Analysis of the electrodeposition process of Fe–Mn films from sulfate electrolytes

Pollyana P Barreiros and Manoel J M Pires

Instituto de Ciência e Tecnologia—Universidade Federal dos Vales do Jequitinhonha e Mucuri (UFVJM), CEP 39100-000 Diamantina, Brazil
E-mail: manoel piires@ict.ufvjm.edu.br

Keywords: electrochemical deposition, alloy deposition, thin film, current transients, nucleation

Supplementary material for this article is available online

Abstract

Fe–Mn alloys with different composition and structure have great importance in a wide range of applications, which requires a detailed knowledge of a variety of production methods. In the present work, Fe–Mn thin films were electrochemically deposited from sulfate aqueous solutions under different conditions on Cu substrates. The effects of several applied potentials for deposition, concentrations of reagents and speed of rotation of the electrode were investigated. Chronoamperometry tests were performed and the curves obtained were analyzed through the models for nucleation and growth from Scharifker et al and from Isaev et al considering apparent diffusion coefficient for the deposition of the alloy. The approach with both these models point to a process close to the instantaneous nucleation limit. Globally, the results indicate a mixed transport-kinetic control for most of the conditions, but a behavior with characteristics of diffusion controlled growth can be established for specific conditions of speed of rotation and concentrations. Koutechký-Levich analysis has been applied to current-potential curves at the rotating-disk electrode providing the determination of the apparent diffusion coefficients and heterogeneous rate constants for electron transfer. Fe is preferentially deposited with a much higher rate of reduction than Mn in the employed solutions. The whole deposition process is very sensitive to the presence of (NH₄)₂SO₄, which affects also the quality of the deposits. The samples were further characterized by scanning electron microscopy and x-ray dispersive energy spectroscopy.

1. Introduction

Due to the great importance of metallic alloys in a wide range of applications, the electrodeposition of alloys has been the focus of many publications for decades [1–7]. The process of electrodeposition has many advantages in specific applications as compared with other methods as fusion or vapor deposition, and furthermore it is usually less expensive. However, many difficulties remain not completely overcome, as the precise control of the alloy composition [1, 2, 7] and a better understanding of the kinetics of the process [8–11]. Fe–Mn, in particular, is an alloy used in several applications from galvanic sacrificial protection of steel [1, 12] to spintronics devices [13], but lacks better methods to be electrochemically deposited in the appropriated composition and structure. Fe–Mn codeposition is very susceptible to changes in the electrolytic baths and is hard to be properly controlled due to the very low potential for the reduction of Mn [7, 14, 15].

An important work about the electrodeposition of metallic alloys is the one from Brenner [1], in which the favorable conditions for alloys deposition were presented and a classification of the different processes has been proposed. The systems were separated in two main types: normal and abnormal alloy plating systems. The normal systems are further classified in regular, irregular and equilibrium codeposition, whereas the abnormal ones are classified in anomalous and induced codeposition. Normal codeposition corresponds to the growth of deposits in which the more noble metal is preferentially deposited. The characteristic of the equilibrium
codeposition is the chemical equilibrium between the two metals of the alloy and the bath. The process is labeled regular if it is diffusion-controlled, otherwise is called irregular. Concerning the abnormal processes, anomalous codeposition is characterized by the preferential deposition of the less noble metal, whereas the induced codeposition involves elements which cannot be individually deposited. Despite the comprehensiveness of Brenner’s book [1], some processes do not fit adequately in that classification. The Fe–Mn codeposition is hard to classify as the results that will be presented here point to. Fe is preferentially deposited and, since it is the more noble metal of this bimetallic alloy, the process is normal, but some behaviors do not properly fit the Brenner normal subclasses. Brenner indicates that irregular codeposition usually occurs for systems which form solid solutions and with static potentials of the parent metals close together [1]. Fe–Mn may form solid solutions [16, 17] but the potentials of Fe and Mn are far apart. Regular codeposition is associated to diffusion control, but our results indicate that a mixed transport-kinetic control occurs, as will be discussed. The results point that only with very specific hydrodynamic condition and concentrations of the reagents there is a diffusion controlled processes.

Other important aspect for the applications is the microstructure of the deposit, not only the composition of the alloy. Therefore, it is very relevant to understand details of the growth processes itself, if it is layer-by-layer or through separated nuclei, if the nucleation is fast or progressive, etc. All these characteristics may influence the microstructure, grain size, besides several mechanical properties [8]. In order to investigate these aspects, we have compared our experimental results with the models from Isaev et al [9, 11] and Scharfert et al [18–20] for current transients during the deposition. Both these models have been used recently in the analysis of single metal electrodeposition [21, 22], as well as for alloys deposition [23]. The model for current transients of alloys is, in fact, an extended approach for diffusion controlled electrodeposition introducing the concept of ‘apparent’ parameters which take into account bimetallic phases [5]. The model for kinetic control, in turn, was recently reviewed by Isaev et al [10].

