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Short Communication

Characterization of Fe-Ni-W Electrodeposits Obtained from Acid Medium

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This paper reports on the study of electrodeposition films of Fe-Ni-W in sodium citrate solution at pH 5.0. Behavior alloys were obtained by cyclic voltammetry at different ion concentration ratios and films were characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). It was concluded from the results of XPS that, during induced co-deposition of the species Fe (II), Ni (II) and W (VI), film growth consisted of a mixture of oxides of W (IV) and (V) doped with Fe and Ni (0), with these coatings analyzed by XPS.

Keywords: electrodeposition; Fe-Ni-W alloys, XPS.

1. INTRODUCTION

Alloys of W with iron group metals have been studied because of their enhanced and specific magnetic, electrical, mechanical, thermal and corrosionless properties [1]. Due to W hardness, they can successfully substitute hard chromium coatings, which are formed in the environmentally hazardous process based on hexavalent chromium [2].

The W electrodeposition is not easily achieved because this metal is only completely reduced in an aqueous solution when an inductor metal is present in the plating bath. The alloy codeposition mechanism is not complete elucidated and the possible multi-step reduction of some Mo and W chemical species has been proposed [3, 4, 5].

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chemical species has been proposed [2]. Very few research works [3-11] are documented about the structural and composition of electrodeposited amorphous and crystalline iron group W alloys.

It has been found that the alloys with tungsten can be deposited in the amorphous form [4]. Several research studies have devoted their attention to binary W alloy deposition with Fe [5, 6], Ni [7, 8] and ternary alloys [10, 11]. The main aspects studied in all of these papers were the properties of deposits as corrosion resistance and hardness. Usually these properties are related to the nanocrystalline or amorphous structure observed in the coatings. Some papers investigated the influence of the composition bath in the composition and morphology of deposits obtained for ternary W alloys. Similarly, in this present work, electrodeposition of Fe-Ni-W alloys will be studied at different deposition conditions by cyclic voltammetry to obtain information about the induced codeposition mechanism during electrodeposition, and their characterization will be carried by X-ray photoelectron spectroscopy (XPS) and scanning electronic microscopy (SEM).

2. EXPERIMENTAL

Electrochemical experiments were performed in a conventional three-electrode cell controlled by an EG&G PARC mod. 273 potentiostat/galvanostat. The voltammetric experiments were performed at 50 mV s^{-1} between -1.8 V to 1.8 V. The Pt discs (0.196 cm^2) were used as working electrodes; the reference electrode was a saturated calomel electrode (SCE) and the auxiliary electrode was a large-surface platinum spiral wire. The chemical reagents were: $FeSO_4·6H_2O$, $NiSO_4·7H_2O$, $Na_2WO_4·2H_2O$ and $Na_3C_6H_5O_7·2H_2O$. All solutions were freshly prepared with water purified in a Millipore Milli-Q system. The bath compositions were 0.01 mol L^{-1} Fe(II) + 0.01 mol L^{-1} Ni(II) + 0.01 mol L^{-1} W(VI) at 0.24 mol L^{-1} $Na_3C_6H_5O_7·2H_2O$ solution and 0.01 mol L^{-} Fe(II)+ 0.10 mol L^{-1} Ni(II) + 0.01 mol L^{-1} W(VI) at 0.24 mol L^{-1} $Na_3C_6H_5O_7·2H_2O$ solution, for molar ratio of the Fe:Ni:W 1:1:1 and 1:10:1, respectively. In all experiments the temperature was kept at 25 °C and electrolyte pH was adjusted to 5.0 with citric acid solution.

The deposition experiments were performed potentiostatically (at -1.2 and -1.5 V) for 60 min and galvanostatically (at 30 mA cm^{-2}) for 30 min, using a steel cathode. The surface morphology of the electrodeposits was analyzed with Philips XL-30 scanning electron microscope (SEM) equipment. The X-ray photoelectron spectroscopy (XPS) experiments were carried out using a VG ESCA LAB MKII (UK). The Mg K$\propto$ X-ray line at 1253.6 eV was used for excitation in all cases. The X-ray supply was run at 11 kV and 20 mA. All measurements were referenced to the C(1s) line binding energy of 284.5 eV. In order to avoid oxidation by air, the sample was protected in high pure nitrogen after deposition and before the XPS experiment.

