

# **Texture and Surface Morphology Development in Zinc and Zinc-Cobalt Electrodeposits**

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The morphology and texture formation in zinc and zinc-cobalt coatings, electrodeposited onto low carbon steel substrate in an acidic sulfate bath, was studied. The predominant texture component of zinc coating at low current density was pyramidal {11.5} and {11.6} nonfiber, while, for zinc-cobalt deposition, a nonfiber {11.0} prism was found as the predominant texture component. Hydrogen adsorption, during the zinc electrodeposition process, inhibited lateral bunching growth and produced a low-angle pyramidal texture component, which developed ridge morphology. Adsorption of cobalt or cobalt-containing species was the reason for promoting a "field-oriented texture"-type growth in zinc-cobalt deposition, which resulted in a coating morphology, consisting of numerous fibers grown almost normal to the substrate surface. At higher overpotentials, the adsorption was hindered. This led to the progression of lateral growth and the development of a sharp (00.2) fiber texture component in zinc and zinc-cobalt electrodeposits.

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Electrodeposited zinc coatings have attracted increased attention because of the flexibility in their properties. By sacrificing itself, zinc offers protection to steel. Studies to improve the corrosion resistance of the zinc coatings are desirable because they are not so resistant to corrosion in marine atmospheres.<sup>1</sup> Under some circumstances, zinc becomes passivated and the protective property is hindered.<sup>2</sup> Hence, the electrodeposition of zinc, alloyed with group eight metals (Ni, Co, and Fe), has attracted considerable interest.<sup>1,3,4</sup> This can be attributed, mainly, to excellent corrosion resistance, paintability, and good formability.<sup>5</sup> These properties are controlled by chemical composition, phase composition, and the microstructure of the deposit. According to recent findings, some of the coating properties, in particular, the corrosion resistance and paintability, are influenced by the morphology and crystallographic texture of the deposit.<sup>6,7</sup>

Various morphologies and textures can be obtained simply by applying different electrochemical conditions to the electrodeposition bath and preparing the steel substrates differently. The properties of the coating, such as corrosion resistance, paintability, and formability, are closely related to the morphology and texture of the coating.<sup>8-14</sup> Although numerous research works have been undertaken to study the electrochemical dependence of the texture and morphology of zinc and zinc alloy electrodeposited coatings, the development of the texture and the morphology and the reasons for their variations, using electrochemical parameters and surface preparations, are still not completely understood. In zinc electrodeposi-tion, Park and Szpunar<sup>13,15</sup> found that the major texture components, developed onto the electropolished steel surface at low current densities, were high-intensity basal (00.2) and low-intensity pyramidal {10.X} planes. Similar results were reported by Vasilakopoulos et al.,<sup>16</sup> using chemically polished steel substrate. A previous study on the zinc electrodeposition by Vasilakopoulos et al. showed that the predominant texture of a nonfiber pyramidal {11.5} and {11.6} type was developed onto an electropolished steel surface at low overpotentials, while at higher overpotentials, a (00.2) fiber texture component dominated.<sup>16</sup> The former texture component produced ridge morphology in the deposit, but platelet morphology was a result of the latter.

Although there have been numerous studies on the electrochemical and morphological aspects of zinc-cobalt electrodeposits, there has not been any significant work on the effect of electrochemical variables on the texture. Carpenter and Farr<sup>17</sup> studied morphology development in a zinc-cobalt alloy deposition from alkaline and acid solutions, systematically. They reported the morphological variation of the resulted coating with increasing cobalt content.<sup>17</sup>

The aim of this work is the comparison of texture development and morphology in zinc and zinc-cobalt electrodeposits onto electropolished low carbon steel from an acidic sulfate bath. For this purpose, an electrochemical impedance spectroscopy was used to study the electrochemical phenomenon occurring at different overpotentials. Orientation distribution function (ODF) and scanning electron microscope (SEM) methods were also applied to evaluate the texture and morphology of the coatings.

## Experimental

The substrate was prepared from a commercial cold-rolled low carbon steel sheet, with a thickness of 1 mm. The specimens were disk shaped, with a surface area of  $0.85 \text{ cm}^2$ . They were mechanically ground down to 800 grit abrasive SiC paper and subsequently electropolished in a solution of 95% acetic acid and 5% percholoric acid for about 2.5–3 min. After electropolishing, the specimens were washed with distilled water and soaked in 10% sulfuric acid for 20 s. Then, the specimens were washed again with distilled water and immediately placed in the electroplating bath.