The addition of (NH₄)₂SO₄ has been pointed out in the literature to benefit the efficiency and uniformity of Fe–Mn deposit [1, 7]. We have also investigated the effects of this additive at different concentrations. In general, it prevents partially the oxidation of the films but reduces the proportion of Mn deposited.

2. Experimental

A standard three-electrode cell has been used for the deposition of the films and for the recording of the polarization curves. A saturated Ag/AgCl reference electrode (from ALS Co.) was used in all the measurements and the results of the next sections will be presented in relation to it. Ultrapure water from a Simplicity UV Merck KGaA system was used, as well as analytical reagents with purity better than 99%. An ALS RRDE-3A Rotating Disk Electrode Apparatus has been used for the hydrodynamically controlled depositions and measurements. A standard copper disk electrode with a diameter of 3 mm was employed as working electrode. Sheets of 0.1 mm of electrolytic copper were used as counter electrodes, which were immersed in HNO₃ (40%) for few seconds immediately before the use. Additionally, to this immersion in HNO₃, the working electrode was polished with 0.05 μm alumina solution and polishing pads, and washed with ultrapure water after that.

The three-electrode cell has been connected to a Microquimica MQPG-01 potentiostat/galvanostat. Voltammograms and polarization curves were recorded at several rates from 2 to 200 mV s⁻¹, starting at −0.9 V versus Ag/AgCl and following to more negative values. Fe–Mn films were potentiostatically deposited on the Cu substrate (working electrode) using different values of applied electrical potential (EDEP). Several distinct concentrations of the reagents were used and the measurements were taken in solutions with different combinations of the reagents MnSO₄, FeSO₄ and (NH₄)₂SO₄. In the following sections, the solution containing the three reagents at concentrations of 0.5 M, 0.6 M and 0.008 M for (NH₄)₂SO₄, MnSO₄ and FeSO₄, respectively, will be referred as ‘complete solution’. The values of pH were kept between 5 and 6, and no significant alterations of its bulk value have been detected along the measurements or deposition procedures, which took place at room temperature in all the cases.

A Tescan Vega 3 microscope was used for scanning electron microscopy (SEM) and for energy-dispersive x-ray spectroscopy (EDS) analysis employing an Oxford INCA system. Complementary analysis were also made with a Carl Zeiss Axio Scope optical microscope and a Shimadzu XRD6000 x-ray diffractometer (Cu–Kα). The kinematic viscosity of the solutions was measured using a glass Cannon-Fenske viscometer tube.

3. Results and discussion

3.1. Polarization curves and basic characterization

Cyclic voltammograms measured with and without FeSO₄ in the solution are presented in figure 1. The curve only with MnSO₄ and (NH₄)₂SO₄ (0.5 M) presents an increasing cathodic current from about −1.1 V as a result
of hydrogen evolution reaction. The reduction of Mn$^{2+}$ becomes significant for potentials more negative than $-1.56$ V. These two reactions are simultaneous, as will be discussed more detailed below. The dissolution peak of Mn is clear in this voltammogram and has a maximum at $-1.34$ V. The other voltammogram in figure 1, obtained with the three sulfates in the solution, does not present the clear dissolution peak of Mn, but only an oscillation in the curve around $-1.3$ V. The marked step below $-1.56$ V, attributed to the onset of significant Mn$^{2+}$ reduction, also is not present. These aspects anticipate results that will be presented in the following, showing that the reduction of Fe$^{2+}$ is much more effective than the reduction of Mn$^{2+}$ under these conditions, despite the smaller concentration of FeSO$_4$ (0.008 M) as compared to MnSO$_4$ (0.6 M). A broad dissolution peak occurs in the range from $-0.85$ to $-0.41$ V, which is associated mainly to the Fe dissolution.

The polarization curve for the (NH$_4$)$_2$SO$_4$ solution at the concentration of 0.5 M, as well as the polarization curves after the inclusion of MnSO$_4$ and FeSO$_4$, are presented in figure 2. Since there was no deposit in the case of pure (NH$_4$)$_2$SO$_4$ solution and the releasing of bubbles was clear, one can attribute the measured current to the hydrogen evolution reaction. The current rises progressively as the potential reaches more negative values, but there are jumps and noise in the curve which are associated to the H$_2$ bubbles formation and release. The inclusion of MnSO$_4$ drastically reduces the current in the range from about $-1.30$ V up to $-1.56$ V. Only for potentials more negative than $-1.56$ V the current presents significant values, which can be attributed to Mn.

Figure 1. Cyclic voltammograms obtained at 100 mV s$^{-1}$ for solutions with and without FeSO$_4$. The curves were displaced vertically for better viewing, and the dotted lines indicate zero current in each case.