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3. RESULTS AND DISCUSSION

The cyclic voltammograms obtained at 50 mVs^{-1} for Fe:Ni:W alloy deposition in solutions with molar ratios of 1:1:1 and 1:10:1 are presented in Figure 1. The voltammograms clearly depicts the well-defined cathodic peaks around -0.7 V for two molar ratio studied and one or two anodic peaks for molar ratio 1:1:1 and 1:10:1, respectively.

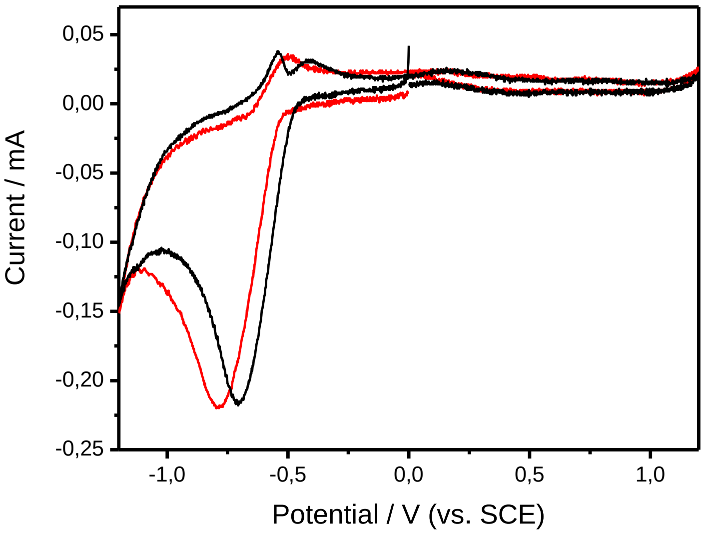


Figure 1. Cyclic voltammograms of molar ratio of Fe:Ni:W 1:1:1 (—) and 1:10:1 (—) at 0.24 mol L^{-1} $Na_3C_6H_5O_7$ solution and pH 5.

On the forward scan, as the Ni concentration increases at 10 times (black line) the cathodic curve varies slightly. The reduction peak shifted at approximately 90 mV to more noble potentials, but the peak current is similar to that for the another molar ratio. Considering that the reduction W(VI), Fe(II) and Ni(II) occurs simultaneously around -0.7 V [14] this shift potential is due the change Ni Nernst potential. As cathodic current no increases with Ni(II) concentration the reduction process is not controlled by diffusion of this ions metals species.

For W deposition with Fe metals group is considered that initially is formed a film consisting that a mixture of polyvalent tungsten oxides and/or nickel and iron hydroxides [12, 13]. Since, the electrodeposition is done under the conditions of excessive hydrogen evolution; the pH value could be increase substantially near the cathode surface. This fact induced the formation of iron or nickel hydroxyl complexes and yields higher weight fraction of iron in the alloy at the beginning of the electrodeposition [15].

Normally, the electrodeposition process of pure metals or Fe-Ni-W alloys only occurs at more negative potentials, simultaneously with the hydrogen reactions. Metallic alloys are thought to be deposited at more negative potentials, as will be argued later in the XPS analysis. The similar behavior could be considered when W(VI) is reduced with Ni(II) and Fe(II). The cathodic peak observed at presence W(VI) also can be attributed formation of HWO_3 with hydrogen incorporations [16].

Following the cathodic potential scan it is observed that the current increases exponentially due to a hydrogen evolution reaction.