The bath composition was  $ZnSO_4 \cdot 7H_2O$  (620 g L<sup>-1</sup>) plus  $Na_2SO_4$  (75 g L<sup>-1</sup>) for zinc deposition and  $ZnSO_4 \cdot 7H_2O$  (620 g L<sup>-1</sup>),  $CoSO_4 \cdot 7H_2O$  (125 g L<sup>-1</sup>), and  $Na_2SO_4$  (75 g L<sup>-1</sup>) for zinc-cobalt deposition. The pH of the bath was adjusted to 2 in both baths with dilute sulfuric acid. Deposition was conducted in a standard corrosion cell with two graphite counter electrodes and a saturated calomel electrode (SCE) used as the reference electrode. This electrode was placed close to the cathode surface via a luggin capillary filled with bath solution. The temperature of the cell was maintained at 25°C. An EG&G (model no. 263A) computer-controlled potentiostat/galvanostat was used to maintain the current density at 10, 100, and 200 mA cm<sup>-2</sup>. The plating time was set to 1100, 110, and 55 s, in order for the above current densities to produce a constant coating thickness of ~5 µm, according to Faraday's law.

Potential vs time curves were plotted during the deposition process. Cathodic polarization tests were run with a scan rate of 40 mV s<sup>-1</sup>. An EG&G AC responser (model no. 1025) was coupled with the potentiostat/galvanostat to measure impedances. AC impedance tests were undertaken in a conventional cell, with platinum counter electrodes and SCE as the reference electrode, with an arrangement similar to the standard corrosion cell. The ac measurements were carried out at 1.05, -1.3, and -1.45 V for zinc and -1.08, -1.57, and -2.02 V for zinc-cobalt deposition.

A Philips XL30 SEM was used to observe the morphology of the

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Figure 1. ODF of the steel substrate sheet at  $\varphi_2 = 45^{\circ}$ .

deposits. The chemical composition of the zinc-cobalt coatings was examined by an energy dispersive spectrometer (EDS) connected to the SEM. A Siemens D500 diffractometer was used to determine the substrate and coatings texture. The diffractometer was operated using Cu K $\alpha$  at an accelerating voltage of 40 kV and a current of 40 mA. For the coatings, three pole figures were measured for the planes of {00.2}, {10.0}, and {10.1} using a reflection technique at 5 ° polar and with angular intervals. The ODF was then calculated using "TexTools" software.

### **Results and Discussion**

Figure 1 shows a cross section of the ODF of the steel substrate sheet at  $\varphi_2 = 45^\circ$ . The main texture component is the so-called  $\gamma$ 



Figure 2. Potential-current plot for zinc and zinc-cobalt deposition at a scan rate of 40 mV s<sup>-1</sup>.

fiber, which is characterized by the {111} plane parallel to the surface of the steel sheet.<sup>18</sup> According to Fig. 1, strong {111} (110) and {111} (112) orientations can be considered for the steel-substrate grains.

Figure 2 shows the cathodic scan plots for the Zn and Zn–Co alloy depositions. It is shown that, as the potential is made increasingly cathodic in the range of, around, -0.6 to -1.0 V, the current density increases rapidly for both cases. This potential range is related to predominant hydrogen evolution.<sup>19</sup> Eventually, hydrogen evolution is suppressed and deposition begins at a potential of around -1.01 V for both Zn and Zn–Co. These plots were used to obtain the values of the corresponding potentials for each applied current density, used as the dc bios potential for ac impedance measurements.

Figure 3 shows the cross sections of the ODF of electrodeposited zinc and zinc-cobalt at 10 mA cm<sup>-2</sup>, at  $\varphi_2 = 30$  and 55°. These cross sections were selected because they can reveal all the texture components of the coatings. With the aid of the location map depicted in Fig. 4, it is noted that a sharp nonfiber pyramidal texture component, which involves  $\{11.5\}$   $\langle \overline{33.1} \rangle$  and  $\{10.3\}$   $\langle \overline{32.1} \rangle$  orienta-



**Figure 3.** ODF section of (a) zinc and (b) zinc-cobalt at  $10 \text{ mA cm}^{-2}$ .



Figure 4. Location map of some texture components in ODF of hexagonal lattice.

tions, is evident as the major texture component for zinc (Fig. 3a). For zinc-cobalt, it is noted that the nonfiber prism {11.0}  $\langle 01.6 \rangle$  orientation should account for the major texture component, besides the basal (00.2) and some low-angle pyramidal {11.5}  $\langle \overline{33.1} \rangle$  and {10.3}  $\langle \overline{32.1} \rangle$  orientations (Fig. 3b).