Figure 2. Polarization curves obtained with the solutions of (NH$_4$)$_2$SO$_4$ before and after the addition of MnSO$_4$ and FeSO$_4$. The concentrations were 0.5 M, 0.6 M and 0.008 M for (NH$_4$)$_2$SO$_4$, MnSO$_4$ and FeSO$_4$, respectively.
This value is below the theoretical value for Mn$^{2+}$ reduction expected from the Pourbaix diagram [24], but close to the normally observed experimentally [7, 14, 15]. A light grey deposit with metallic aspect is clear seen when the applied potential is below $-1.56$ V. It should be noted that the amount of MnSO$_4$ included in the solution ($C_{\text{Mn}} = 0.6$ M) is of the same order of magnitude of the amount of (NH$_4$)$_2$SO$_4$, in a way that its addition changes significantly the solution viscosity affecting the diffusion. It may also interfere in the possible intermediate reactions, altering the behavior of the solution as a whole. The addition of FeSO$_4$ in the solution containing (NH$_4$)$_2$SO$_4$ and MnSO$_4$ restores high values of current, higher even than the case with only (NH$_4$)$_2$SO$_4$, despite the low concentration of FeSO$_4$ ($C_{\text{Fe}} = 0.008$ M). Both the formation of the deposit and the hydrogen evolution starts at less negative potentials than in the case without FeSO$_4$. The difference between the currents in the polarization curves with and without FeSO$_4$ evidences the rather distinct rate of reduction of Mn$^{2+}$ and Fe$^{2+}$ in the present conditions. Although there is a large predominance of Fe in the most of the deposited alloys, the presence of Mn has been unequivocally detected by EDS (spectra are presented in figure S1 of the supplementary material is available online at stacks.iop.org/MRX/7/016403/mmedia). The relative amounts of Fe and Mn are very sensitive to several solution parameters, particularly to the presence of (NH$_4$)$_2$SO$_4$.

(NH$_4$)$_2$SO$_4$ affects several aspects of the process and of the quality of the deposits. Figure 3 presents MEV images of two samples obtained with and without (NH$_4$)$_2$SO$_4$. The Fe–Mn films deposited in the presence of (NH$_4$)$_2$SO$_4$ are more homogeneous and presents a better adhesion to the substrate than the ones produced without (NH$_4$)$_2$SO$_4$. The adhesion was qualitatively verified when the samples were removed from the solution and by altering the speed of rotation immediately after the deposition. Furthermore, the deposits produced without (NH$_4$)$_2$SO$_4$ presents a number of cracks and thickness irregularities much more pronounced than the films produced with (NH$_4$)$_2$SO$_4$, as can be seen in figure 3. Although the relative amount of Mn in the deposited alloy was larger without (NH$_4$)$_2$SO$_4$ in the solution, the oxidation of the film was rather accelerated as compared with the case with (NH$_4$)$_2$SO$_4$. The darkening of the films was noticeable even during the deposition at constant potential. The appearance of the films is opaque dark gray immediately after the removal from the solution without (NH$_4$)$_2$SO$_4$. EDS results pointed out that the amount of oxygen in the samples produced without (NH$_4$)$_2$SO$_4$ is about 2 times larger than the samples deposited in the presence of (NH$_4$)$_2$SO$_4$ (EDS spectra are presented in the supplementary material [25]).

The presumed positive ions available in the complete solution are Fe$^{2+}$, Mn$^{2+}$, H$^+$ (H$_2$O$^+$) and NH$_4^+$. During the deposition or along the polarization to negative potentials, Fe$^{2+}$, Mn$^{2+}$ tend to be reduced and H$^+$ is consumed in the hydrogen evolution reaction. Then NH$_4^+$, which is an equilibrium specie at the potentials and pH employed [24], remain in the solution able to attract oxygen ions. This effect is believed to be the related to the reduced amount of oxygen in the films produced with (NH$_4$)$_2$SO$_4$ as compared with the ones obtained without (NH$_4$)$_2$SO$_4$ in the solution.

Representative samples were analyzed by x-ray diffraction using the conventional Bragg-Brentano configuration. The diffractograms for samples deposited with $E_{\text{DEP}} = -1.8$ V and $E_{\text{DEP}} = -2.1$ V are presented in figure S2 of the supplementary material. The diffraction peaks of the copper substrate are the main characteristics of the diffractograms. Only one additional peak in the 2θ range between 44° and 45° can be
attributed to the FeMn film from the deposited film. This unique peak does not permit an unequivocal identification of the alloy phase because both $\alpha$ and $\gamma$ FeMn phases present diffraction peaks in this range [16, 17]. The presence of other compounds or phase was not detected in the diffractograms.

