

Electrodeposition of Zn-TiO₂ Dispersion Coatings: The Effect of Anionic and Cationic Surfactants on Particle Incorporation

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Nowadays there is a great need for chromium(VI)-free coating processes. For that reason, the development of environmental friendly alternative materials with applications in the field of protective coatings is in the focus of research. In this context, Zn-TiO₂ coatings are promising materials that can be prepared by co-depositing TiO₂ nano-particles with zinc during the electrodeposition process. This work presents a study of the influence of plating additives on both the dispersion behavior of TiO₂ nanoparticles and particle incorporation. Commercial anionic and cationic surfactants were chosen as plating additives since they are used for conventional zinc deposition. The structural and morphological characterization of the layers is discussed as well.

Galvanische Abscheidung von Zink-TiO₂-Dispersionsschichten: Einfluss von anionischen und kationischen Zusätzen auf den Partikeleinbau

Derzeit besteht erheblicher Bedarf an chrom(VI)freien Beschichtungsprozessen. Deshalb laufen Entwicklungsarbeiten zur Abscheidung von umweltfreundlichen, alternativen Schichtwerkstoffen für den Einsatz als Schutzschichten. In diesem Zusammenhang sind Zink-TiO₂-Schichten interessant, bei denen Titandioxid-Nanopartikel bei der Zinkabscheidung in die Schicht eingebaut werden. Hierzu wurden Untersuchungen zum Einfluss von Zusätzen auf das Dispersionsverhalten von Titandioxid-Nanopartikeln und den Partikeleinbau durchgeführt. Verwendet wurden kommerzielle anionische und kationische oberflächenaktive Stoffe, wie sie für die Zinkabscheidung im Einsatz sind. Die Struktur und morphologische Charakterisierung der Schichten wird diskutiert.

1 Introduction

Chromium(VI) compounds have been widely used to increase the corrosion resistance of zinc layer surfaces through conversion coating processes. Due to regulations intended to protect health and environment against the potential hazards of the chromium(VI) compounds [1-4], the zinc plating industry must face the challenge to develop novel alternative products that accomplish those new legislations. At the same time, the zinc plating industry must assure a suitable performance of the novel products at reasonable costs. As alternative material, chromium(VI)-free systems (e.g. chromium(III) based conversion layers) have been proposed. Nevertheless, despite the enhancement of corrosion resistance achieved with chromium(VI)-free systems, most of them are not self-healing. For that reason, damage resistance requires to be enhanced.

In order to overcome the problems mentioned above, the focus of research must be placed not only on post plating treatments for zinc but also on the enhancement of the zinc coating properties. A promising alternative is the development of zinc dispersion layers by electro co-deposition method (Fig. 1). Zinc dispersion coatings (Fig. 2)

consist of hard micro/nano-particles which are incorporated and dispersed in a metallic matrix during the electrodeposition process. These layers can lead to an enhancement of properties such as hardness, wear and corrosion resistance. The successful improvement of such properties is directly related to the amount of incorporated particles, their uniform distribution within the metal matrix as well as microstructural changes of the matrix material.

The development of dispersion coatings requires a systematic study of particle properties, dispersion behavior of particles in the electrolyte, electrodeposition parameters (e.g. chemical composition of the bath, pH, current density, particle concentration and type of agitation of the bath) as well as composite properties (surface morphology, particle incorporation, microstructure, hardness, wear and corrosion resistance etc.).

The use of additives for the zinc plating industry is very important since they influence electrocrystallization processes of the metal. Therefore, small concentrations of additives can change considerably the microstructure and morphology of zinc providing some benefits such as promoting brightness and leveling to the layers [5].