In order to understand the electrochemical factors involved in the development of the mentioned texture components, electrochemical impedance spectroscopy was used. Figure 5 compares the Nyquist plots obtained at -1.05 and -1.08 V, corresponding to the current density of 10 mA cm<sup>-2</sup>, for zinc and zinc-cobalt deposition, respectively. Figure 5 shows the electrochemical aspects of zinc and zinc-cobalt alloy depositions at the mentioned current density. A high-frequency capacitive loop, due to the charge transfer resistance of the deposition, in parallel with the double-layer capacitance, is observed on the Nyquist plots for both zinc and zinc-cobalt depositions. Two possible inductive loops are observed at low frequencies for zinc electrodeposition. According to previous works, the two low-frequency inductive loops could correspond to the relaxation of Zn<sup>+</sup><sub>ad</sub> and ZnH<sup>+</sup><sub>ad</sub> coverage, in order of decreasing frequencies.<sup>20,21</sup> As mentioned by Ichino et al.,<sup>20</sup>



**Figure 5.** Nyquist plot at -1.05 V for zinc ( $\blacksquare$ ) and -1.08 V for zinc-cobalt ( $\blacktriangle$ ) deposition.

entire surface of the zinc deposit growing near the zinc redox potential.<sup>22</sup> For zinc-cobalt electrodeposition, a different feature of the ac impedance spectrum is observed. An inductive loop, followed by a capacitive loop, is observed at lower frequencies, instead of the two inductive loops observed for zinc deposition. The inductive loop, which appeared at medium frequencies, may again correspond to the relaxation of  $Zn_{ad}^+$  coverage on the substrate surface. However, the capacitive loop obtained at low frequencies may be the result of the relaxation of cobalt or cobalt containing species onto the growing surface of the deposit, similar to previous work on zinc-nickel deposition<sup>23</sup> and zinc deposition from baths with small amounts of lead.<sup>22</sup>

It is well known that the lateral mode of electrogrowth, which is common at low overpotential, can proceed only through the progress of two-dimensional (2D) nucleation-dependent macrosteps, via di-rect incorporation of adions (adatoms).<sup>24</sup> However, some degree of inhibition can encourage 2D nucleation and lead to bunching during lateral growth. The bunching only comes about because younger microsteps overtake the older ones during lateral growth, and then, all microsteps coalesce to form macrosteps. For this purpose, the older steps in their lateral growth must be hindered (inhibited) more than the younger ones.<sup>25</sup> This succeeds by the time dependency of inhibitor adsorption.<sup>25</sup> It seems that the adsorbed hydrogen  $\text{ZnH}_{\text{ad}}^+$ occurred in zinc electrodeposition at low overpotential could be con-sidered as an interfacial inhibitor adsorbate,<sup>26</sup> which satisfies all requirements for acting as an effective inhibitor for bunching growth. Therefore, bunching growth can be promoted by the presence of adsorbed hydrogen. Finally, the lateral aggregation of the created macrosteps results in the ridge morphology, as seen in Fig. 6a. This kind of growth is characterized previously by Itoh et al.<sup>24</sup> and is expected to occur only on surfaces that are electrolytically polished, which consists of microsteps.<sup>27,28</sup> In this way, a fully epitaxial growth of zinc onto the electropolished steel substrate can be obtained.<sup>29-31</sup> Eventually, it can be considered that the steel substrate microsteps have been transformed into zinc deposit macrosteps through bunching and resulted in low-angle pyramidal texture components, such as {11.5} and {10.3}, as seen from the ODF results in Fig. 3a. The development of the low-angle pyramidal planes in zinc deposition is shown, schematically, in Fig. 7a.

Successive 2D nucleation, on top of a growing microstep, can disturb microstep progression and cease its growth. This situation can be achieved by a high degree of inhibition.<sup>25,26</sup> The adsorbed cobalt or cobalt-containing species, which occur in the zinc-cobalt electrodeposition at a low cathodic overpotential, can be considered as a blocking adsorbate for microsteps growth. Thus, it can be deduced that, at a high coverage of cobalt and/or cobalt-containing species, lateral growth of microsteps should be inhibited. In fact, the adsorbed inhibitor decreases the specific edge free energy and facilitates 2D nucleation.<sup>25</sup> Then, the system undergoes an intensive 2D nucleation and, thus, a different type of growth, other than lateral growth, is expected to develop. This kind of growth, based on a



Figure 6. Morphology of (a) deposited zinc and (b) zinc-cobalt at current density of 10 mA cm<sup>-2</sup>.

high-frequency 2D nucleation, resulted by a high coverage of the surface with an interface inhibitor and is called field-oriented texture.  $^{25,26}$  It can create numerous crystal fibers almost normal to the substrate surface. Each fiber consists of many macrosteps



Figure 7. Schematic representation of (a) lateral growth of zinc crystallites and (b) perpendicular growth of zinc-cobalt crystallites onto steel substrate surface.