As commented above, there is a large predominance of Fe in the deposited alloys obtained with $(\text{NH}_4)_2\text{SO}_4$ in the solution, and the polarization curve of the complete solution (figure 2) does not present any clear aspect (peak, step or fluctuation) which can be directly associated to the onset of Mn$^{2+}$ reduction. However, Mn has been detected by EDS at different amounts in the films depending on the concentration of the solutes and on the applied potential. Subtracting the polarization curve of the pure $(\text{NH}_4)_2\text{SO}_4$ solution from the polarization curve of the complete solution we can obtain a curve evidencing the behavior of both metallic ions in the complete solution. Figure 4 presents these curves for different speeds of rotation ($\omega$). Although the curves resulting from this subtraction must be seen only as rough estimates for the partial current, a tendency to stabilization of the partial current associated to the reduction of the metallic ions is clear below $-1.5 \text{ V}$, mainly for $\omega < 1000 \text{ rpm}$. The stabilization of the current in the polarization curve is a characteristic of diffusion limited current [8, 26]. In our case, this behavior is not easy to notice due to the overlap of the hydrogen evolution reaction. From 1000 rpm and above, there is also a significant change of the curves around $-1.3 \text{ V}$. The current in the complete solution in this range of potential is larger than the current in the $(\text{NH}_4)_2\text{SO}_4$ solution for $\omega < 1000 \text{ rpm}$, but smaller for $\omega \geq 1000 \text{ rpm}$. This behavior is showing that there is a partial inhibition of the hydrogen evolution at high speeds of rotation associated to the presence of the metal ions.

In order to better identify the aspects discussed above, polarization curves and depositions at constant potentials were made at several speeds of rotation. The values of the cathodic current ($I_C$) at the applied largest negative potential ($-1.7 \text{ V}$) are plotted as a function of $\omega$ in figure 5(a). One can see in figure 5(a) that the values of $I_C$ increase as the rotation speed increases, and the increasing rate is larger for low $\omega$ values and diminishes progressively. Concerning the curve for the pure $(\text{NH}_4)_2\text{SO}_4$ solution, $I_C$ continues to increase at high speeds, differently from the other solutions for which the current tends to stabilize. The behavior for the complete solution is very similar to the case only with $(\text{NH}_4)_2\text{SO}_4$ and FeSO$_4$, but the values of current are much larger than in the case only with $(\text{NH}_4)_2\text{SO}_4$ and MnSO$_4$. Then, despite the relatively small concentration of Fe$^{2+}$ ions, the contribution of its partial current is clearly predominant over Mn$^{2+}$ ions.

Figure 4. Comparison between the polarization curves obtained with the complete solution and with the $(\text{NH}_4)_2\text{SO}_4$ solution for distinct rotation speeds. The curves labeled ‘difference’ correspond to the difference between the currents of the complete solution and of the $(\text{NH}_4)_2\text{SO}_4$ solution.
Since the amount of Mn in the deposits is very sensitive to the applied potential, the curve \( I_{C} \times \omega \) obtained only with \((\text{NH}_4)_2\text{SO}_4\) and \(\text{MnSO}_4\) for \(-1.6\) V is also shown in figure 5. This curve has a rather distinct dependence on \(\omega\), the current increases reaching a maximum at 200 rpm, decreases continually up to 1000 rpm, and practically stabilizes at very low value after that. This behavior shows that there is a range of speeds more adequate for the codeposition of Fe–Mn at \(-1.6\) V. In this way, the amount of Mn in the deposit can be controlled by choosing a specific speed.

In order to investigate the type of rate control, the limiting current curve as a function of the square root of the angular velocity \((\omega)\) can be analyzed. The linear increase of the steady-state limiting current \((i_L)\) is expected for diffusion-controlled mechanism and is described by the Levich equation [8, 26, 27]:

\[
i_L = 0.2nFAD_c^{1/2}\omega^{1/2}\nu^{-1/6}
\]

The terms \(F, n, A_{RD}, D, \nu\) and \(c\) in equation (1) correspond, respectively, to the Faraday constant, the number of electrons involved in the reaction, the exposed area of the rotating disk, the diffusion coefficient, the kinematic viscosity of the solution and the bulk concentration of the reagent. All the parameters are in cgs units but \(\omega\) is in rpm. Levich equation applies for fast electron-transfer at the electrode surface. In case of mixed transport-kinetic controlled mechanisms, a typical approach is the use of Koutecký–Levich equation, which can be expressed as [26, 27]:

\[
\frac{1}{I_{C}} = \frac{1}{I_k} + \frac{1}{0.2nFAD_c^{2/3}\omega^{1/2}\nu^{-1/6}}
\]
Table 1. Parameters 'a' and 'b' (described in the text) obtained through different approaches. Solutions with concentrations 0.5 M, 0.6 M and 0.008 M respectively for (NH₄)₂SO₄, MnSO₄ and FeSO₄.

