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Electrodeposition of Zn-Ni-ZrO₂, Zn-Ni-Al₂O₃ and Zn-Ni-SiC Nanocomposite Coatings from an Alkaline Bath

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Zn-Ni-ZrO₂, Zn-Ni-Al₂O₃ and Zn-Ni-SiC nanocomposite coatings were obtained on mild steel substrate by electrodeposition technique from an alkaline bath. ZrO₂, Al₂O₃ and SiC nanoparticles were added to the bath with concentrations of 5 and 10 g dm⁻³. The effect of current density and particles concentration on the deposit composition, morphology, structure and microharness was studied. The results show that the addition of nanoparticles to the plating solution does not affect significantly Zn-Ni electrodeposition process and alloy Ni percentage. X-ray diffraction patterns of the coatings show only the presence of cubic γ -phase Ni₅Zn₂₁. With ZrO₂ or Al₂O₃ nanoparticles, homogeneous and compact deposits with low grain size were obtained. On the contrary, SiC nanoparticles incorporation perturbs the growth of the alloy matrix by reducing γ -phase orientation. ZrO₂ and Al₂O₃ lead to an increase in the coating microhardness, whereas SiC leads to a decrease, due to the strong modification induced in the alloy structure.

Keywords: electrodeposition; Zn-Ni alloy; nanocomposite coatings; ceramic nanoparticles.

1. INTRODUCTION

In the last few decades, several investigations on the electrodeposition of metallic coatings containing ceramic micro or nanoparticles have been performed in order to improve their mechanical, tribological and corrosion properties [1-5]. The electrochemical production of composites, less expensive than other preparation techniques [6], can be used for new application fields, as energy storage, electrocatalysis and photoactive materials [1].

Although much research on ceramic particles incorporation in the metal electrodeposits has been carried out [1, 2, 7, 8, 9], the mechanism of this process is not yet well understood. The first model has been developed by Guglielmi [10] and it is based on a two-step absorption mechanism of

the particles. Other theories are based on mechanical entrapment, electrophoresis, adsorption and convective-diffusion [2].

Many deposition parameters influence the characteristics of the electrodeposited composite, like bath composition, presence of additives, particle type, size and concentration, bath agitation, pH, temperature and current profile [2,6,11-13]. The composite properties, such as wear resistance and corrosion protection, are mainly determined by the incorporated particles content [6]. The operating parameters, which enhance the incorporation of ceramic particles in the deposit, are: high particles concentration in the bath, smaller sized particles, low concentration of the electroactive species and pulsed current [2]. Furthermore, some authors found that the use of ultrasound during electrodeposition reduces agglomeration and leads to a more uniform distribution of the particles [14].

Zn-Ni alloy is widely used for the corrosion protection of steel, especially in the automotive industry [15]. However, zinc and its alloys have low hardness and abrasion resistance, which could be improved by ceramic particle incorporation.

Several investigations on the electrodeposition of zinc and zinc alloy composite coatings from acidic baths have been performed. Tulio et al. studied the deposition of Zn, Zn-Co [16] and Zn-Ni [17] in presence of SiC or Al₂O₃ micro-particles from sulphate baths. Electrodeposition of Zn-Ni-Al₂O₃ nanocomposite coatings has been studied from different baths [18,19]. Hammami et. al. electrodeposited Zn-Ni alloy coatings containing SiO₂ nanoparticles [20]. Carbon nanotubes (CNT) have been used to obtain Zn-Ni-CNT composite coatings from a sulphate bath [21].

Even though the alkaline baths are widely used by galvanic industry because they give more uniform plating than acid ones [23], only few works have been performed using alkaline solutions and Al_2O_3 or SiC particles. Blejan and Muresan investigated the corrosion behaviour of Zn-Ni-Al₂O₃ nanocomposite coatings electrodeposited from alkaline commercial electrolytes (Performa 280.5) [22]. Müller et al. studied the codeposition of α -SiC micro-sized particles with Zn-Ni alloy in an alkaline solution containing diethylentriamine [23]. To the best of our knowledge, no report has been published on the electrodeposition of Zn-Ni-ZrO₂ coatings.

