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Zn–TiO₂ composite films prepared by pulsed electrodeposition

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Abstract The preparation of a Zn–TiO₂ composite film has been performed by pulsed electrodeposition, from acidic zinc sulphate solutions, on an Fe support. The influence of the bath pH and the presence of a cationic surfactant (CTAB) on the composite's structural and morphological characteristics has been investigated. The characterization of the samples was made by X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS) and atomic force microscopy (AFM). The experimental data show that for the composites prepared at pH 2, the metallic matrix presents a (0 0 2) preferential orientation. At pH = 4, the deposit loses the preferred *c*-axis orientation and in addition a higher content of TiO₂ particles is obtained. The use of the surfactant modifies the shape of the metallic grains, but little effect is observed on the dispersion of the semiconductor particles.

Keywords TiO₂ · Composite materials · Thin films · Electron microscopy · Crystal structure

Introduction

Electrolytic co-deposition is widely used for preparing metal matrix composites due to its low cost and versatility [1]. By electrolysis of plating solutions in which micron or sub-micron size particles are suspended, it is possible to obtain solid materials with improved and/or combined properties, which make them interesting for applications such as environmental remediation.

The electrolytic co-deposition of oxide particles with metals is a very complex process. It occurs under non-

equilibrium conditions and is accompanied by a flow of ions across the solution [2]. During the electrodeposition a progressive development of the texture and the roughening of the deposit take place.

The composite characteristics, are influenced by the deposition parameters, namely current profile, bath composition, pH, particle concentration and temperature [3]. The presence of additives has a marked influence on the rate of incorporation of the particles [4].

Composites containing occluded TiO₂ particles are interesting materials, due to the semiconducting properties of TiO₂, with applications as photocatalysts, particularly in the treatment of polluted water [5].

In recent years a lot of work has been performed on the TiO₂ co-deposition process, with Ni, Cu, Ag and Zn as the metallic component [6, 7, 8]. Most of these studies were carried out under potentiostatic conditions.

In this work, studies on the preparation of Zn–TiO₂ composite films on a Fe substrate are presented. Pulsed electrolysis has been used, due to the fact that the deposit's properties could be tailored when a rectangular current waveform is imposed in a periodic manner [9]. Zimmerman et al. have applied this technique successfully for the electrodeposition of Ni–SiC nanocomposites [10].

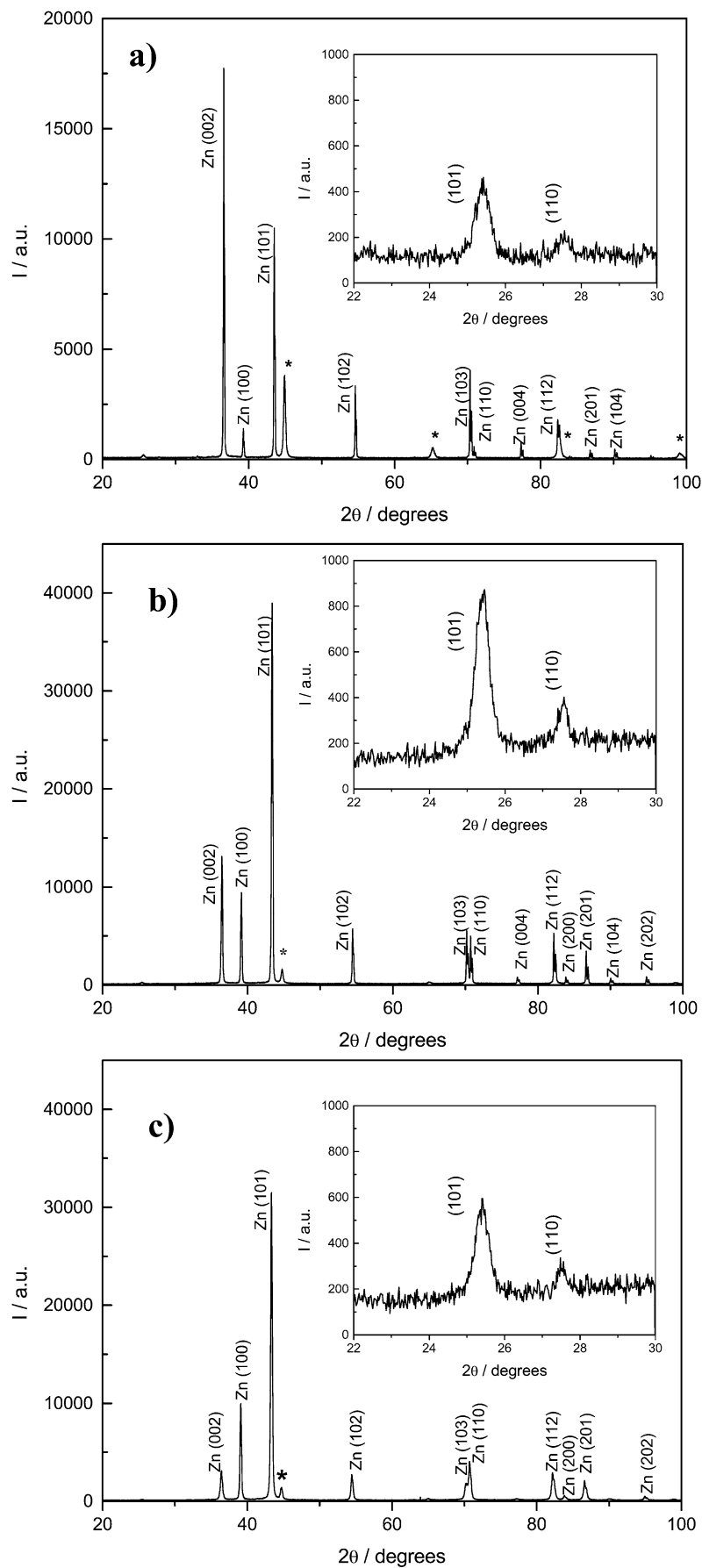
The goal of the work reported here is to investigate the influence of pH and the presence of a cationic surfactant on the structural and morphological characteristics of the as-deposited composites, which is crucial to the photocatalytic performance of the films [11].