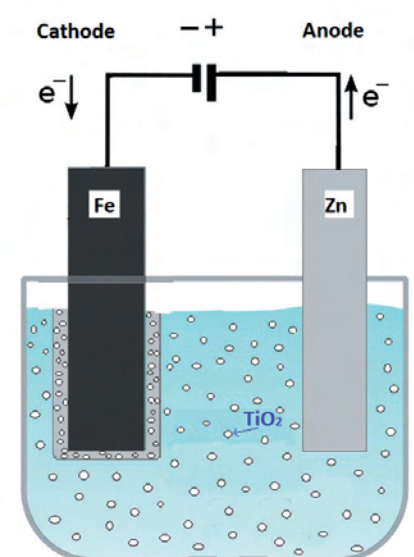


Fig. 1: Electro-codeposition process schema

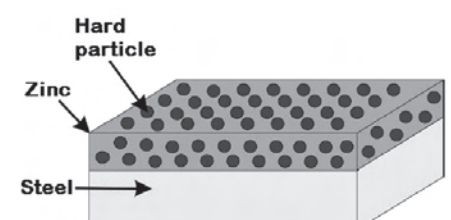


Fig. 2: Schematic representation of a zinc dispersion layer

Nevertheless, the formulation of plating baths that are intended to be used for the plating of composite layers should be carefully designed. It must be considered that the presence of additives (e.g. cationic, anionic surfactants) in the plating bath might change not only the properties of the metal being deposited but also the surface chemistry of the particles. Therefore, additives can play an important role during the co-deposition process.

This work focuses on the electrodeposition of Zn-TiO₂ dispersion layers. The aim was to study the influence of commercial additives for zinc deposition (anionic and cationic surfactants) on

- the dispersion behavior of TiO₂ nanoparticles and
- particle incorporation.

The Zn-TiO₂ layers were characterized in order to study their morphological and structural properties.

2 Experimental part

A zinc chloride (ZnCl₂) based electrolyte was selected as plating bath. The dispersion stability of TiO₂ nanoparticles (average primary size 21 nm) in water and diluted zinc chloride electrolyte was studied by Dynamic Light Scattering (DLS) technique (Malvern, Nano ZS ZEN3600) and Laser Diffraction technique (LD) (Sympatec, Helos&Quixel) respectively. In this work, the DLS technique has been found more suitable for measurements at the nano-scale range whereas the LD techniques allowed measuring wide size distributions at submicro- and micro-scale ranges.

Zeta potential studies of TiO₂ in diluted plating bath as electrolyte media were performed using Laser Doppler Electrophoresis (LDE) technique (Malvern, Nano ZS ZEN3600). The influence of the presence of commercial cationic and anionic surfactants in the electrolyte was studied as well. In all the cases the plating baths (with/without additives) were diluted in order to reach an electrolyte with a concentration of about 1 mM ZnCl₂. For both size distribution and zeta potential measurements, the samples were placed in an ultrasonic bath for 10 minutes just before each measurement.

The electrodeposition experiments were carried out galvanostatically at different current densities at pH 5.3. Hull cell (256 mL electrolyte volume, air bubbling agitation) and rotating disk electrode (RDE) setup (50 mL electrolyte volume, rotation speed 600 rpm and an interchangeable steel disk electrode with a 2.54 cm² area) were used to perform the electrodeposition experiments. Low carbon steel panels were used as cathodes and a pure zinc (99.95 %) plate as anode. The concentration of TiO₂ nanoparticles in the plating bath was 15 g/L. The concentration of surfactants in the plating bath was chosen according to the information provided by the supplier: 0.3 g/L cationic surfactant and 1 g/L anionic surfactant. These concentrations were optimal for conventional zinc plating.

Chemical depth profile analyses using Glow Discharge Optical Spectroscopy (GD-OES) were carried out to study particle incorporation. A GDA 750 spectrometer

(Spectrums Analytik GmbH) was used. A spot with a diameter of 4 mm was analyzed. The analyses were performed in constant voltage and current mode with 1000 V and 25 mA. X-ray diffraction (XRD) characterizations were made using a diffractometer Bruker AXS D 5000 operating with Cu-K α radiation. A Hitachi S4800 scanning electron microscope was used to study the morphology of the layers.

3 Results and discussion

3.1 Dispersion stability

Generally it is assumed that a good dispersion stability of particles in the plating bath leads to a higher probability to promote particle incorporation during electrodeposition. The dispersion stability of particles in a defined electrolyte can be characterized by parameters such as the particle size distribution and zeta potential.