| Solution                  | Fitting $I_C \times \omega$ equation (3), figure (a) | Linearized Koutecký-Levich $1/I_C \times \omega^{-1/2}$ ($\omega \geq 1000$ rpm) | Levich plot $I_C \times \omega^{3/2}$ ($0 < \omega \leq 1000$ rpm), figure (c) |
|---------------------------|-------------------------------------------------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------------------|
| (NH₄)₂SO₄ + MnSO₄ + FeSO₄ | 77 ± 6                                                 | 49 ± 2                                                                            | (32 ± 3)-10                                                                     |
| (NH₄)₂SO₄ + FeSO₄         | 56 ± 6                                                 | 34 ± 10                                                                          | (295 ± 1)                                                                        |
| (NH₄)₂SO₄ + MnSO₄         | 64 ± 6                                                 | 42 ± 8                                                                            | (55 ± 1)-10                                                                      |
| (NH₄)₂SO₄                | 161 ± 12                                               | 58 ± 4                                                                            | (123 ± 4)-10                                                                     |

In equation (2), $I_C$ and $I_K$ represent the cathodic electrode current and the current in the absence of mass-transfer effects, respectively. $I_K = nFeAE_kb$; being $k_b$ the heterogeneous rate constant for electron transfer. The terms in (2) can be rearranged and written as equation (3), where $a = 1/(0.2nFA_{k_B}D^{2/3} \nu^{-1/6}c)$ and $b = 1/I_{K_c}$.

$$I_C = \frac{1}{a \cdot \omega^{-1/2} + b}$$  \hspace{1cm} (3)

The equations above are deduced from simplified models but can be used for the diagnosis of mechanisms involved in more complex processes as the ones implied in our case [8, 26, 27]. Here we are dealing, at least, with the reduction of both Fe⁺³ and Mn²⁺, as well as the hydrogen evolution reaction, simultaneously. Therefore, the measured $I_C$ corresponds to the sum of the partial currents related to each of these reactions, and $D$ and $k_b$ are weighted average terms, or ‘apparent’ parameters as named by Díaz-Morales et al [5]. The discussion of references [8, 26, 27] can be summarized in the following statements. A linear response in the $I_C \times \omega^{3/2}$ plot (Levich plot) over a large range of $\omega$ indicates the predominance of a single-step fast electron transfer, case where the current at high overpotentials will be limited by diffusion. Linearity in the $I_C \times \omega^{-1/2}$ plot (Koutecký-Levich plot) over extended $\omega$ range indicates mixed transport-kinetic control of a single-step mechanism, otherwise multi-step mechanisms are probably involved.

Note that the parameter ‘a’ defined above is the inverse of the angular coefficient of the Levich plot (equation (1)). In a way that its value can be obtained by the two models. A coincidence of the values of $a$ obtained by these two methods is a reliable indicative of one-step mechanism and the parameter can be used for the determination of the terms $n$, $D$ or $\nu$, depending on which of them are known through other methods [27]. By the other hand, if the value of $a$ obtained from the Koutecký-Levich plot for high values of $\omega$ is smaller than the value obtained from the Levich plot for low values of $\omega$, it is an indicative of two or more consecutive charge transfer steps.

The data obtained for $I_C \times \omega$ presented in figure 5(a) were fitted with equation (3) and the obtained ‘a’ and ‘b’ parameters are presented in table 1. The uncertainties of the parameters are relatively high, but equation (3) provides a reasonable representation of the whole behavior, therefore evidencing mixed transport-kinetic controlled mechanisms. The resulting squared correlation coefficient ($R^2$) were between 0.960 and 0.982, the best fit was obtained for the complete solution with $R^2 = 0.982$. Some experimental points are apart from the fitted line, mainly for high $\omega$ in the cases of the complete solution and of the solution only with FeSO₄ and (NH₄)₂SO₄. In order to better analyze these data, Levich and Koutecký-Levich plots were made with the same data as presented in figures 5(b) and (c).

In figure 5(b) one can see that, except for the (NH₄)₂SO₄ pure solution, the curves can be well described by two linear ranges, below $\omega^{-1/2} \approx 0.316$ rpm $^{-1/2}$ (i.e. $\omega = 1000$ rpm) and from this value and above. Such a change in the slope is indicating the process is not a single-step mechanism. Both ranges were fitted. For low values of $\omega$, the fitted parameters agree with the ones obtained from figure 5(a) considering the uncertainties ranges. For high values of $\omega$, the resulting parameters are significantly distinct, as presented in table 1.

In the Levich plots presented in figure 5(c), one can see there is a linear increase of $I_C$ only for specific ranges at intermediary values of $\omega$, except for the (NH₄)₂SO₄ pure solution, which is clearly linear only at high values of $\omega$. The current $I_C$ tends to a finite value as $\omega$ tends to zero and stabilizes for high $\omega$, except for pure (NH₄)₂SO₄. In fact, Levich approach is adequate for the limiting diffusion current ($I_{L}$), therefore the fact that $I_C$ increases linearly as a function of $\omega$ is only indicating there is a Levich-like contribution to the whole mechanism in specific ranges of speeds. There are few points in the linear ranges, but they were fitted for comparison of the coefficients. The parameters $a$ for each case obtained in figure 5(c) are also presented in table 1. Their values are much larger than the ones obtained by the Koutecký-Levich plot for high $\omega$, which is a signature of the occurrence of multi-step mechanisms, following the review from Treimer et al [27].
Table 2. Apparent diffusion coefficient ($D$), kinematic viscosity ($\nu$) and heterogeneous rate constant for electron transfer ($k_h$) determined for the solutions with concentrations 0.5 M, 0.6 M and 0.008 M respectively for (NH$_4$)$_2$SO$_4$, MnSO$_4$ and FeSO$_4$.