Experimental

The electroplating bath was a mixture of 0.6 mol dm⁻³ ZnSO₄·7H₂O (Merck p.a.) + 0.1 mol dm⁻³ (NH₄)₂SO₄ (M & B p.a.) + 0.1 mol dm⁻³ TiO₂ (Degussa P25, particle size: 25 nm). The bath pH as prepared was 4. In some experiments the pH was adjusted to 2 by adding H₂SO₄. For the studies on the influence of the presence of the cationic surfactant in the electrodeposition process, 1 × 10⁻³ mol dm⁻³ cetyltrimethylammonium bromide (CTAB (C₁₆H₃₃N⁺(CH₃)₃·Br⁻), Aldrich) was added. The

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Fig. 1 X-ray patterns of Zn–TiO₂ composite films prepared from an electroplating bath with pH=2 (a), and pH=4 in the absence (b), and in the presence (c) of 1×10^{-3} mol dm⁻³ CTAB. *: reflections due to the substrate (Fe). Inset: diffractograms showing the most intense peaks due to the TiO₂



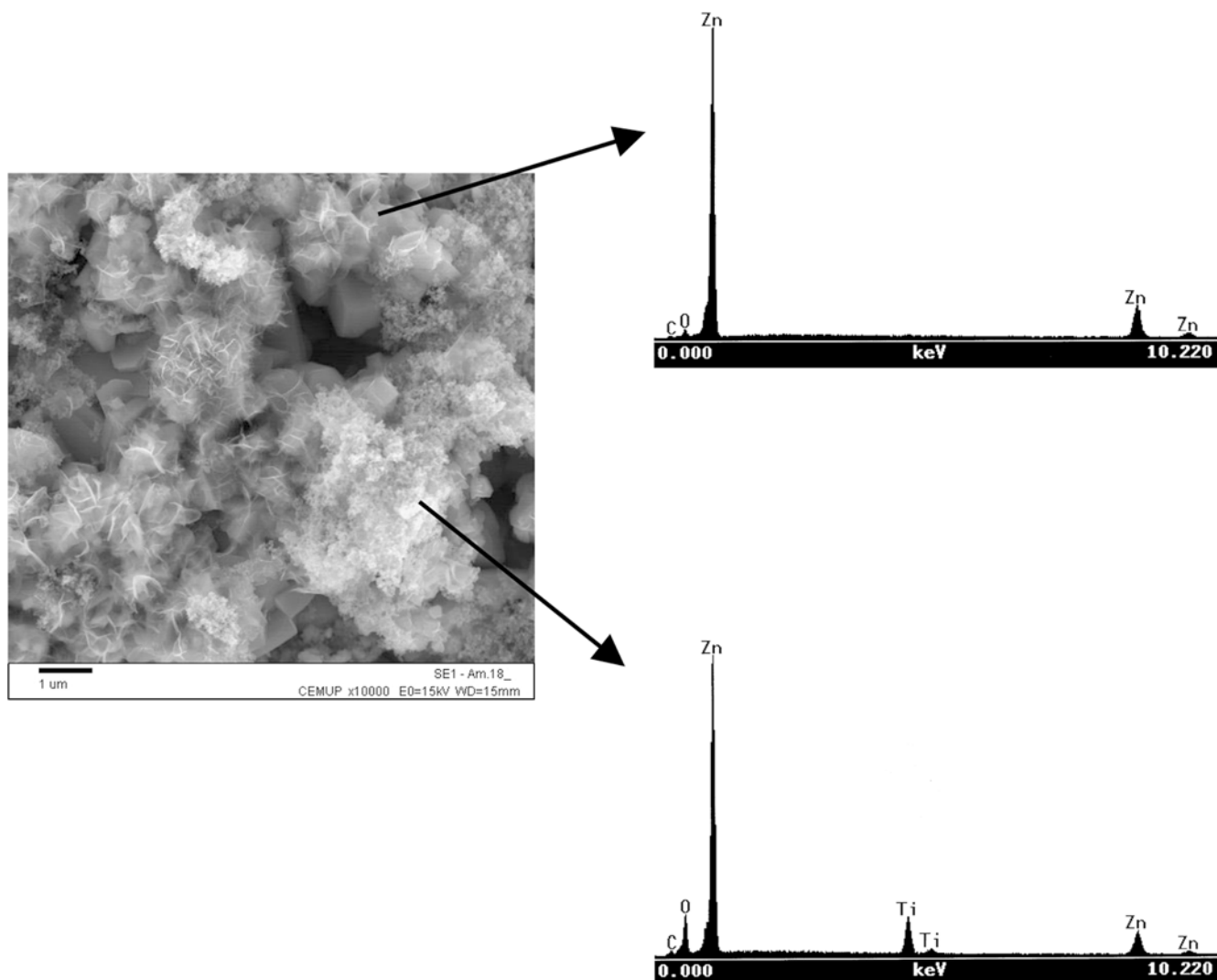


Fig. 2 SEM micrograph and EDS spectra for different points of the surface of a Zn-TiO₂ composite film prepared from an electroplating bath with pH = 4

solutions were made daily without further purification, followed by deaeration with nitrogen before and during the electrodeposition.

A glass cell with two compartments was used, with a Pt spiral as counter electrode and a commercial SCE as reference. The working electrode was a Fe disc (Goodfellows) with a 10 mm diameter. The Fe disc was mechanically polished with abrasive paper with different grades, followed by a chemical etching with a mixture of H₂O and HCl (1:1), prior to use.

Table 1 Electroplating conditions and average mass deposited

Electroplating conditions	Average mass of deposit (mg cm ⁻²)
pH 2	2.44 ± 0.21
pH 4	12.75 ± 0.66
pH 4 + CTAB	12.53 ± 0.48

The electrochemical measurements were carried out using an EG&G Princeton Applied Research potentiostat/galvanostat, Model PAR 263.

The Zn-TiO₂ composite films were prepared by pulse electrodeposition, using a galvanostatic cathodic square wave with a pulse peak current density of -125 mA cm⁻² and a current on-time and off-time of 4 and 40 ms, respectively. The deposition was performed under magnetic stirring at room temperature for 1 h. When finished the electrode was removed from the cell, rinsed with deionised water (18 MΩ cm) and dried under a nitrogen atmosphere.

The mass of the composite films was evaluated by weighing the samples before and after the electrodeposition.