Figure 3 and Figure 4 depict examples showing how the size distribution of TiO₂ nanoparticles (primary average size: 21 nm) dispersed in water (Fig. 3) differs notably from the size distribution in diluted zinc electrolyte media (Fig. 4). The size distribution of particles in water falls in the nano-scale range (20 nm to 100 nm) which means that the level of particle agglomeration in water is not so high. Figure 4 shows that the presence of ions has an influence on the surface properties (e.g. zeta potential) of the particles and the tendency to aggregate is higher as in the first case. The size distribution of particles in diluted electrolyte falls in a range between 200 nm and 20 μ m. The smaller particle agglomerates might be the

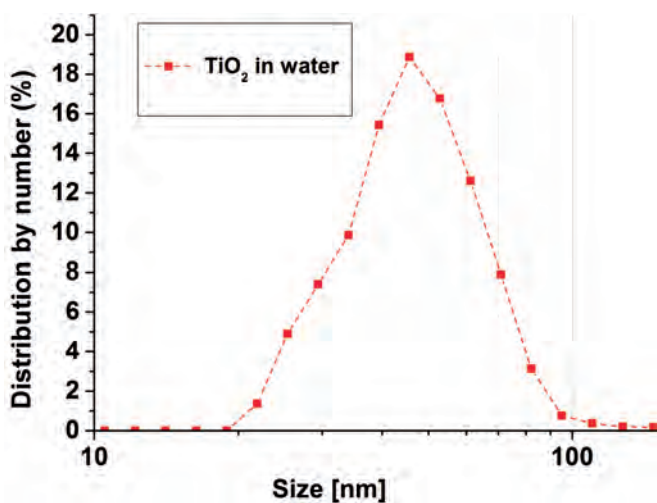


Fig. 3: Particle size distribution of TiO₂ nanoparticles in water at pH 5 after 10 minutes ultrasound treatment determined by DLS technique (Malvern, Nano ZS ZEN3600)

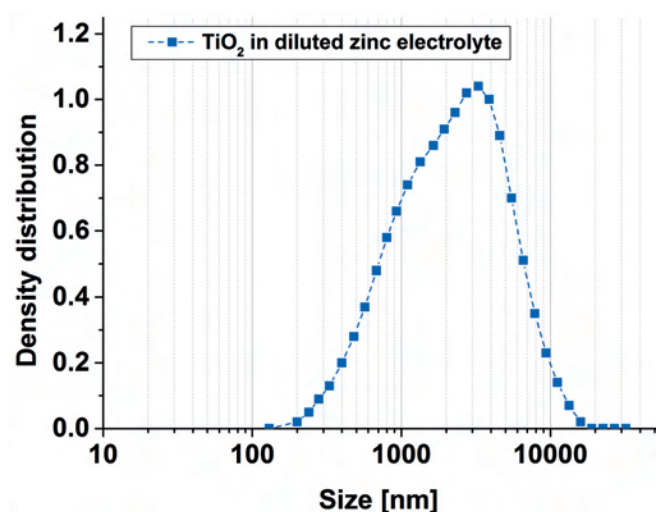


Fig. 4: Particle size distribution of TiO₂ nanoparticles in diluted zinc chloride electrolyte at pH 5 after 10 minutes ultrasound treatment determined by LD technique (Sympatec, Helos&Quixel)

ones with higher probability to take part on the co-deposition process whereas the larger ones will tend to sediment.

The zeta potential is proportional to the particle surface charge and gives information about the electrostatic stability of the dispersion. The surface charge in metal oxide particles such as TiO₂ results from the ionization (protonation or deprotonation) of surface groups. The presence of ions, surfactants as well as the ionic strength and pH of the medium strongly influence the zeta potential. Generally particles having enough surface charge will repel each other. If not, particle aggregation might take place [6, 7]. Due to technical limitations of the LDE technique, the zeta potential study was restricted to measurements in low ionic strength media. A rigorous study of zeta potential values in *real media* (plating baths) was not possible with this technique. However, despite of this restriction, zeta potential determination might help to understand differences in the dispersion behavior in distinct media.