**Figure 8.** Nyquist plots (a) for zinc at -1.3 ( $\blacksquare$ ) and -1.45 V ( $\Box$ ) and (b) for zinc-cobalt at -1.57 ( $\blacktriangle$ ) and -2.02 V ( $\triangle$ ); the mentioned potentials correspond to 100 and 200 mA cm<sup>-2</sup>, respectively.

that are piled one on the other but cannot merge with each other.<sup>25</sup> Therefore, a large number of elongated crystals normal to the substrate surface are expected to be formed, creating a coherent deposit.<sup>25</sup>

Figure 6b shows the morphology of the zinc-cobalt coating deposited at 10 mA cm<sup>-2</sup>. From Fig. 6b, it can be seen that a large number of elongated crystals are grown normal to the substrate without merging. Figure 7b shows a schematic representation, which describes this kind of growth onto the electropolished steel surface. As was mentioned, this morphology develops under the strong inhibition that resulted by the adsorption of cobalt or cobalt-containing species, which increases 2D nucleation frequency. With this kind of growth, narrow macrosteps are grown normal to the substrate without merging with each other and create the nonfiber prism {11.0} (01.6) orientation, as seen in Fig. 3b. Some blocky crystals are also seen on top of the resulted prism crystals (Fig. 6b), which indicates that perpendicular growth supported by the substrate is degraded by increasing the deposit thickness. It seems that random threedimensional (3D) nucleation is responsible for the development of these blocky crystals on top of the prisms. The low-intensity basal and pyramidal texture components represented in ODF (Fig. 3b) can also be related to the incorporation of these blocks into the morphology

Figure 8 shows the Nyquist plots corresponding to the zinc and zinc-cobalt deposition at 100 and 200 mA cm<sup>-2</sup>. Increasing the overpotential results in quite a different feature for both zinc and zinc-cobalt electrodepositions. The inductive or capacitive loops observed at medium and low frequencies, at 10 mA cm<sup>-2</sup> (Fig. 5a and b), are replaced by some scattered points. The absence of any inductive loop at medium frequencies implies that a direct discharge of Zn<sup>2+</sup> ions, which differs from that two-step discharge observed at 10 mA cm<sup>-2</sup>, may have happened. The absence of any capacitive or inductive loops on the Nyquist plot (Fig. 8) at low frequencies indicates that there is no hydrogen adsorption (inhibition) in zinc deposition and, also, no adsorption of cobalt or cobalt-containing



Figure 9. ODF section of (a) zinc and (b) zinc-cobalt at 100 mA  $cm^{-2}$ .

species for zinc-cobalt deposition. It is believed that the presence of adsorbates during the electrodeposition of metal and alloys is confined to the low overpotentials.<sup>25</sup> Therefore, the interfacial inhibition could be reduced by increasing the overpotential to 100 and  $200 \text{ mA cm}^{-2}$ .

Figure 9 shows the cross sections of the ODF of electrodeposited zinc and zinc-cobalt at 100 mA cm<sup>-2</sup>. In addition to the sharp, nonfiber pyramidal texture component observed at the deposition current density of 10 mA cm<sup>-2</sup>, a basal (00.2) fiber texture component was also obtained for zinc deposition. Nevertheless, only a sharp texture intensity of basal (00.2) planes, with a maximum plane intensity of 19.7 times random, was obtained for zinc-cobalt electrodeposition. The absence of any pyramidal texture component in zinc-cobalt electrodeposit could be related to the higher overpotential obtained during its electrodeposition, as can be seen in Fig. 2. The basal (00.2) fiber texture component is expected to develop after 3D nucleation and lateral growth.<sup>25,29</sup> According to Li and Szpunar,<sup>32,33</sup> the development of a fiber texture is possible during the growth of 3D nucleation, due to the surface energy differences, which are responsible for the selective growth of grains that have the lowest surface free energy. The lowest surface energy in a hexagonal zinc or zinc-cobalt crystal is for the basal (00.2) plane, due to its higher compactness. It seems that the higher overpotential, created at 100 mA cm<sup>-2</sup> during the zinc-cobalt electrodeposition, is responsible for obtaining a single texture component of (00.2) basal planes.