| Solution                  | $D$ (cm$^2$ s$^{-1}$) 10$^{-6}$ | $\nu$ (cm$^2$ s$^{-1}$) 10$^{-2}$ | $k_h$ (cm s$^{-1}$) 10$^{-4}$ | $N_r$/A/cm$^2$ |
|---------------------------|---------------------------------|----------------------------------|-----------------------------|----------------|
| (NH$_4$)$_2$SO$_4$ + MnSO$_4$ + FeSO$_4$ | 3.2 ± 0.4                      | 1.59 ± 0.01                      | 1.35 ± 0.06                 | 0.005 at 400 rpm |
| (NH$_4$)$_2$SO$_4$ + MnSO$_4$               | 4.2 ± 0.6                      | 1.52 ± 0.01                      | 0.55 ± 0.01                 | 1340 at 400 rpm |
| (NH$_4$)$_2$SO$_4$ + FeSO$_4$                | 15 ± 2                         | 1.173 ± 0.004                    | 2.49 ± 0.09                 | —              |
| (NH$_4$)$_2$SO$_4$                         | 3.2 ± 0.4                      | 1.16 ± 0.01                      | 2.5 ± 0.2                   | —              |

Multi-step mechanisms are expected in codeposition of non-monovalent metal ions in aqueous solutions, as the cases of FeNi, NiCo, FeCo and MnZn alloys [2–4, 23]. The proposed mechanisms usually include a first step of reduction of the divalent ions in solution to a monovalent adsorbed ion, followed by the reduction of the adsorbed ion to solid neutral metal, as indicated by the partial reactions (4)–(7) below. Hydrogen evolution is also considered a multi-step mechanism represented by the reactions (8) and (9) [4].

$$\text{Mn}(\text{II})_{\text{aq}} + e^- \rightarrow \text{Mn}(\text{I})_{\text{ads}} \quad (4)$$
$$\text{Mn}(\text{I})_{\text{ads}} + e^- \rightarrow \text{Mn}^0 \quad (5)$$
$$\text{Fe}(\text{II})_{\text{aq}} + e^- \rightarrow \text{Fe}(\text{I})_{\text{ads}} \quad (6)$$
$$\text{Fe}(\text{I})_{\text{ads}} + e^- \rightarrow \text{Fe}^0 \quad (7)$$
$$\text{H}^+_{\text{aq}} + e^- \rightarrow \text{H}_{\text{ads}} \quad (8)$$
$$2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \quad (9)$$

In our case, the results above indicate multi-step reactions in all the solutions. Simultaneously, copper oxide is formed on the surface of the counter electrode. For the case of pure (NH$_4$)$_2$SO$_4$ solution, in which hydrogen evolution is the predominant reaction, there is no limitation of the current as a function of potential or as a function of $\omega$. However, the solutions after the addition of MnSO$_4$ and FeSO$_4$ present a limitation behavior in the current, both as a function of applied potential and $\omega$, and the relatively short range of linear dependence of $I_c$ over $\omega^{1/2}$ in fact corresponds to a diffusion controlled process in this intermediate range of $\omega$. This conclusion is corroborated by the results of the next section for the current-time transients.

The kinematic viscosity of the solution has been measured at 16 °C with a conventional Cannon-Fenske viscometer tube, and the results are presented in table 2. Naturally, the viscosity is larger for the complete cases of FeNi, NiCo, FeCo and MnZn alloys. For the case only with charging of the double-layer renders an initial peak in the current in all the cases, but the subsequent behavior depends on several factors. For the case only with (NH$_4$)$_2$SO$_4$, the current reaches an approximately steady state value immediately after the initial peak. The fluctuations in the current can be attributed to the release of bubbles resulting from the hydrogen evolution reaction [22]. The behavior is very similar for several speeds, but the value of the almost steady current increases with the increase of $\omega$. None significant alterations of the electrodes could

3.2. Current-time transients

In figure 6, chronoamperometric curves recorded under constant applied potential of −1.7 V are presented. The charging of the double-layer renders an initial peak in the current in all the cases, but the subsequent behavior depends on several factors. For the case only with (NH$_4$)$_2$SO$_4$, the current reaches an approximately steady state value immediately after the initial peak. The fluctuations in the current can be attributed to the release of bubbles resulting from the hydrogen evolution reaction [22]. The behavior is very similar for several speeds, but the value of the almost steady current increases with the increase of $\omega$. None significant alterations of the electrodes could
be noted after the procedure with this solution. The dependence on the speed of rotation is much more accentuated in the solutions after the inclusion of the metal ions, both the shapes of the curves and the value of the final current change significantly as \( \omega \) increases.