Figure 5 shows the zeta potential curves as a function of pH of TiO₂ dispersions as well as the influence of plating additives (surfactants). It can be seen that TiO₂ particles in diluted chloride electrolyte exhibit high positive zeta potential values at low pH values and therefore a good dispersion stability. The addition of a small quantity of a commercial cationic surfactant had no significant influence on the zeta potential of TiO₂ at low pH while at high pH range a small increment of charge can be seen. On the other hand, the dispersion stability of the system is negatively affected by the addition of a small quantity of a commercial

anionic surfactant since the zeta potential values decreased due to the adsorption of anionic surfactant at the particle surface.

3.2 Particle incorporation

3.2.1 Galvanostatic electro-deposition performed using a Hull Cell

In order to see the influence of current density on TiO₂ particle incorporation, our first attempt was to perform experiments at the Hull cell in absence of surfactants. Due to the trapezoidal geometry of the Hull cell, the study of a current density range (1 to 6 A/dm²) into a single experiment was possible. Figure 6 shows a macroscopic view of the zinc layer. Four current density zones (1, 2, 4 and 6 A/dm²) were selected to study particle incorporation.

Figure 7 shows the GD-OES depth profile analysis of the sample zones mentioned above. The sample analysis areas differ in thickness since they were deposited at different current densities. In all the cases, using additive-free bath, TiO₂ particle incorporation (< 0.6 wt.%) took place throughout all the layer thickness. Slightly higher particle incorporation was found at the higher current densities. Furthermore, higher amounts of TiO₂ at both the zinc top surface and near the substrate surface can be distinguished. This can be ascribed to adsorption phenomena of TiO₂ at the surface of the metals. The early occurrence of

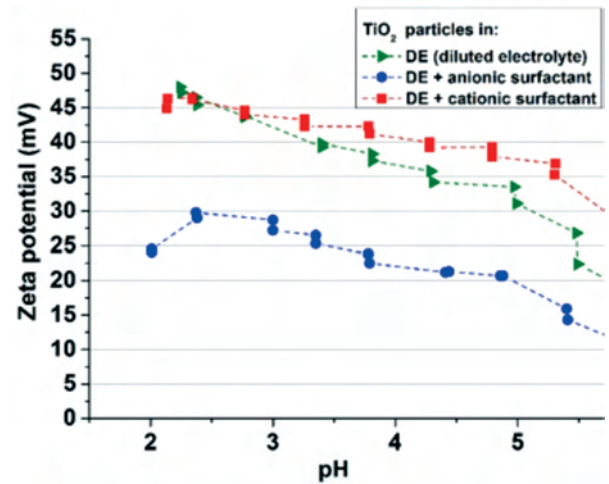


Fig. 5: Zeta potential as a function of pH of TiO₂ particles in diluted plating baths in the absence and the presence of anionic and cationic surfactant

the iron signal at the low current densities (1 and 2 A/dm²) is due to the non-homogeneous thickness of the deposits obtained at those current densities.

3.2.2 Galvanostatic electrodeposition performed using RDE setup

In order to perform depositions at well-defined hydrodynamic conditions, further experiments were carried out using a rotating disk electrode (RDE) setup (rotation speed: 600 rpm). The influence of surfactants was studied at low and high current densities (2 and 20 A/dm²). Figure 8 and Figure 9 show the GD-OES depth profile analysis of zinc layers deposited at 2 and 20 A/dm² respectively.

