Fig. 7. SE images obtained in SEM of the electrodeposited Mn–Bi films in a chloride bath $(0.4 \text{ mol dm}^{-3} \text{ MnCl}_2 4H_2\text{O}, 10^{-3} \text{ mol dm}^{-3} \text{ BiCl}_3, 3 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl})$ on Cu/Si at various deposition potentials, (a) -1.6 V vs SCE, (b) -1.65 V vs SCE, (c) -1.75 V vs SCE, (d) -1.8 V vs SCE, corresponding to the following deposition charge: (a) Q = -6.7 C, (b) Q = -11.17 C, (c) Q = -19.14 C, (d) Q = -26.73 C.

3.2.2. Electrodeposition of bismuth

The electrochemical reactions taking place in the chloride bath with the presence of bismuth cations were also studied on vitreous carbon RDE. Fig. 4 plots show the cyclic voltammograms obtained at several cathodic limit potential.

Starting from the rest potential (-0.2 V vs SCE), in the direction of cathodic scan, a plateau of weak current, corresponding to bismuth reduction is observed at small potentials. Up to -1.05 V vs SCE, one observes current fluctuations generated by the process of hydrogen evolution. In the reverse scan, the dissolution peak of Bi is observed up to -0.16 V vs SCE. Its intensity increases as a function of the cathodic limit potential, in other words as the increase of the deposit. No displacement in the peak position is observed, which means that there is no change in the deposit composition. For better illustrating the kinetic of the bismuth deposit, we carried out a linear sweep voltammograms as a function of the speed ω of the RDE, at a cathodic limit potential of -0.55 V vs SCE and two different sweep rates 5 mV s^{-1} and 20 mV s^{-1} (Fig. 5a and b). The voltammograms show a region where the current is approximately constant. This is the limiting current plateau where the Bi³⁺ reduction is under complete mass-transport control. When the potential is made more negative (up to -0.35 V vs SCE), a secondary cathode reaction, hydrogen evolution, takes place in addition to the Bi³⁺ reduction. For the Levich plots, the limiting current values were taken from the cross of the vertical line at -0.3 V vs SCE in each current potential curve. The experimental points (Fig. 5c) are on straight lines through the origin, this indicates that the process of bismuth ions reduction was under diffusion control. It can also be



Fig. 8. BSE images obtained in a SEM and corresponding EDX spectra of the Mn–Bi films electrodeposited on Cu/Si in 0.4 mol dm⁻³ MnCl₂ 4H₂O, 10⁻³ mol dm⁻³ BiCl₃, 3 mol dm⁻³ NH₄Cl, at two different deposition potentials: (a) –1.6 V vs SCE, (b) –1.8 V/vs SCE.

seen that the increase of the scanning rate did not have a significant effect on the Levich plot, this indicates that the current is at or near the steady state.

3.2.3. Electrodeposition of the Mn-Bi system

Manganese and bismuth reduction kinetics have been studied simultaneously in a solution containing Mn^{2+} and Bi^{3+} under the same conditions, the ammonium chloride concentration is fixed at 3 mol dm⁻³ according to the last study. On the voltammograms displayed in Fig. 6a a plateau of weak current corresponding to bismuth reduction is observed when scanning towards small cathodic potential, starting from -0.2 V vs SCE. As the cathodic potential increases (E < 1.57 V vs SCE), a significant current corresponding to manganese deposition and hydrogen evolution is observed. In the reverse scan two anodic peaks are observed. Peak A, the more significant, observed at -1.44 V vs SCE is attributed to manganese dissolution whereas the peak B at -0.2 V vs SCE is attributed to bismuth dissolution. The relative intensity of the two dissolution peaks is related to the species concentration in the electrolysis bath.

3.3. Physicochemical and morphological characterization

According to the electrochemical study of Mn–Bi deposition, different samples are elaborated on (Cu/Si) electrode, at various potentials corresponding to different current densities (Fig. 6b). The SEM images of the deposited films are shown in Fig. 7 (SE images). They illustrate that the deposit is granular, it consists of a large shaped of small crystallites which grain size is less than 5 μ m. The number and the coalescence of these particles increase with increasing the imposed potential.

The deposit composition is heterogeneous according to the BSE images and the corresponding EDS spectra (Fig. 8). It reveals that the deposit presents separate grains of manganese and bismuth. The relative intensities of each element peak vary with the position on the sample and the applied potential.

Several cases have been observed according to the deposition potential (*E*): in the Fig. 8a (E = -1.6 V vs SCE), some large Mn grains (dark area) and small Bi grains (white area) have been observed. The Cu substrate is not completely recovered by the deposit. This fact is clearly seen in the EDS spectra where mainly Cu is detected with minor element of Mn and Bi.

In Fig. 8b (E = -1.8 V vs SCE), we have always some large Mn grains (spectrum 1) with a thin isolated Bi grains (spectrum 2).

The chemical analysis is difficult due to the fact that the volume of analysis is around $1\,\mu\text{m}^3$ and the deposit is heterogeneous.

3.4. X-rays analysis

Fig. 9a shows the XRD pattern of the Mn–Bi films obtained at various deposition potentials. We note peaks related to copper and silicon which is used as a substrate. Concerning the deposit, the spectra obtained reveal two different manganese phases α -Mn (body centred cubic system) and γ -Mn (body centred tetragonal system), this is in agreement with results obtained from the literature [20]. XRD spectrum reveals the presence of characteristic peaks of bismuth in its rhombohedral system with a predominant [012] texture, in agreement with others works [29,30]. A small amount of manganese oxide is also detected in XRD spectra (Fig. 9b), it was probably formed later on the surface of the deposit.

It is important to note that the intensity of the peak related to each element notably evolves according to the deposition potential. So, at more cathodic potential, the manganese corresponding



Fig. 9. (a) X-ray diffraction pattern (Cu K α radiation) of Mn–Bi electrodeposited on Cu/Si at various deposition potentials in (0.4 mol dm⁻³ MnCl₂ 4H₂O, 10⁻³ mol dm⁻³ BiCl₃, 3 mol dm⁻³ NH₄Cl, (a) Cu/Si substrate, (b) –1.6 V vs SCE, (c) –1.65 V vs SCE, (d) –1.75 V vs SCE, (e) –1.8 V vs SCE. (b) Zoom of the X-ray diffraction pattern between 2θ =35° and 2θ =45°.

peak intensity increases with increasing potential whereas the peak related to bismuth decreases. These results are in agreement with those obtained in the electrochemical study.

4. Conclusions

The electrodeposition of Mn–Bi system from acidic chloride bath was studied. It is found that the electrodeposition of Mn–Bi is possible in this bath. It is important to note that, the presence of an optimal concentration of the ammonium chloride as additive is a decisive parameter to obtain manganese deposit with a good efficiency, to improve the electrolysis bath conductivity and also to inhibit the formation of manganese hydroxide.

The electrodeposition of manganese occurs at more cathodic potentials than bismuth, thus the BSE observations and its corresponding EDS analysis show that the Mn–Bi deposits have a heterogeneous composition. It consists of separate grains of manganese and bismuth. Further the crystal structure analysed by XRD indicates the presence of two manganese phases, α -manganese

body centred cubic system and γ-manganese body centred tetragonal system. We have also observed characteristic peaks of bismuth in its rhombohedral system.

Annealing of the samples is required to induce interdiffusion of the two elements (Mn and Bi) and to form homogenous Mn_xBi_{1-x} alloy. Actually these experiments are in progress.

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