The aim of the present work was to investigate the electrodeposition of composite Zn-Ni coatings containing ZrO_2 , Al_2O_3 and SiC nano-sized particles from an alkaline bath in order to improve their microhardness. The influence of the nanoparticles type and concentration in the bath on deposition potential, current efficiency and alloy composition was studied. The morphology, structure and microhardness of the obtained nanocomposite coatings were also investigated. The results were compared between them and with those relative to Zn-Ni coatings without ceramic particles.

2. EXPERIMENTAL

Zn-Ni alloy was electrodeposited on mild steel substrate from an alkaline bath, with the following composition: 12.5 g L⁻¹ ZnO, 9.8 g L⁻¹ NiSO₄·6H₂O, 185 g L⁻¹ NaOH, additives Protedur Ni 75TM by Atotech. Zn-Ni composite coatings were obtained by adding to the deposition bath 5 or 10 g L⁻¹ of the following particles: yttria stabilized ZrO₂ (Aldrich, particle size < 100 nm, 10.14 wt% Y₂O₃), Al₂O₃ (Aldrich, primary particle size: 13 nm) and SiC (Cometox, average crystallite size: 60 nm).



Figure 1. X-ray diffraction patterns of the used nanoparticles: a) ZrO₂; b) Al₂O₃.

X-ray diffraction pattern of ZrO₂ nanoparticles (Fig. 1a) indicates that they are primarily constituted by cubic zirconia (JCPDS 27-997), with the presence of baddeleyite (JCPDS 36-0420, monoclinic structure). The X-ray diffraction pattern of Al₂O₃ nanoparticles is shown in Fig. 1b: the 2 θ angles of all the peaks correspond to those of δ alumina (JCPDS 16-394, tetragonal structure). SiC nanoparticles were the same used in a previous work [24], which showed that they are prevalently constituted by β SiC (JCPDS 29-1129, cubic structure), with small amount of α Si (JCPDS 29-1130, hexagonal structure) and Si (JCPDS 5-565).

All the baths were prepared with analytical grade reagents and double distilled water. In order to have well dispersed and disaggregated particles, the deposition bath was magnetically stirred for at least 24 h before the experiment.

Zeta potentials of ZrO_2 , Al_2O_3 and SiC nanoparticles in the alkaline solution were determined at 25 °C using a Malvern Nano-ZS apparatus. All measurements were performed at least four times. Zeta potentials were calculated from the electrophoretic mobility, by applying the Helmholtz-Smoluchowski equation; the obtained data show an unimodal distribution. The results reported in Tab. 1 show that ZrO_2 , Al_2O_3 nanoparticles have low negative Zeta potentials, whereas SiC show a potential value more negative than -30 mV, generally considered the limit between uncharged and charged particles [25].

Nanoparticles	Zeta potential mV			
SiC	-39.3 ± 0.8			
Al ₂ O ₃	-11.1 ± 1.5			
ZrO ₂	-25.2 ± 2.1			

Table 1. Zeta potentials of the nanoparticles in the alkaline plating solution.

Electrodepositions were carried out at 25 ± 1 °C under constant magnetic stirring (about 250 rpm). The plating cell was a 0.5 L glass beaker. A mild steel disk, 1 mm thick, was used as cathode. Before electrodeposition, steel disk was mechanically smoothed with different emery papers (320, 500 and 800 grit) degreased with acetone, rinsed with double distilled water and dried. The disk was mounted in a flat specimen holder in order to have an exposed area of 3.14 cm². A 99.5 % nickel wire (area 11 cm²) was used as anode. The distance between the two electrodes was 4 cm. A SCE electrode (241 mV vs NHE), to which all the potentials are referred, was used as reference. After the electrodeposition tests, the cathode was extracted from the cell and rinsed with distilled water. The disk was removed from the specimen holder and then immersed in an ultrasonic bath for 10 min, in order to remove the nanoparticles weakly adsorbed on the alloy surface; finally, the cathode was washed with acetone and dried.

The electrodeposition tests were carried out galvanostatically with direct current density in the range from 10 to 30 mA cm⁻², by using a Gamry Reference 600 potentiostat. Electrodeposition time was changed as a function of current density in order to obtain coatings about 10 μ m thick. For the deposits to be submitted to microhardness measurements, the deposition time was prolonged until the thickness was about 30 μ m, to avoid the influence of the steel substrate. All the tests were repeated three times.