Generally, it can be seen that the presence of either the cationic surfactant or the anionic surfactant caused a decrease of particle incorporation. At 2 A/dm² current

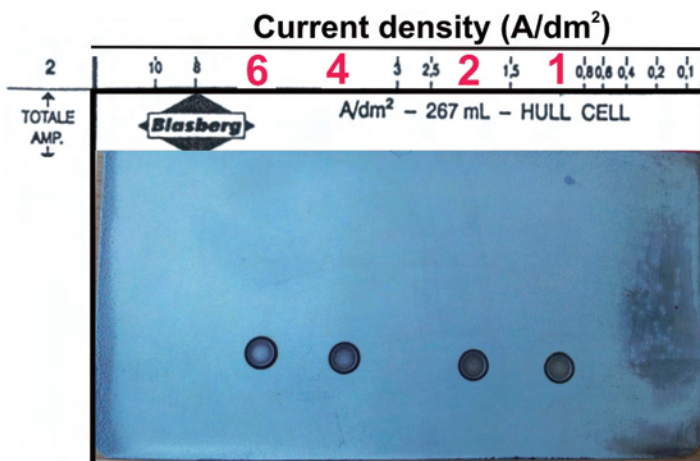


Fig. 6: Macroscopic view of zinc layer plated at a 267 mL Hull Cell. The circular areas (each one at a defined current density) correspond to the GDOES analysis areas

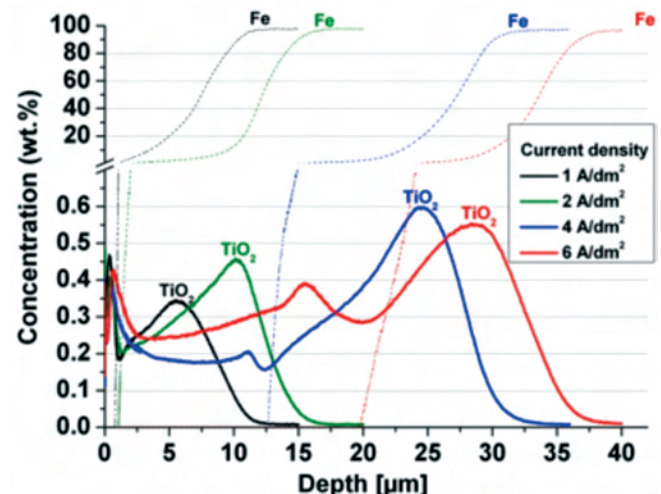


Fig. 7: TiO₂ incorporation (wt.%) in zinc deposits at different current densities by GD-OES. Deposition conditions: Hull cell set up (Fig. 6), pH 5.3

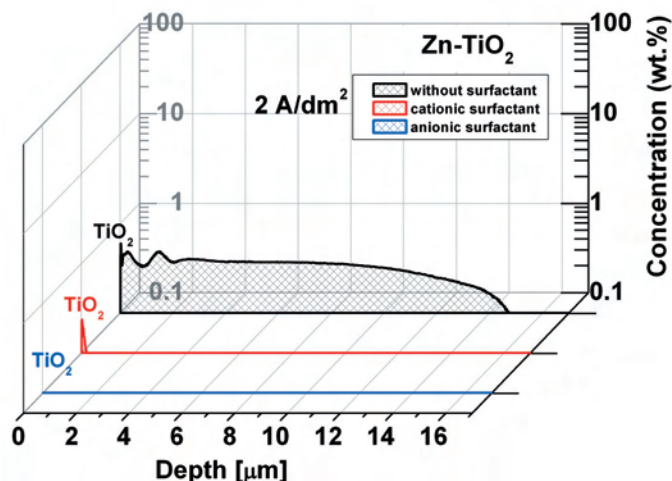


Fig. 8: Influence of surfactants on the incorporation of TiO_2 (wt.%) in zinc deposits plated at 2 A/dm^2 by GD-OES; RDE setup, pH 5.3