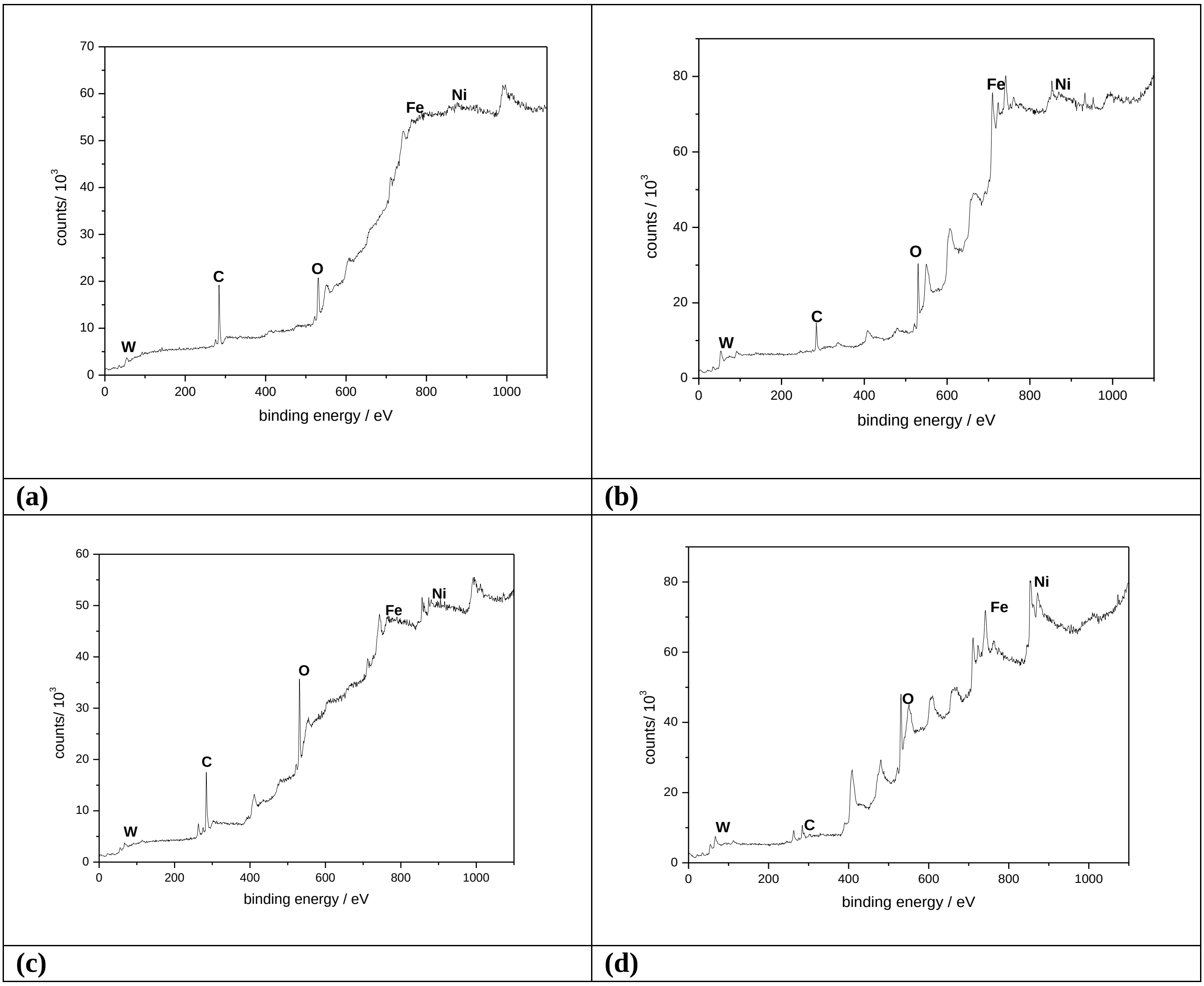


Figure 2. XPS spectra of the films obtained by potentiostatic (a,b) and galvanostatic (c,d) electrolysis for of Fe:Ni:W.1:10:1. a , c: before and b, d: after sputtering process on the surface samples with argon atmosphere

In the anodic scan, for 1:1:1 molar ratio, one very low current peak is observed at -0.5 V followed at flat and wide peak at 0.15 V that is reference to the Fe element. Comparing the peak potentials with observed at presence of individuals metals W(VI), Fe(II) and Ni(II) the first process can be attributed by the Fe dissolution and either to the process of the passivation phenomena of the Ni that was deposited during the cathodic sweep [15]. When the Ni concentrations increases on the bath, its possible to observe two anodic peaks is observed at -0.55 and -0.42 V, attributed to Fe and Ni dissolution.

XPS studies of solid material offer very useful information on elemental composition and their oxidation states, both on the surface and in the bulk of the sample (up to few layers). Similarly, this technique was used to evaluate the surface deposits, which were obtained galvanostatically at 30 mA cm^{-2} (corresponding -1.5 V) and potentiostically for 60 min at -1.2 and -1.5 V, at bath containing molar ratios of Fe:Ni:W 1:1:1 and 1:10:1 in the solution.