X-ray diffraction analysis was carried out by using a Philips X-ray diffractometer (PW 1710) with Cu-Kα radiation, working at 30 mA and 40 kV and automatic data acquisition (APD Philips (v 3.5 B) software). The diffractograms were obtained in the 2θ range of 20 to 100°, using a 0.02° step and acquisition time of 2 s/step. Measurements with an acquisition time of 10 s/step were made in the 2θ range of 22 to 30°. General information about

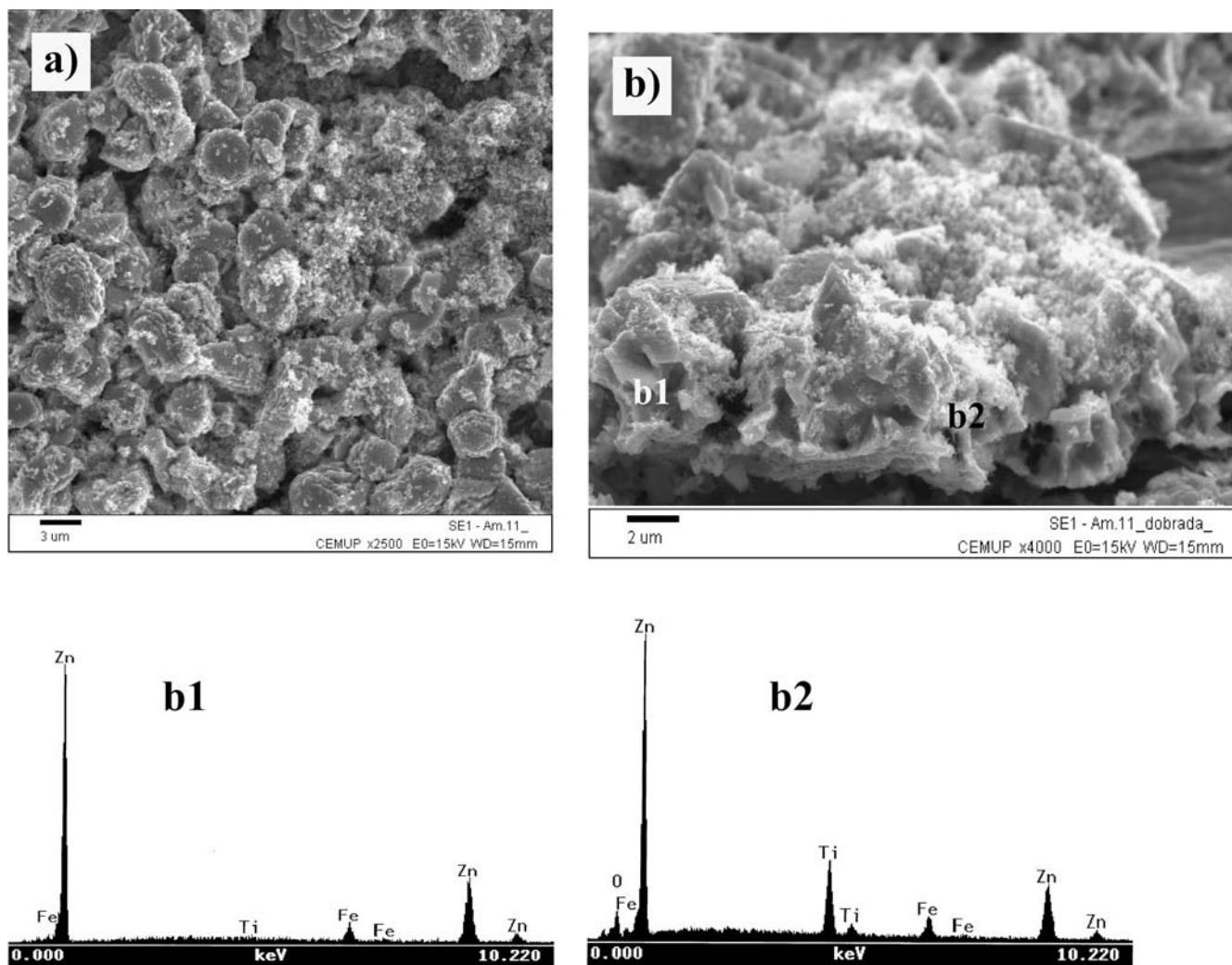


Fig. 3 SEM micrographs of the surface (a) and cross section (b) of a Zn-TiO₂ composite film prepared from an electroplating bath with pH=2. EDS spectra are shown for the Zn-TiO₂ cross section

the metallic matrix texture was obtained by comparison of the X-ray diffraction pattern of the studied sample with the ICDD file for zinc powder in accordance with the methodology indicated by Bérubé et al [12].

Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) analysis was performed with a JEOL (JSM-6301F) microscope with a electron beam voltage of 15 kV, in order to characterise the films surface and to estimate their thickness by investigations of the cross-sections. AFM images (DI Nanoscope IIIa, Santa Barbara) were recorded in the tapping mode. Silicon cantilevers with a resonance frequency of 300 kHz were used.

Results and discussion

The amount of the deposit obtained from the different plating solutions used in this work is presented in Table 1. The data show the strong influence of the electroplating bath's pH value. At pH 2 the amount depos-

ited is roughly five times less that deposited at pH=4. This fact is attributed to the hydrogen evolution reaction that occurs simultaneously with the zinc electrodeposition from acidic sulphate electrolytes and affects the current efficiency [13]. Indeed, the low value of pH in addition to the substrate composition enhances the hydrogen adsorption inhibiting the zinc deposition.

The results also show that the presence of the additive has no effect on the amount of the Zn-TiO₂ deposited.

Figure 1 presents the XRD patterns of Zn-TiO₂ composite films prepared at pH 2 (a) and pH=4 in the absence (b), and in the presence (c) of 1×10^{-3} mol dm⁻³ CTAB. The analysis of the diffractograms shows that the majority of the diffraction lines can be ascribed to the Zn hexagonal structure [14].

The XRD patterns indicate changes on the texture of the metallic phase, which are dependent on the bath pH. Its decrease led to a change of the zinc crystal orientation from (101) to a (002) direction, which is consistent with the results obtained by Raeissi et al. [15], for the galvanostatic deposition of zinc at pH 2.

From the width of the zinc diffraction lines presented in Fig. 1b and c it can be concluded that the grain size of the metallic matrix is smaller when the CTAB is present.