The mass of the obtained coating was determined by weighing the cathode before and after the electrodeposition. Coatings were chemically analysed by means of energy dispersive X-ray analysis (EDX); from the deposit weight and the percentages of Si, Zr and Al, the amount of incorporated particles was calculated. Then, the weight of the nanoparticles was subtracted from that of the deposit and hence the weights of deposited Zn and Ni were calculated.

The following reactions occur on the cathode:

$Zn^{2+} + 2e^{-} \rightarrow Zn$	(1)
$Ni^{2+} + 2e^- \rightarrow Ni$	(2)
$2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2$	(3)

Zn and Ni partial current densities (i_{Zn} and i_{Ni} respectively) were calculated as described previously [26]. Hydrogen partial current density (i_{H2}) was calculated as the difference between total current density and ($i_{Zn} + i_{Ni}$); current efficiency was calculated as percentage of ($i_{Zni} + i_{Ni}$) with respect to the total current density.

Preferred crystallite orientations of the coatings were studied by means of X-ray diffraction analysis (XRD). A Philips PW 1730 diffractometer with Cu K α radiation (λ =0.154 nm) was used. Morphological characterization and chemical analysis of the coatings were performed by scanning electron microscopy (SEM) coupled with EDX. A Zeiss Supra 40 microscope and a Bruker Quantax serie 5000 L N₂-free XFlash device were used.

Vickers microhardness measurements were carried out on deposit surface by applying a 100 g load for 10 s. A HX-1000 Remet equipment was used.

3. RESULTS AND DISCUSSION

Table 2. Cathode potentials (mV) of Zn-Ni electrodepositions carried out from baths with and without nanoparticles.

i mA cm ⁻²	Without nanoparticles	ZrO_2 5 g L ⁻¹	ZrO ₂ 10 g L ⁻¹	$\begin{array}{c} Al_2O_3\\ 5 \text{ g } \text{L}^{-1}\end{array}$	Al ₂ O ₃ 10 g L ⁻¹	SiC 5 g L ⁻¹	SiC 10 g L ⁻¹
10	-1589 ± 8	-1591 ± 9	-1584 ± 10	-1586 ± 9	-1588 ± 8	-1595 ± 9	1589 ± 11
20	-1689 ± 10	-1691 ± 11	-1694 ± 9	-1698 ± 12	-1696 ± 8	-1681 ± 12	1683 ± 10
30	-1761 ± 12	-1763 ± 9	-1759 ± 11	-1766 ± 9	-1758 ± 10	-1764 ± 11	1769 ± 9

Table 3. Current efficiencies (%) of Zn-Ni electrodepositions carried out from baths with and without nanoparticles.

i mA cm ⁻²	Without nanoparticles	ZrO ₂ 5 g L ⁻¹	ZrO ₂ 10 g L ⁻¹	Al ₂ O ₃ 5 g L ⁻¹	Al ₂ O ₃ 10 g L ⁻¹	SiC 5 g L ⁻¹	SiC 10 g L ⁻¹
10	93.7 ± 2.2	93.0 ± 2.7	93.2 ± 2.0	91.4 ± 3.1	89.9 ± 3.7	91.5 ± 2.6	90.9 ± 3.0
20	85.6 ± 2.9	85.9 ± 1.4	86.3 ± 2.1	83.0 ± 2.7	82.5 ± 2.9	84.3 ± 2.7	86.0 ± 1.8
30	72.8 ± 2.2	74.1 ± 2.1	75.1 ± 3.1	71.9 ± 2.6	71.8 ± 2.4	73.4 ± 1.8	74.2 ± 2.0

Tables 2 and 3 report the potentials and the current efficiencies respectively for the electrodepositions carried out with and without nanoparticles in the bath at different current densities.

The cathode potential (Tab. 2) decreases from about -1590 mV to about -1760 mV on increasing the current density from 10 to 30 mA cm⁻²; the addition of the nanoparticles to the plating bath scarcely affects the deposition potential, which changes only for few mV. The current efficiency decreases strongly on increasing the current density (Tab. 3). Also in this case no significant difference has been found by adding nanoparticles to the bath.