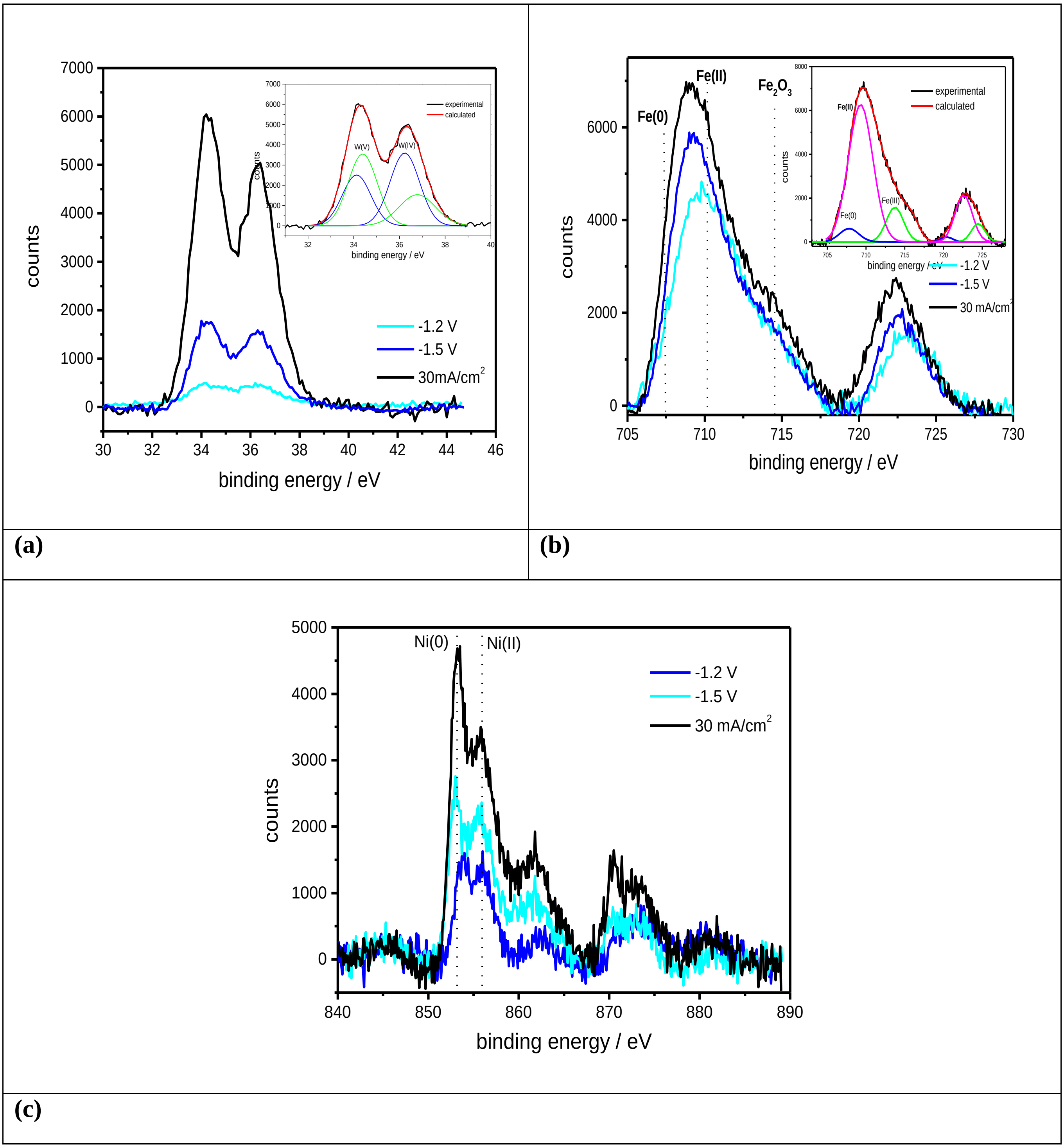
XPS spectra showed the presence of O and C as well as Ni, Fe and W, see Figure 2 The presence of carbon is due to contamination by hydrocarbons/dust adsorbed from the atmosphere during storage of the samples in air. After the sputtering process on the surface samples with Argon atmosphere until 75 s, there is the removal of C elements, however O content no decrease, indicating that the oxides are presence on the deposits.