The curves for the solution with \((\text{NH}_4)_2\text{SO}_4\) and \(\text{MnSO}_4\) present the typical behavior associated to the models for nucleation and growth, showing a local maximum (in modulus) for the current after the peak of the double layer charging followed by a slow decreasing behavior. These general characteristics are similar for both the kinetic controlled and the diffusion controlled growths [9–11], but the shape and the asymptotic behavior after a long period of deposition are different and can permit the identification of the specific type of growth, as will be discussed below.

For the solution with \((\text{NH}_4)_2\text{SO}_4\) and \(\text{FeSO}_4\) (figure 6(c)) the transient curves are noisy and do not follow the typical behaviors. For 1000 rpm particularly the curve presents a step at about 3 s, which seems to indicate a change in the regime of growth. Although the curves have these characteristics and the hydrogen evolution was much accentuated, the films deposited present good uniformity and metallic aspect. The noise can be attributed to the release of bubbles as commented. Concerning the curves obtained with the complete solution (figure 6(d)), up to 200 rpm, the characteristics are similar to the ones for the solution only with \((\text{NH}_4)_2\text{SO}_4\) and \(\text{FeSO}_4\) but above 200 rpm they are less noisy and present a behavior which can be associated to the typical models of nucleation and growth. The current efficiency for alloy deposition varies from 28 to 56% depending on the speed of rotation, the maximum occurring at 400 rpm.

Different nucleation and growth models are normally used for the interpretation of the current-time transient curves of electrodeposition [5, 6, 8–11, 28–31]. The more detailed three-dimensional approach has not a simple analytical solution and has been recently reviewed [10, 11]. A common approach is based on the growth of planar diffusion zones [18–23, 29–31], and is called standard model or Scharifker-Hills model [8, 10, 11, 20]. This last model has the advantage to present a single analytical expression for the time \( t \) dependence of the current density, represented in equation (10) (current density \( \dot{i} \) in modulus). This expression can be directly fitted to the experimental curve for diffusion-controlled growth.
In equation (10), $A$ represents the nucleation frequency (nucleation rate, assumed constant), $N_0$ represents the initial number of electroactive sites per area of the electrode surface, the product $zF$ is the molar charge transferred, $\rho$ is the density of the deposit, and $M$ its molar mass.

A modification of equation (4) has been also proposed to deal with the deposition of alloys where the parameters are weighted averages of the parameters of each metal [5, 23]. However, both the Scharifker–Hills model (SH) as its modified version for alloys, as well as the three-dimensional approaches involve many parameters which are hard to determine experimentally. Here we have opted to compare the SH fits with the Isaev et al approaches (IGZ) considering the known parameters in each case. In the IGZ model [9–11, 22] the growth follows the law of hemispherical diffusion and not planar diffusion zones as in the SH model. Consequently, there is no a single expression like equation (10) to be fitted and the transient curve is calculated recursively.

Figure 7 presents the results for the complete solution and for the solution only with $(\text{NH}_4)_2\text{SO}_4$ and MnSO$_4$ for rotation speeds in the intermediate range, which closely follow the models for nucleation and growth. Equation (10) has been fitted with a common Levenberg-Marquardt non-linear least squares algorithm. The typical values for $\gamma$-FeMn and $\alpha$-Mn were considered for $\rho$ and $M$ in each case. The $D$ values presented in table 2 were used, reducing the free parameters to $A$ and $N_0$. In order to take the hydrogen evolution into account, a constant term was added to equation (10), in the same sense as it has been done in recent works [21, 22]. This is also an approximation since the results of figure 6(a) show the contribution from hydrogen evolution is not constant at the beginning of the deposition, but tends to a steady state after about 5 s. For the IGZ model, the curves were generated using the software Wolfram Mathematica considering the approach presented in references [10, 11] (refer to supplementary material for an example of Mathematica file with the calculations). The experimental values of current density and time at the maximum ($i_{\text{m}}, t_{\text{m}}$) were used to determine the

\[
i(t) = \frac{zFD^{1/2}c}{\pi^{1/2}t^{1/2}} \left[1 - \exp \left(-N_0 \pi D \frac{8\pi cM}{\rho} \left(t - \frac{1 - e^{-At}}{A} \right)\right)\right]
\] (10)
parameters needed to do the numerical integrations. The integrations were made point by point along the deposition interval, and the addition of constant was also necessary to take the hydrogen evolution in account.