Table 4. Nickel percentages (wt%) in Zn-Ni coatings electrodeposited at different current densities from baths with and without nanoparticles.

i mA _c m ⁻	Without nanoparticle s	ZrO_2 5 g L ⁻¹	ZrO_2 10 g L ⁻¹	Al_2O_3 5 g L ⁻¹	$\begin{array}{c} Al_2O_3 \ 10\\ g \ L^{-1} \end{array}$	SiC 5 g L ⁻¹	SiC 10 g L ⁻¹
10	13.0 ± 0.7	12.8 ± 0.6	12.9 ± 0.7	12.7 ± 0.7	12.8 ± 0.5	12.9 ± 0.5	13.0 ± 0.5
20	16.7 ± 0.5	16.5 ± 0.7	16.6 ± 0.5	16.4 ± 0.6	16.7 ±0.7	16.5 ± 0.6	16.5 ± 0.7
30	17.1 ± 0.7	16.8 ± 0.6	17.4 ± 0.5	17.2 ± 0.6	17.3 ± 0.5	16.8 ± 0.6	17.0 ± 0.6

Table 4 shows the effect of nanoparticles concentration in the bath on Ni percentage in the deposits obtained at different current densities. In absence of nanoparticles, Ni content in the coatings significantly increases (from 13.0 wt% to 16.7 wt%) on increasing current density from 10 to 20 mA $\rm cm^{-2}$, while changes very little from 20 to 30 mA $\rm cm^{-2}$. At all the used current densities, alloy composition is not significantly affected by the addition of nanoparticles to the plating solution in the studied range of concentration.

The above results agree with those of Muller et al. who studied the electrodeposition of Zn-Ni composite coating containing α -SiC micro-particles; they found that the addition of the particles to the alkaline plating solution does not affect significantly both the alloy electrodeposition process and the Ni percentage in the deposit [23]. From literature, papers on the effect of alumina on Zn-Ni electrodeposition process and alloy composition in alkaline baths have not yet published.

In acidic baths, different results have been found by other authors. A slight increase in Ni percentage of the coating (from 12.1 to 13.3 wt%) with the increase in nanoalumina content from about 4.3 to 11 wt% has been observed by Zheng et. al [15]. Ghaziof and Gao found that low concentrations of Al_2O_3 in a sulphate bath do not modify alloy Ni content, while high concentrations decrease it [19]. Tulio et al. indicate that alumina microparticles do not influence the composition of Zn-Ni coating, while SiC microparticles decrease the Ni percentage in the alloy [17]. These differences suggest that the influence of the ceramic particles on the alloy composition depends on many factors, such as bath composition and nanoparticles type, size and concentration.



Figure 2. Effect of deposition current density on ZrO_2 (a), Al_2O_3 (b) and SiC (c) percentages in Zn-Ni coatings electrodeposited from baths containing 5 (curve a) and 10 g L⁻¹ (curve b) nanoparticles.

The weight percentage of incorporated nanoparticles in the coating as a function of the current density at the two concentrations used in this work is shown in Fig. 2. The trend of the curves changes depending on the particles type: on increasing current density, ZrO_2 percentage slightly increases (Fig. 2a), Al_2O_3 percentage remains almost constant (Fig. 2b), while SiC percentage decreases (Fig. 2c). The content of all the studied nanoparticles increases on increasing their concentration in the bath. The incorporation rate of the nanoparticles does not seem to be determined by their zeta potential: ZrO_2 nanoparticles show the lowest percentage despite their intermediate potential and the negative zeta potential of SiC (-39 mV) does not hinder its incorporation. This latter result could be explained on considering that high absolute values of zeta potential lead to better dispersed particles and that the negatively charged particles are dragged to the cathode surface by stirring. In the studied bath, ZrO_2 and Al_2O_3 can be considered uncharged particles because they have a zeta potential value less negative than -30 mV [25]; the higher incorporation rate of alumina with respect to zirconia could be due to its lower size [2].

The different trends of the nanoparticles percentage with the current densities shown in Fig. 2 can be explained taking into account that the incorporation rate depends on the various particles

characteristic (type, size and shape) [2]. As reported in literature, the influence of current density can vary with electrolyte composition [2]. In fact, a decrease in alumina percentage on increasing current density in the range from 5 to 30 mA cm⁻² has been found by Tulio et al. using a slightly acidic bath and micrometric particles [17]. The decrease in SiC percentage in Zn-Ni alloy, observed on increasing current density from 10 to 30 mA cm⁻² (Fig. 2c), agrees with the results obtained by other authors in an alkaline bath [17,23]. This trend has been attributed to the fact that an increase in current density leads to a more rapid deposition of the metallic matrix [23].