The tungsten W 4f spectra obtained at -1.2 and -1.5 V and 30 $mAcm^{-2}$ for Fe:Ni:W molar ratio 1:10:1 are showed at Figure 3a. The peaks corresponding to $4f_{7/2}$ and $4f_{5/2}$ are observed at 34.2 eV and 36.3 eV for all deposition conditions. A spectrum deconvolution is represented in insert in Figure 3a. The fitting analysis allows to identify two doublets of the overlapped spectra with energies close to those expected for tungsten oxides present in the mixed valences of W(VI), W (V), W (IV). The signals of metallic tungsten, observed usually at 31 eV and 33 eV, is not observed in any of the deposition conditions used in this study. Therefore, it is evident that the tungsten in the electrodeposited is present only as polyvalent tungsten oxides.

The spectra for the Fe region, on the same conditions specified previously, are represented in Figure 3b. In this figure, one doublet is well defined; this was observed to be independent of the deposition conditions, as there were peaks at 710.0 eV (Fe $2p_{3/2}$) and 723.3 eV (Fe $2p_{1/2}$) that correspond to different Fe species. The first peak can be deconvoluted at three peaks at energies of 707.0, 710.0 and 715.0 eV, which represent the species Fe (0), Fe (II) in FeO and Fe (III) in Fe_2O_3, respectively. In this case, a good fitting between the experimental and calculated curves was obtained (insert Figure 3b). The peak intensity of iron oxide is higher than iron metallic and from qualitative analysis, that amount of oxides in the film is larger than that of metallic iron. Also in Figure 3b can be observed for deposition at more negative potentials (-1.5 V and 30 mA/cm^2) to facilitate the deposition of Fe metal. This fact is in agreement with that proposed in the analysis of voltammograms.

The Figure 3c shows the spectra for the region of the Ni for deposits of the Fe-Ni-W 1:10:1 obtained from different deposition conditions used in this study. It is possible to identify two species, nickel metallic (Ni(0)) and nickel oxide (NiO), which was evidenced by the peak at 852.9 eV (Ni 2p 3/2) and at 856.0 eV, respectively. Whereby in the case of iron, but more clearly, we can identify that the deposition of metallic Ni is favored at -1.5 V and 30 mA/cm^2.

Although the literature has been proposed that the process of induced codeposition of W or Mo with Fe group metals is formed by a metal alloy [8,10]. The presented data shows the dependence of the deposition conditions is absent in our case. Considering the results of the XPS in this study, its possible to predict that from codeposition of Fe(II), Ni (II) and W (VI) is obtained an reasoning leads that the oxide films with a small amount of Fe and Ni metallic.



(a) **(b)**

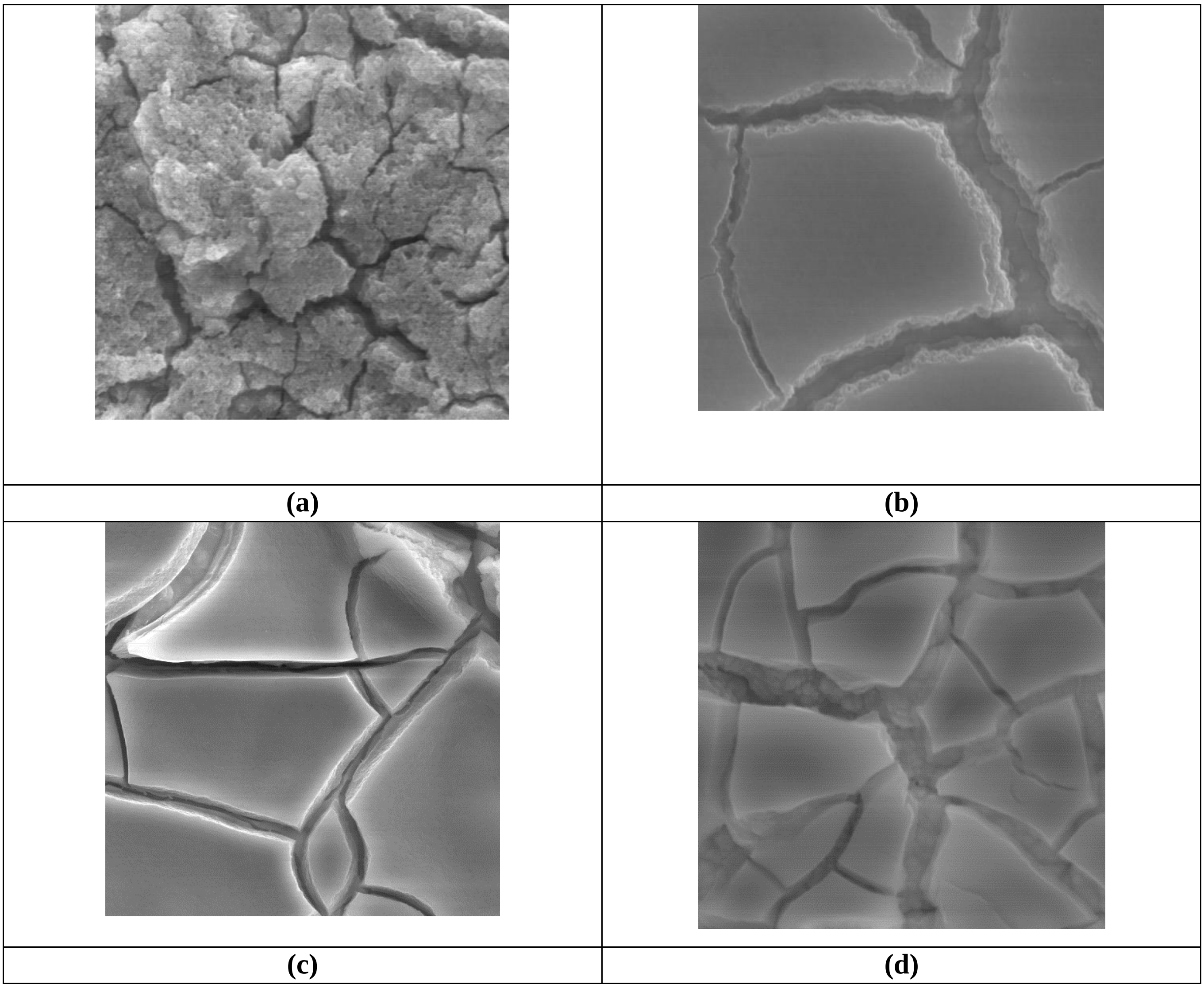
(c)