Figure 10 shows the morphology of zinc and zinc-cobalt coating obtained at 100 mA cm<sup>-2</sup>. Numerous crystals having platelet morphology are grown almost parallel to the substrate in order to produce a (00.2) fiber texture component. It can be seen that the ridge morphology in the zinc-cobalt deposit, which is evidence for the development of a pyramidal texture component in the coating, is reduced in amount and expected to be less than the random level.

On increasing the overpotential (current density of 200 mA cm<sup>-2</sup>), the pyramidal texture component could no longer be detected in the zinc deposit (Fig. 11a). It seems that the overpotential at this current density is high enough to develop 3D nuclei all over the steel substrate surface, even in zinc electrodeposition. This confirms the effect of overpotential on the (00.2) fiber texture component. Therefore, the basal (00.2) planes could be grown by lateral growth in both zinc and zinc-cobalt electrodeposits and as seen in Fig. 11, a (00.2) fiber texture is developed as the major texture

component in zinc and zinc-cobalt electrodeposits. Thus, the cross sections of the ODF of zinc and zinc-cobalt deposits, obtained at 200 mA cm<sup>-2</sup>, look very similar (Fig. 11a and b).

Figure 12 shows the morphology of zinc and zinc-cobalt deposits obtained at 200 mA cm<sup>-2</sup>. In zinc deposits, the crystallites are predominantly parallel, or nearly parallel, to the steel substrate surface and show the basal (00.2) planes parallel to the substrate surface. A



Figure 10. Morphology of deposited (a) zinc and (b) zinc-cobalt at current density of 100 mA cm<sup>-2</sup>.





similar feature could be observed in the zinc-cobalt coating, but, numerous needle-shaped crystallites are also dispersed on top of the thin platelets. These needle crystallites should have, essentially, a different crystallographic lattice structure from the platelets because of their different morphology. It seems that the additional counter



Figure 12. Morphology of deposited (a) zinc and (b) zinc-cobalt at current density of 200 mA cm<sup>-2</sup>.

lines observed on  $\varphi_2 = 30^\circ$  section of zinc-cobalt ODF should be related to distribution of these needle crystallites on top of the coating.

Figure 13 shows EDS spectra for zinc-cobalt coating at different current densities. The cobalt percentages extracted from the spectra are shown in Fig. 14. From Fig. 14, it can be seen that, by increasing the current density to 200 mA cm<sup>-2</sup>, the cobalt percentage in the coating is increased to 4.3%, compared to the value of ~1.7% obtained at 10 and 100 mA cm<sup>-2</sup>. The higher percentage of cobalt in the coating deposited at 200 mA cm<sup>-2</sup> is evidence for the presence of the  $\Gamma$  phase, which appeared as needlelike crystallites on top of the  $\eta$ -phase crystallites. According to Gomez et al., <sup>34</sup> the hexagonal zinc-cobalt  $\eta$  phase, which grows at low overpotentials, contains ~1% cobalt. High current densities produce a body-centered-cubic  $\Gamma$  phase of zinc-cobalt, besides the  $\eta$  phase, with a cobalt content of between 4 and 10% in the coating.

#### Conclusion

1. Hydrogen adsorption, during the zinc electrodeposition process at 10 mA cm<sup>-2</sup>, developed a nonfiber low-angle pyramidal,  $\{11.5\}$  and  $\{10.3\}$ , texture component through lateral bunching growth. This developed ridge morphology in the zinc deposit.

2. A nonfiber  $\{11.0\}$  prism was the major texture component in the zinc-cobalt coating, obtained at 10 mA cm<sup>-2</sup>. A field-oriented texture–type of growth resulted under the influence of the adsorbed cobalt or cobalt containing species and produced a morphology consisting of numerous fibers grown normal to the substrate without merging.

3. By increasing the current density to 100 mA cm<sup>-2</sup>, the presence of adsorbates during the deposit growth was hindered. Therefore, lateral growth led to a texture component of basal (00.2), which created platelet morphology in both zinc and zinc-cobalt coatings.

4. Further increasing the current density to  $200 \text{ mA cm}^{-2}$  resulted in a complete basal texture and platelet morphology in the zinc deposit. However, in the zinc-cobalt coating, numerous needle-shaped crystallites were dispersed on top of the thin platelets.



Figure 14. Effect of current density on cobalt percentage in zinc-cobalt electrodeposit.

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