Figure 3. SEM images of Zn-Ni alloys electrodeposited at 10 mA cm⁻² from: a) bath without nanoparticles (Ni 12.9 %); b) bath containing 10 g L⁻¹ ZrO₂ (Ni 12.9 wt%, ZrO₂ 0.7 wt%); c) bath containing 10 g L⁻¹ Al₂O₃ (Ni 12.8 wt%, Al₂O₃ 1.3 wt%); d) bath containing 5 g L⁻¹ SiC (Ni 13.0 wt%, SiC 1.1 wt%);

Figure 3 shows SEM images obtained on Zn-Ni coatings electrodeposited at 10 mA cm⁻² from baths with and without nanoparticles. Zn-Ni-ZrO₂ and Zn-Ni-Al₂O₃ were electrodeposited from baths containing 10 g L⁻¹ nanoparticles, whereas Zn-Ni-SiC was obtained from a bath with 5 g L⁻¹ SiC, in order to have deposits with low particles percentage. Zn-Ni alloy is homogeneous and compact, with low grain size (Fig. 3a). The incorporation of 0.7 wt% ZrO₂ (Fig. 3b) or 1.3 wt% Al₂O₃ (Fig. 3c) does not lead to a marked change in the coating morphology; only a slight increase in roughness is visible in the figures. On the contrary, a strong change in morphology is produced by the incorporation of 1.1 wt% SiC nanoparticles (Fig. 3d): SEM image shows nodular agglomeration of grains. Even though the coating shown in Fig. 3d was obtained by using β SiC nano-sized particles in place of α SiC micro-sized ones and contains a lower particles percentage (1.1 in place of 8 wt%), the same worsening in morphology found by Muller et. al [23] can be observed in Fig. 3. No significant difference in morphology was found by Tulio et al. [17] for Zn-Ni-Al₂O₃ and Zn-Ni-SiC micro-composites electrodeposited from a slightly acidic solution, therefore the nodular agglomeration of grains observed in the present work and by other authors [23] have to be attributed to the use of an alkaline bath. In the bath used in the present research, SiC particles have a high negative zeta potential (~-39 mV); on the contrary, a low positive charge has been measured previously in a slightly acidic bath [24].

According to the model of Bund and Thiemig [27], negatively charged particles are dragged to the surface of the cathode by mechanical factors, such as the stirring, and they are preferentially attracted by the excess of positive charge in the electrolytic part of the cathode electrical double layer. When the particles come closer to the electrode the shell of adsorbed ions surrounding them is stripped off and the particles becomes incorporated into the growing metal layer. This mechanism can perturb the growth of the coating, leading to the nodular agglomeration of grains.



Figure 4. X-ray diffraction patterns of the Zn-Ni alloys electrodeposited at 10 mA cm⁻² from: a) bath without nanoparticles (Ni 12.9 wt%); b) bath containing 10 g L⁻¹ ZrO₂ (Ni 12.9 wt%, ZrO₂ 0.7 wt%); c) bath containing 10 g L⁻¹ Al₂O₃ (Ni 12.8 wt%, Al₂O₃ 1.3 wt%); d) bath containing 5 g L⁻¹ SiC (Ni 13.0 wt%, SiC 1.1 wt%);

Fig. 4 shows X-ray diffractograms of Zn-Ni alloy coatings with and without nanoparticles; all deposits show only the presence of cubic γ -phase Ni₅Zn₂₁ (JCPDS 6-0653). The pattern related to the alloy without nanoparticles (Fig. 4, curve a) indicates a strong orientation of the deposit, with the reflection from the (330) plane largely predominant. This is in agreement with the results of other authors for Zn-Ni alloy electrodeposited from an alkaline bath similar to that used in the present work [23]. The incorporation of 0.7 wt% ZrO₂ or 1.3 wt% Al₂O₃ (Fig. 4, curves b and c respectively) leads to a further orientation of γ -phase, while the incorporation of 1.1 wt% SiC (Fig. 4, curve d) reduces the

deposit orientation. As found also by other authors [23], the presence of SiC nanoparticles perturbs the growth of the Zn-Ni matrix, leading to an increase of the random orientation of the grains.