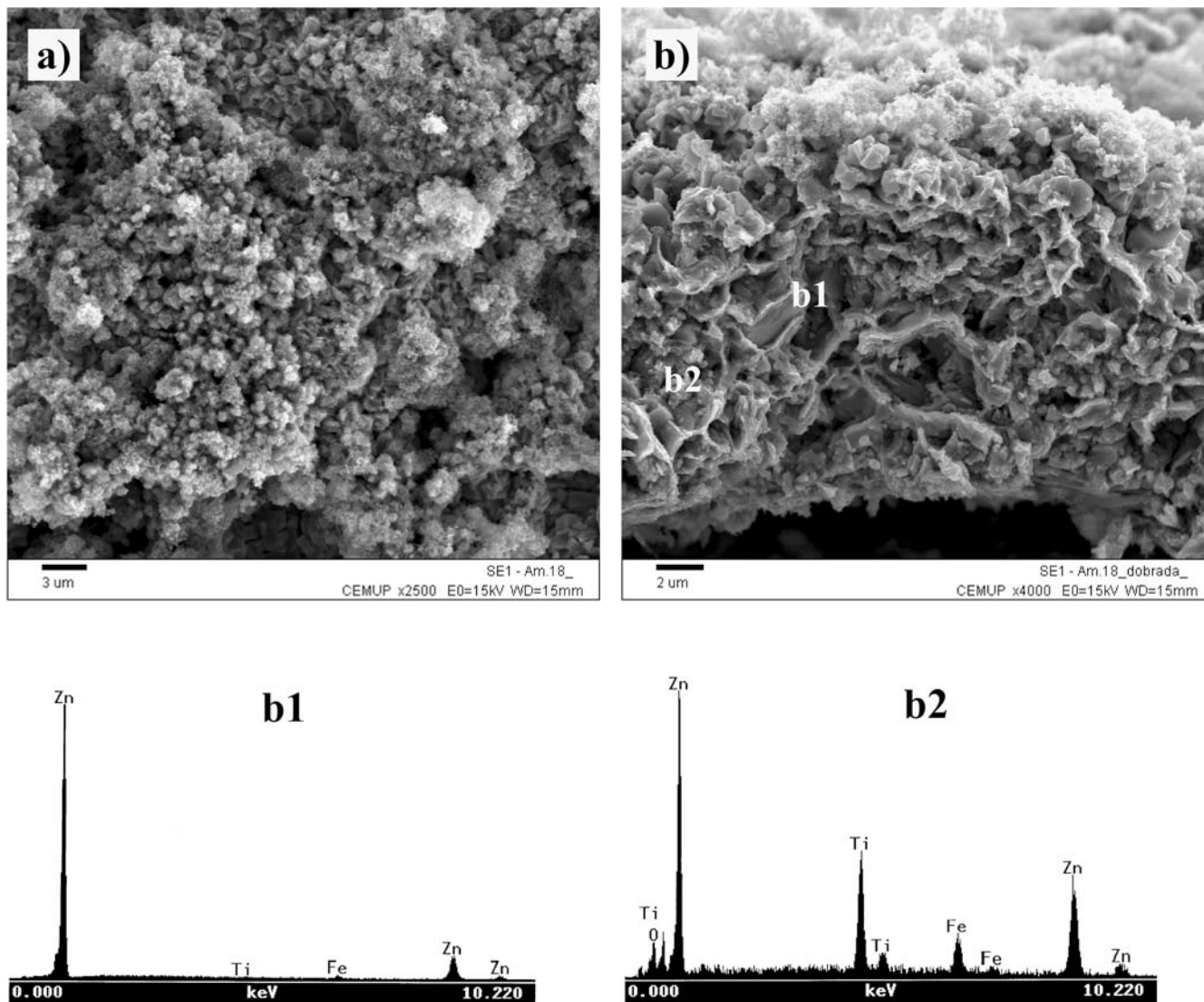


Fig. 4 SEM micrographs of the surface (a) and cross section (b) of a Zn-TiO₂ composite film prepared from an electroplating bath with pH=4. EDS spectra is shown for the Zn-TiO₂ cross section

This fact can be mainly related to the inhibition of growth of the zinc crystallites due to the surfactant molecules present on the cathode surface [16].

For all the deposits obtained, the (1 0 1) and (1 1 0) diffraction lines for anatase and rutile phases, respectively, were observed between 24° and 28° 2θ, which confirms the formation of the Zn-TiO₂ composite [17].

The films morphology and elemental composition were investigated by SEM/EDS. From the chemical analysis performed with EDS for all electrodeposited films, it was possible to identify the areas where the presence of Ti and an increase of the oxygen content occur, indicating the deposition of the TiO₂ particles which is in accordance with the XRD data. Figure 2 illustrates this result for an electrodeposit obtained at pH=4, where a SEM image is presented as well as the corresponding EDS spectra.

The morphology and thickness of the composites are greatly dependent on the electrodeposition conditions

tested, as the micrographs of the coatings surface and cross-section presented in Figs. 3, 4 and 5 show. In general the electrode surface is covered by a polycrystalline zinc film with randomly dispersed TiO₂ particles. These particles are grouped in agglomerates, presenting a spongy morphology, whose size and number are dependent on the pH of the solution.

In the case of the samples prepared from the more acidic solution, relatively large plate-like zinc crystals were obtained, with the TiO₂ particles uniformly dispersed in this matrix, as Fig. 3 shows. The thicknesses of the coatings was estimated as 5 μm by SEM analysis.

For the deposition bath of pH 4, the size and number of TiO₂ agglomerates increases and the Zn matrix grain size decreases (Fig. 4). A thickness of 22 μm was estimated for the coatings. The coating thickness values are in accordance with the amount deposited for the two pH values used and presented in Table 1.

EDS spectra obtained at different points in the cross-sections of the films show that the TiO₂ particles are present in the metal matrix.