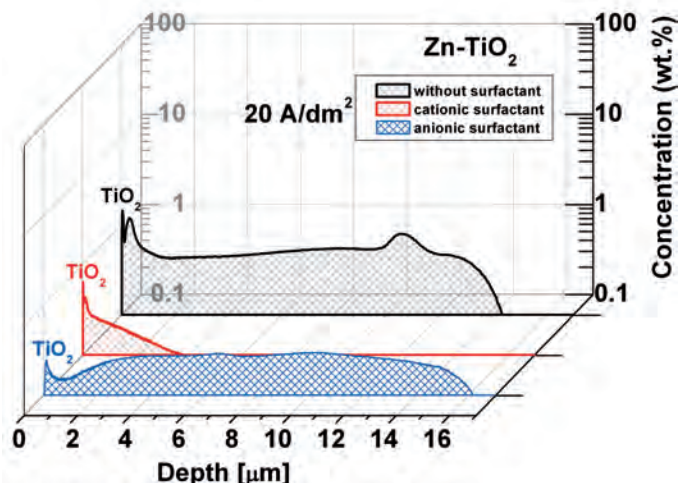


Fig. 9: Influence of surfactants on the incorporation of TiO_2 (wt.%) in zinc deposits plated at 20 A/dm^2 by GD-OES; RDE setup, pH 5.3

density no significant TiO_2 incorporation can be seen for zinc deposits plated in presence of surfactants. According to zeta potential studies, the presence of the anionic surfactant cause a decrease on the zeta potential whereas the presence of the cationic surfactant causes a small increase of the zeta potential at slightly acid pH values. It can be assumed that in both cases the surface chemistry of the particle was changed. Therefore adsorbed surfactant at the particle surface might inhibit particle incorporation. According to the literature [8, 9] the adsorption of metal cations (Zn^{2+}) at the particle surface promotes particle incorporation. In this work, the presence of surfactants at the particle surface might inhibit the adsorption of Zn^{2+} on TiO_2 and, therefore, particle incorporation.

At high current density, it is still possible to observe some incorporation in the presence of anionic surfactant, probably the microstructure obtained at this current density is playing a role.

3.3 Surface morphology

As shown in Figure 10 the morphology of the layers is influenced strongly by presence of surfactants. Furthermore, the morphology changes with the current density. The morphology of the deposits plated in the absence of surfactants is weakly affected by the current density. In the presence of surfactants in the plating bath produced needle like and not compact deposits at the low current density, whereas the morphologies became more compact at the higher current density.