The analysis of grain size by means of Scherrer equation indicates that the incorporation of both ZrO_2 and Al_2O_3 leads to an increase from 55 nm (alloy without nanoparticles) to about 100 nm, while SiC incorporation does not change appreciably grain size.

On increasing deposition current density from 10 to 20 mA cm⁻², Zn-Ni alloy morphology changes slightly (Fig. 5a); this is related to the increase in Ni percentage in the alloy from 12.9 to 16.9 wt%. Also in this case, the incorporation of ZrO_2 (1.0 wt%) or Al_2O_3 (1.5 wt%) leads to an increase in roughness (Fig 5b and 5c respectively). As found for the alloy electrodeposited at 10 mA cm⁻², the incorporation of SiC (0.8 wt%) leads to the formation of nodular agglomeration of grains (Fig. 5d); in this case, the effect is slightly less marked than that shown in Fig. 3d, due probably to the lower SiC percentage in the coating.



Figure 5. SEM images of the Zn-Ni alloy coatings electrodeposited at 20 mA cm⁻² from: a) bath without nanoparticles (Ni 16.9 wt%); b) bath with 10 g L⁻¹ ZrO₂ (Ni 16.8 wt%; ZrO₂ 1.0 wt%); c) bath with 10 g L⁻¹ Al₂O₃ (Ni 17.0 wt%; Al₂O₃ 1.5 wt%); d) 5 g L⁻¹ SiC (Ni 16.7 wt%, SiC 0.8 wt%).

The increase in deposition current density from 10 to 20 mA cm⁻² modifies the orientation of γ -phase (Fig. 6 curve a) and the reflection from the (600) plane becomes predominant. This change is due to the increase in nickel content of the alloy. The incorporation of ZrO₂ or Al₂O₃ nanoparticles

does not modify appreciably the structure of Zn-Ni alloy (Fig. 6, curves b and c respectively). Similarly to that found at 10 mA cm⁻² (Fig. 4), the incorporation of SiC leads to a more disordered grains growth.



Figure 6. X-ray diffraction patterns of the Zn-Ni alloy coatings electrodeposited at 20 mA cm⁻² from: a) bath without nanoparticles (Ni 16.9 wt%); b) bath with 10 g L⁻¹ ZrO₂ (Ni 16.8 wt%; ZrO₂ 1.0 wt%); c) bath with 10 g L⁻¹ Al₂O₃ (Ni 17.0 wt%; Al₂O₃ 1.5 wt%); d) 5 g L⁻¹ SiC (Ni 16.7 wt%, SiC 0.8 wt%).

Zn-Ni alloy morphology does not appreciably change on increasing deposition current density from 20 to 30 mA cm⁻² (Fig. 7a); this can be considered an expected result, because in this range of current density the Ni percentage remains almost constant.

Also the effect of the incorporation of ZrO_2 or Al_2O_3 particles is almost the same observed at 20 mA cm⁻², due to the fact that the nanoparticles percentage remains almost constant (Fig. 7b and 7c). On comparing Fig. 7d with Fig. 5d, a decrease in the formation of the nodular grains with respect to that obtained at 20 mA cm⁻² can be observed, due to the decrease in SiC percentage incorporated in the deposit.

According to the morphological observations, the structure of Zn-Ni, Zn-Ni-ZrO₂ and Zn-Ni-Al₂O₃ coatings (Fig. 8, curves a, b and c respectively) does not appreciably change with respect to that found at 20 mA cm⁻² (Fig. 6, curves a, b and c respectively). Also in this case, SiC incorporation decreases γ -phase preferential orientation.



Figure 7. SEM images of the Zn-Ni alloy coatings electrodeposited at 30 mA cm⁻² from: a) bath without nanoparticles (Ni_d 17,1 wt%); b) bath with 10 g L⁻¹ ZrO₂ (Ni 17.3 wt%; ZrO₂ 1.1 wt%); c) bath with 10 g L⁻¹ Al₂O₃ (Ni 17.0 wt%; Al₂O₃ 1.4 wt%); d) 5 g L⁻¹ SiC (Ni 16.9 wt%, SiC 0.5 wt%).