In the four cases presented in figure 7, the shape of the curves and the fittings show diffusion controlled growths. For the solution only with (NH₄)₂SO₄, MnSO₄, the SH approach has resulted in the best fits (figures 7(a) and (b)). At 400 rpm (figure 7(a)), SH is just a little better but almost equivalent to the curve from the IGZ approach for diffusive controlled process at the instantaneous nucleation limit. The values of \( \frac{N_v}{A} \) obtained with SH were 1340 and 970 s cm⁻², for 400 rpm and 600 rpm, respectively. In the case of the complete solution (figures 7(c) and (d)), the results of SH fits and IGZ curve for diffusive control at the instantaneous nucleation are equivalent, but SH is also a little better at 400 rpm. The values of \( \frac{N_v}{A} \) obtained for these last two cases were 0.005 s cm⁻² and 0.010 s cm⁻². These slightly better results of SH approach are related to the fact that the curves were fitted, where the curves from the IGZ were calculated for limiting situations (instantaneous and progressive nucleation limits correspond to \( \frac{N_v}{A} \rightarrow 0 \) and \( \frac{N_v}{A} \rightarrow \infty \), respectively). The values of \( \frac{N_v}{A} \) obtained indicate the growth in the solution with MnSO₄ is at an intermediate regime, whereas in the solution with MnSO₄ and FeSO₄ it is tending to the instantaneous limit. Although \( D \) was kept fixed in the SH fits, the uncertainties of these \( \frac{N_v}{A} \) values are relatively high, thereby they should be seen only as estimates which represent the general behavior of the system.

The four examples of figure 7 show that the type of growth can be identified using any of the models, SH or IGZ, but the limiting regimes of progressive or instantaneous nucleation may not fit adequately the experimental data in some situations. Considering the experimental uncertainties of our measurements, we can use the SH model without loss of generality, since the fitting procedure is more straightforward than the use of the complete 3D growth of IGZ model, furthermore the simple kinetic controlled growth has not occurred in the conditions tested here.

In figure 8(a), one can see the transient curves for the deposition using the complete solution and the same rotation speed but employing different applied potentials. The curves were fitted with equation (4) letting \( D \) as a free parameter, as well as \( A \) and \( N_v \), and the resulting parameters are plotted in figure 8(b). The fittings describe adequately the major behavior of the experimental data, which are in diffusion controlled regime. The value of \( D \) increases slightly as the value of deposition potential (\( E_{DEP} \)) increases. The values of \( \frac{N_v}{A} \) ratio are close each other for the smaller values of \( E_{DEP} \), but increases when \( E_{DEP} \) passes to \(-1.85 \) V. Although all these values of \( \frac{N_v}{A} \) indicate almost instantaneous nucleation, the rising tendency is showing the increase of \( E_{DEP} \) approximates the behavior to an intermediary nucleation regime.

The effects of the three different concentrations of (NH₄)₂SO₄ (0.5, 0.8 and 1.0 M) also have been analyzed keeping \( E_{DEP} = -1.65 \) V and the concentrations of the other components fixed (0.6 M for MnSO₄ and 0.008 M for FeSO₄). The fits and the corresponding parameters are presented in figure 9. There is a reduction of the \( \frac{N_v}{A} \) ratio as the concentration of (NH₄)₂SO₄ increases, but all the three cases are close to the instantaneous limit and the changes in \( N_v/A \) value are within the uncertainties, which are of the order of 0.1 s cm⁻². The value of \( D \) increases one order of magnitude when the NH₄⁺ concentration pass to 1.0 M, which corresponds to \( \frac{C_{NH4}}{C_{Mn}} = 1.67 \). That means the length of the diffusion layer increases as the \( C_{NH4}/C_{Mn} \) ratio pass to 1.67, a case for which a significantly better SH fit was obtained.
4. Conclusions

Fe–Mn thin films were electrochemically deposited from sulfate baths under different conditions. The effects of several applied potentials for deposition, concentrations of the reagents MnSO4 and FeSO4, as well as of the additive (NH4)2SO4, were investigated. The results indicate that the codeposition occurs at a mixed transport-kinetic control with multi-step mechanisms. The composition of the alloy can be controlled by choosing the specific concentrations and speed of rotation of the working electrode, despite the occurrence of hydrogen evolution reaction in a relatively large scale.

Using a specific hydrodynamic condition with speed of rotation in an intermediate range, approximately from 100 to 800 rpm, the deposition takes place as a system under diffusion control, and the current-time transients can be analyzed in light of the typical models for nucleation and growth. In this range of rpm, the nucleation tends to the instantaneous limit with diffusion coefficient of the order of 10−5 to 10−6 cm² s⁻¹. The value of the rate of reaction obtained for the solution with (NH4)2SO4 and FeSO4 is much larger than the one for (NH4)2SO4 and MnSO4, confirming why Fe is preferentially deposited as the analysis of the composition has shown.

Acknowledgments

This work is supported by FAPEMIG Foundation (Project APQ-01987-18). P. P. Barreiros is a grantee of the CAPES Foundation (501100002322). Authors wish to thank the supports from LMMA sponsored by FAPEMIG (501100004901), (CEX-112-10), SECTES/MG and RQ-MG (FAPEMIG: CEX-RED-00010-14), and the help from Caíque L. Macedo.

ORCID iDs

Manoel J M Pires © https://orcid.org/0000-0001-8115-7517

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