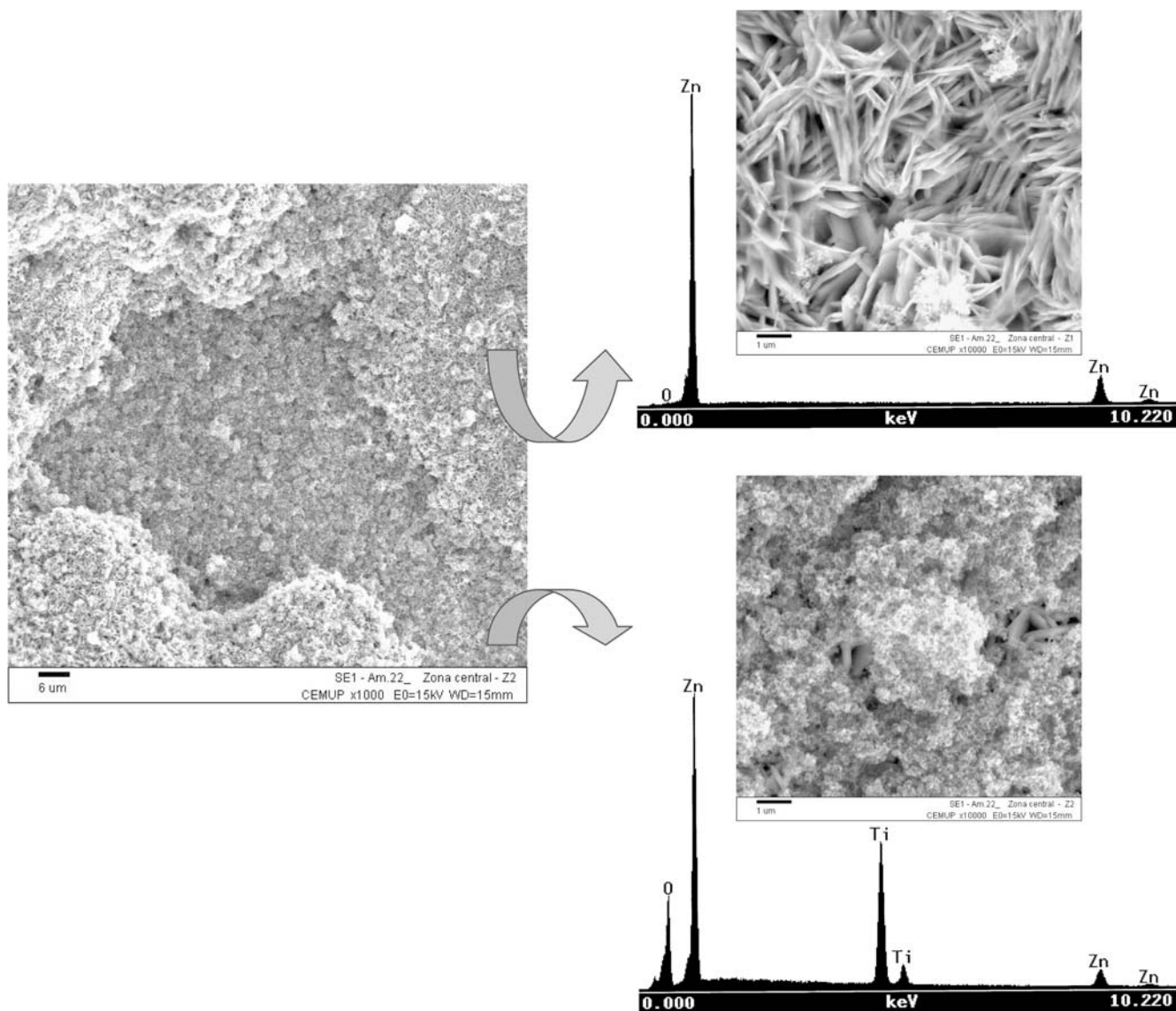


Fig. 5 SEM micrographs and EDS spectra for different areas on the surface of a Zn-TiO₂ composite film prepared from an electroplating bath with pH=4, in the presence of 1×10^{-3} mol dm⁻³ CTAB

In the presence of the surfactant, modifications of the homogeneity of the deposits as well as a change on the shape of the Zn crystallites are clearly seen, as Fig. 5 illustrates for the surface of a Zn-TiO₂ composite.

The modification of the metal crystal shape is common for acid sulphate solution used for zinc electrodeposition when organic additives are present, and is due to the adsorption of the additives on the electrode, inhibiting the surface diffusion of ad-atoms and consequently the growth of the Zn crystals [18].

EDS analysis performed at different surface points shows that the films present areas where the Zn needles are the main component and other areas where the main component is TiO₂.

The surface of the films prepared at pH 2 and 4 without CTAB has been also observed by AFM (Fig. 6).

In both cases very rough surfaces are observed, although the film obtained at higher pH presents a smoother surface (Fig. 6b). This fact could be due to the larger size and amount of the TiO₂ aggregates.

Conclusions

Zn-TiO₂ composites were successfully prepared by pulse electrolysis using a zinc plating bath with homogeneously dispersed TiO₂ particles with and without the addition of a surfactant.

The crystal orientation of the zinc matrix changes from a (101) to a (002) texture when the pH value of the electroplating bath is decreased.