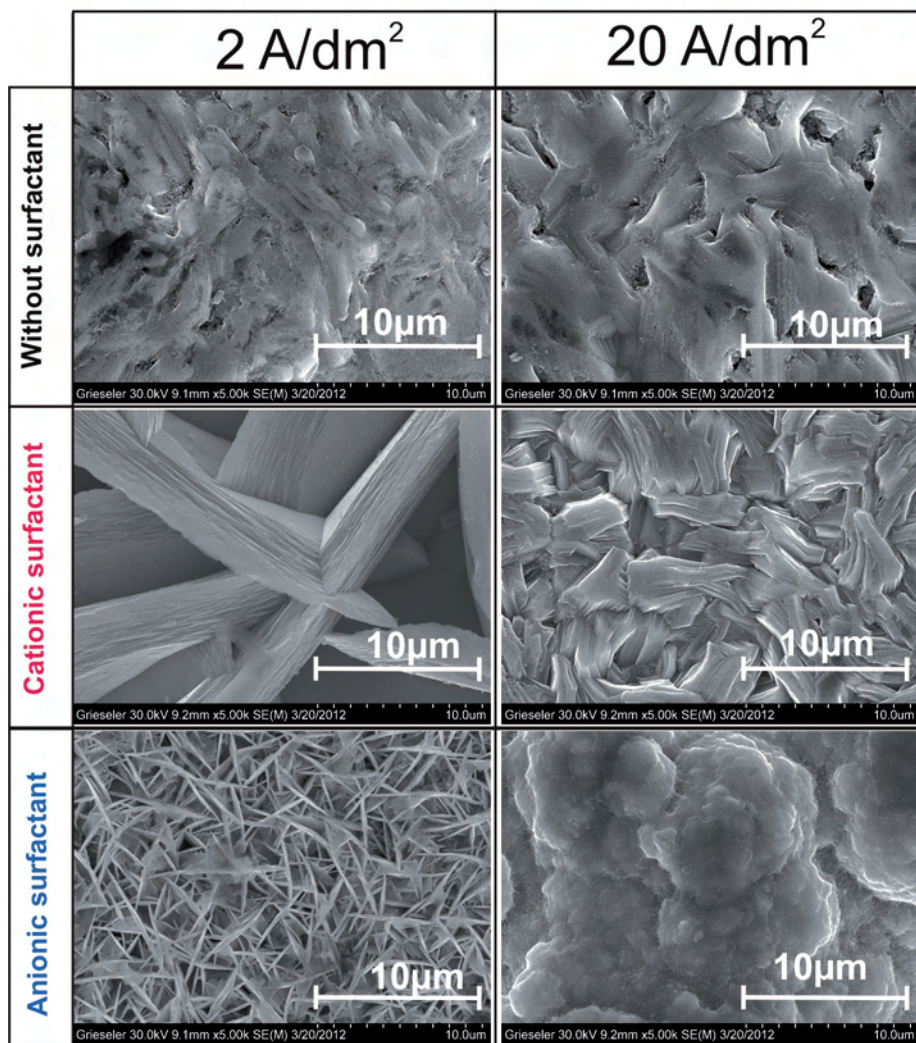


Fig. 10: Influence of surfactants on the surface morphology of Zn-TiO_2 layers plated depending on the current density; RDE setup, pH 5.3

It is interesting to notice that, despite the high heterogeneous morphology of the layers deposited in the presence of surfactants at 2 A/dm², the particles did not remind trapped or incorporated in the layer. It might be assumed that during the co-deposition process some particles could have been trapped within the growing layer but at the same time they were kicked out by the electrolyte streaming since a non-closed structure was formed.

3.4 Microstructure of the deposits

The microstructural characterization involves a comparative analysis of the texture of deposits. The zinc layers were characterized by XRD method and the relative texture coefficient (RTC) values were calculated for the first eight peaks [(002), (100), (101), (102), (103), (110), (004) and (112)] taken from the XRD patterns according to the method developed by Berúbé et al. [10]. RTC values higher than 12.5 % can be considered as preferred orientations (textures).

Figure 11 shows a comparative analysis of the texture of pristine Zn and Zn-TiO₂ layers plated at two different current densities. For both current densities (2 and 20 A/dm²), it can be seen that despite the low particle incorporation (less than 1 wt.%) observed for the composite layers, the microstructure of Zn-TiO₂ layers differs from the zinc layers. For the Zn-TiO₂ layers it can be distinguished up to three common preferred orientations [(102), (103) and (112)], those textures might be arisen due to either the presence of particles in the plating bath or the incorporation of particles in the layer.

Figure 12 shows the influence of surfactants on the texture of the zinc composite layers. As expected, the presence of surfactants in

the plating bath composition produced strong changes in the microstructure of the layers. However, from the results shown in Figure 11, part of those changes might be also ascribed to the presence of particles in the plating baths. At 2 A/dm² (Fig. 12a), the presence of both cationic and anionic surfactant promoted deposits with an elevated (110) preferred orientation. In the case of the anionic surfactant the (110) texture was even more present. On the other hand, at 20 A/dm², the presence of the cationic surfactant influenced a high (100) preferred orientation. The presence of the anionic surfactant promoted the (101) preferred orientation but with a significant presence of all other 7 textures (including the (102), (103) and (112) characteristic textures observed for the composite deposits plated in absence of surfactants). This might be the reason why at high current density was still possible to get some TiO₂ incorporation (Fig. 9).

4 Summary

According zeta potential measurements, the dispersion stability of particles in diluted zinc chloride based electrolytes changes with the presence of plating additives since they modify the surface chemistry of TiO₂ particles. The cationic surfactant did not affect strongly the surface RTC of TiO₂ and

therefore its zeta potential. On the other hand, the anionic surfactant (negative charged molecules) produced a decrease in the zeta potential values due to electrostatic interaction and partial neutralization of the charge at the TiO₂ surface.

Using additive-free electrolytes the incorporation of TiO₂ particles throughout zinc layers was possible. According to experiments carried out at both the Hull cell set up and RDE setup, particle incorporation slightly increases the current density rises. Incorporation of TiO₂ reached values up to 0.6 wt.%, the low amount of incorporation can be ascribed to the high degree of particle agglomeration in electrolyte.

