Analysis of Initial Stages of Electrocrystallization and Composition of Fe-Co Deposits

Elena Charipova, Fábio R. Bento and Lucia H. Mascaro
Depto. de Química - Universidade Federal do Paraná
C.P. 19081. 81531-990 – Curitiba. PR- Brazil

1. Introduction

According to Brenner's classification (1) the electrodeposition of Fe + Co alloys belongs to the category of anomalous codeposition in which a normally less noble metal (Fe) deposits the more noble one (Co) as the potential is driven negative. In the case anomalous codeposition it is impossible to predict the composition of the alloy, so that the former must the determined by some other technique for a given conditions of alloy deposition. The anodic linear sweep voltammetry (ALSV) for phase structure determination of binary alloys and quantitative assessment or phases in the alloy has been developed.

In this work the objective was investigate the Fe-Co alloy electrodeposition in a different metal ratio molar in a solution content simple chloride using ALSV technique for determination Fe-Co alloy composition. Also studied initial stages of alloy deposits by potentials steps.

2. Experimental

A three-electrode Pyrex® cell was used to perform the experiments with an approximate volume of 25 mL. The working electrode was obtained sealing a Pt disk and polishing in aluminum powder. The auxiliary electrode was Pt foil and all potentials quoted in this work were refereed to the saturated calomel electrode (SCE).

The electrolyte bath consisted of a 0.1 M $FeCl_2$ + 0.1 M de $CoCl_2$ in molar ratio 1:5, 1:1 and 5:1 in 1,0 M KCl solutuion. The electrochemical experiments were performed with Microquímica potentiostat-galvanostat linked to PC microcomputer. The software used to control the experiments was the MQPG.exe.

3.Results and Discussion

Fe-Co alloy electrocrystallization was studied by potential steps (range –0.9 to –1.1 V) in three solutions mentioned. Taking into account the equations for instantaneous and progressive 3D nucleation and growth process under kinect control mechanisms, the transients current were normalized representing non-dimensional plots $(I/I_{max})^2$ vs. t/t_{max} (fig. 1). Is observed that experimental results fitting the curve to instantaneous nucleation for 5:1 ratio and progressive for 1:5 ratio. In 1:1 ratio an intermediate behaviour is observed.

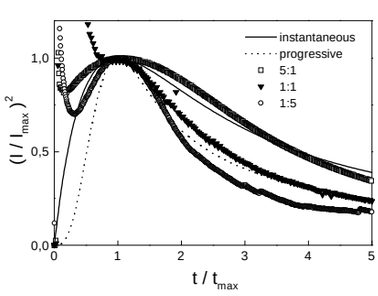
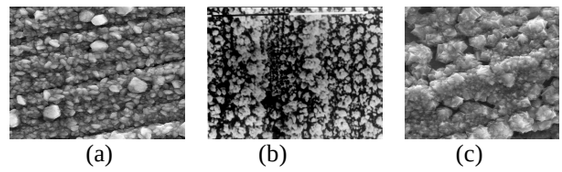


Figure 1: Non-dimensional $(I/I_{max})^2$ vs. t/t_{max} plot for Fe-Co alloys in different molar ratio, E_{step} = -1.02 V .

The morphology of alloys is modified when content Fe in solution is change. To 5:1 ratio deposits present crystals with the same size but 1:5 ratio these have size different that is according the nucleation process.



(a) (b) (c)

Figure 2: MEV of Fe-Co alloys deposits obtained in different molar ratio (a) 1:5, (b) 1:1 and (c) 5:1, 5000X.

ALSVs of Fe-Co alloys electrodeposited at a different molar ratio are shown in Fig. 3.

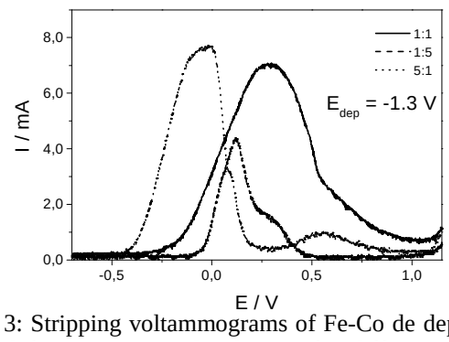


Figure 3: Stripping voltammograms of Fe-Co de deposits obtained from 1,0 M KCl solutions for different molar ratio of Fe:Co in solution, v= 50 mVs^{-1}.

The deposit stripping obtained for 1:5 ratio show two well-defined peaks in – 0.05 and 0.6 V. When Co percentage in solution is lower the first peak disappear and new peak is observed in 0.25 V for 1:1 and 0.12 V for 5:1. These results indicate that different composition alloys were formed.

The quantity total alloy deposits is lower in 5:1 ratio, as shown by decrease charge dissolution observed in ALSV curve. Therefore we can to say the efficiency of deposition process is lower when content Fe is higher.

Alloys composition corresponding Fig. 2 were determined by atomic absorption and presents in Table 1. Comparing ALSV curves with data in Table 1 and based in ALSV pure metals is possible to define that rich Co alloys presented more negative potential dissolution and anomalous deposition occurs to 1:5 ratio, in another ratios the deposition process is regular.

Table 1: Dependence of Fe and Co content in the deposits as a function of the molar ratio Fe:Co in solution.

Fe:Co ratio	% at/at Fe	% at/at Co
1:5	29.3	70.7
1:1	34.3	65.7
5:1	41.3	58.7

4. Conclusions

In this work was observed that nucleation process and deposits morphology is modified with Fe content in solution. The ALSV technique permitted indicate rich Co alloys.

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