Figure 8. X-ray diffraction patterns of the Zn-Ni alloy coatings electrodeposited at 30 mA cm⁻² from: a) bath without nanoparticles (Ni 17,1 wt%); b) bath with 10 g L⁻¹ ZrO₂ (Ni 17.3 wt%; ZrO₂ 1.1 wt%); c) bath with 10 g L⁻¹ Al₂O₃ (Ni 17.0 wt%; Al₂O₃ 1.4 wt%); d) 5 g L⁻¹ SiC (Ni 16.8 wt%, SiC 0.5 wt%).



Figure 9. SEM image (a) and EDX map of Zr (b) of the cross section of a Zn-Ni-ZrO₂ coating containing 1.1 wt% zirconia.

SEM image of a cross sectional area of a Zn-Ni-ZrO₂ coating shows that the deposit is homogeneous and compact (Fig. 9a). The particles are not clearly visible in the photo, but EDX map of Zr, performed on the cross section, shows that ZrO₂ is distributed within the whole coating layer (Fig. 9b). A similar result has been obtained on a Zn-Ni-Al₂O₃ coating (Fig. 10 a and 10b). It is noteworthy that EDX map shows a particle size higher than that expected (about 13 nm), indicating that the nanoparticles were not completely disaggregated due to their low Zeta potential. SEM observation of a cross sectional area of Zn-Ni-SiC (Fig. 11) highlights its indented surface. In this case, the nanoparticles are clearly visible within the entire coating layer because they have dark colour, as shown in the inset.



Figure 10. SEM image (a) and EDX map of Al (b) of the cross section of a Zn-Ni-Al₂O₃ coating containing 1.4 wt% alumina.



Figure 11. SEM image of the cross section of a Zn-Ni-SiC coating containing 1.1 wt% SiC. Inset: magnification of a coating area with SiC nanoparticles.

The results of microhardness measurements, performed on coatings electodeposited at different current density from baths with and without nanoparticles, are reported in Fig. 12. Measurements on Zn-Ni-SiC deposits were carried out after mechanical smoothing of the surface. The values obtained on Zn-Ni alloy without nanoparticles are in good agreement with those reported in literature for alloys with similar Ni percentage [28]. Microhardness of all deposits slightly increases on increasing current density, due to the higher Ni content in the alloy. Incorporation of both zirconia and alumina induces a significant increase in hardness, in agreement with the results obtained by other authors for Zn-Ni-Al₂O₃ coatings obtained from a slightly acidic bath [15]. On the contrary, the incorporation of SiC leads to a decrease in hardness, due to the strong worsening induced in the alloy morphology.



Figure 12. Vickers microhardness of the coatings obtained at different current densities: a) without nanoparticles; b) Zn-Ni-SiC (SiC 5 g L^{-1}); c) Zn-Ni-ZrO₂ (ZrO₂ 10 g L^{-1}); d) Zn-Ni-Al₂O₃ (Al₂O₃ 10 g L^{-1}).

4. CONCLUSIONS

Zn-Ni-ZrO₂, Zn-Ni-Al₂O₃ and Zn-Ni-SiC nanocomposite coatings have been obtained by electrodeposition on mild steel substrate from an alkaline bath. The electrodepositions were performed under galvanostatic control with current density in the range 10-30 mA cm⁻². From the results, the following conclusions can be drawn:

1) The addition of ZrO_2 , Al_2O_3 and SiC nanoparticles to the plating solution scarcely affects the electrodeposition process of Zn-Ni alloy. Deposition potential, current efficiency and Ni percentage of the alloy are almost the same as that obtained without nanoparticles.

2) X-ray patterns of all the coatings show only the presence of cubic γ -phase Ni₅Zn₂₁.

3) The incorporation of SiC perturbs the growth of the Zn-Ni matrix by reducing the orientation of γ -phase.

4) The incorporation of ZrO_2 or Al_2O_3 does not reduce the orientation of γ -phase. With these last nanoparticles, homogeneous and compact coatings with low grain size have been obtained.

5) Vickers microhardness measurements showed that the incorporation of ZrO_2 and Al_2O_3 leads to an increase in hardness, while SiC leads to a decrease.

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