In general the incorporation of TiO₂ particles was negatively affected by the presence of both cationic and anionic surfactants. It was not possible to determine the zeta potential, and consequently the surface charge, of particles in real plating

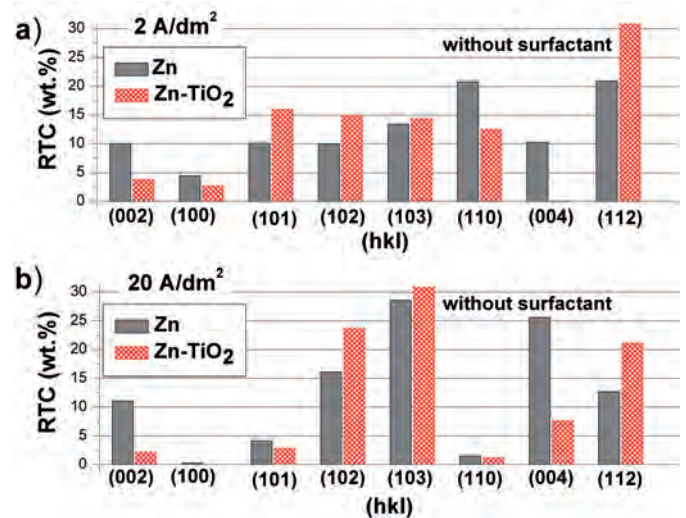


Fig. 11: Texture analyses of pristine Zn and Zn-TiO₂ deposits plated in the absence of surfactants at different current densities: a) 2 A/dm² and b) 20 A/dm²; RDE setup, pH 5.3

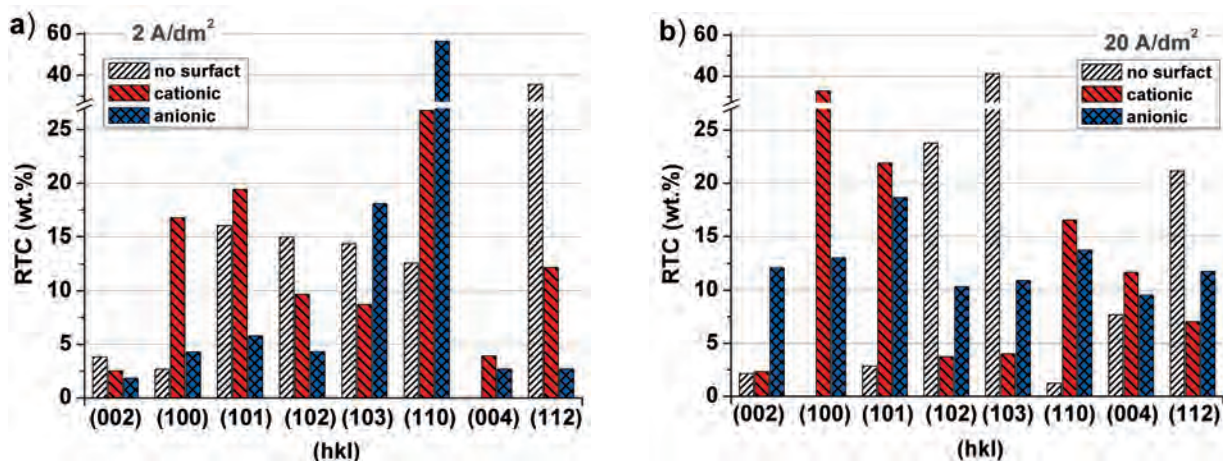


Fig. 12: Influence of surfactants on the texture of Zn-TiO₂ deposits plated at 2 A/dm² (a) and 20 A/dm² (b); RDE setup, pH 5.3

baths (with high ionic strength). However, without taking into account the nature of TiO_2 surface charge in this medium, it is clear that the adsorption of either negative or positive charged molecules (surfactants) at the particle surface had an inhibition effect on particle co-deposition. As expected, the presence of surfactants has a strong influence on the microstructure of the layers. Furthermore, the zinc layers containing co-deposited TiO_2 presented the (102), (103) and (112) planes as preferred orientations.

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