In the absence of a surfactant (CTAB) in solution, the highest content of TiO₂ particles in the composite is achieved when the pH of the electroplating bath is 4.

The presence of a surfactant (CTAB) led to a decrease in the grain size of the zinc matrix; however, no effect in the dispersion of semiconductor particles is observed.

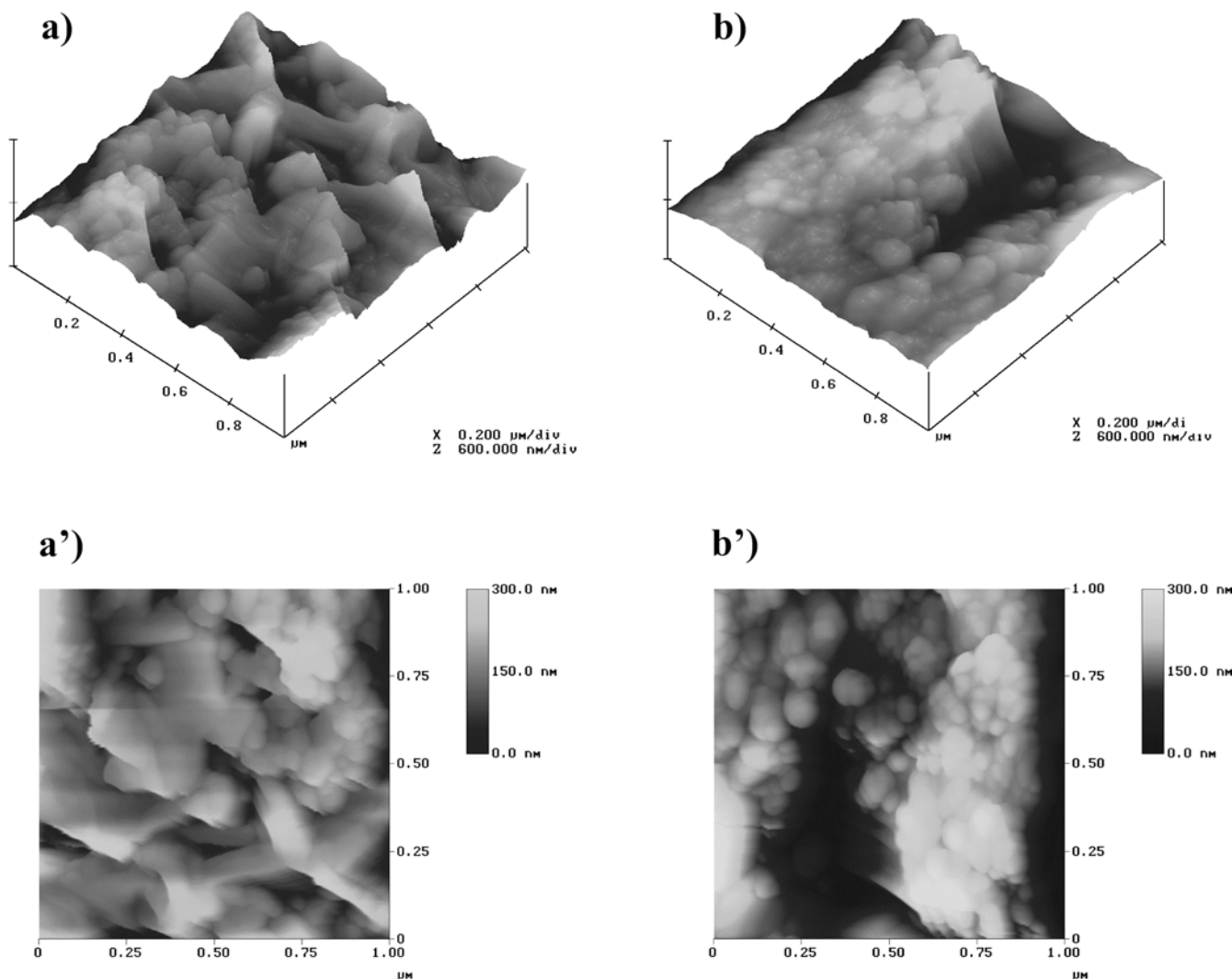


Fig. 6 AFM images of Zn-TiO₂ composite films prepared from an electroplating bath with pH = 2 (a) 2D and (a') 3D view and pH = 4 (b) 2D and (b') 3D view

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