Figure 3. XPS spectra of the films obtained by potentiostatic and galvanostatic electrolysis for W (a), Fe (b) and Ni (c) region, from molar ratio of Fe:Ni:W.1:10:1. Insert: modeled fitting spectra.

Thus, this film obtained is a composite consisting of an array of oxide doped with Fe and Ni metallic. The same behavior was observed by Valles *et al*. in the deposition of Co-Mo alloy [17] and Sanches *et al.* for Ni-Mo and Fe-Mo co-deposition [14, 15] .

Electrodeposited Fe-Ni-W films have an appearance of grey-white and shiny. The SEM images for Fe-Ni-W alloys eletrodeposited from electrolyte pH 5.0 and molar ratio of Fe:Ni:W 1:1:1 and 1:10:1 are presented in Figure 4. The samples were prepared on steel foil electrodes at current density of 30 mA/cm^2 and -1.5 V. Electrodeposited films at low molar ratio and -1.9 V were roughness with globular structure and presented thin cracks; similar that observed by Balaraju *et al.* for nanoparticule tungsten oxide [18]. This morphology is characteristic of the formation of an amorphous structure.

For all other deposition conditions have the formation of two layers. A superior layer is extremely smooth and a close examination of the surface shows that the inferior layer is consisted of globular and roughness regions.



(a) **(b)** **(c)** **(d)**

Figure 4. SEM image of the film obtained potentiostatically at - 1,5 V, t = 3600 s (a, b) and galvanostatically (c,d) at - 30mA cm^{-2} , t = 1800 s from molar ratio of Fe:Ni:W.1:1:1 (a, c) and 1:10:1 (b,d).

Thicker cracks are observed on the surface, which may result either from hydrogen embrittlement or from residual stresses. Donten *et al.* [8,10] related similar cracking in amorphous Ni–W deposits mainly to high residual stresses. The smooth layer may be due to deposition of a metal film and is observed only in conditions of more negative potential, or where it has a higher content of Ni in the film, which facilitates the deposition of metal. The layer roughness is characteristic of tungsten oxides that exist in large quantities in deposits.

4. CONCLUSIONS

The formation of the Fe-Ni-W alloy does not occurs with W(0) in pH equal to 5 and the 1:10:1 and 1:1:1 deposition ratios. From the XPS analysis, it was possible to conclude that the doped oxide deposition was obtained with small concentrations of Ni e Fe metallic. The morphologic aspects do not presents a relationship with the deposition method for Fe-Ni-W.

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