

# Texture and morphology of pulse plated zinc electrodeposits

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Zinc coatings were deposited under pulse-current plating conditions from an acidic sulphate bath on low-carbon steel cathodes. The effect of the (peak) deposition current density, duty cycle and pulse frequency on the microstructural texture and morphology of the deposits was studied by X-ray diffractometry and scanning electron microscopy. The zinc films consisted of crystallites having an average size controlled by deposition current density, and oriented mostly with basal (00.2) and high index (10.3), (10.4), (10.5) pyramidal planes parallel to the surface. Pulse plating resulted in coatings which were microstructurally different to those prepared under similar conditions by direct current deposition. Texture and grain size modification is illustrated. The effect of pulse current is explained in terms of enhanced nucleation and inhibited growth. © 2006 Springer Science + Business Media, Inc.

## 1. Introduction

Zinc and zinc alloy-coated steel sheets are widely used in order to protect automotive body panels. The resistance in corrosion, along with other mechanical and physical properties of the coatings such as hardness and ductility are influenced by the predominant texture and the microstructural morphology of the polycrystalline metal, which in turn depend on the specific procedure used for preparation. Various approaches have been addressed for the electrochemical (EC) deposition of zinc, depending on the application purposes. The diversity of the EC operating conditions leads to the preparation of coatings which may differ both in their macro and microstructure, therefore in their properties. This is often due to grain size effects [1], thus associated mainly with the employed current density, otherwise to their textural features which are determined mostly by the chemical composition of the bath and the material and structure of the substrate. The combined effect of texture and grain size on the properties of a coating remains to be investigated.

The electrocrystallization of zinc can be described as a weakly inhibited process involving a fast electron transfer [2], as having a high exchange current density ( $>1 \text{ A}\cdot\text{dm}^{-2}$ ), low overvoltage for charge transfer, low surface tension and high hydrogen overvoltage. The zinc surface diffusion coefficient for ad-atoms is high, thus inducing a low sensitivity to inhibition by adsorption of

foreign species [3]. Commonly, direct current (DC) electrolysis of acidic sulphate or alkaline cyanide baths is used for zinc deposition, although techniques employing pulsed currents (PC) can be advantageously used since they provide multiple controllable parameters and a variety of electrocrystallization conditions can be readily configured.

The present work constitutes a study on the effect of pulse electrolysis parameters (peak current density, frequency, duty cycle; d.c.) on the crystallographic texture and the surface morphology of electrogalvanized zinc layers. It is complementary to a DC plating related research [4] and may serve as a reference base within the presently investigated experimental conditions.

## 2. Experimental

Zinc coatings, typically of  $25 \mu\text{m}$  thickness, were electrodeposited from an additive-free aqueous acidic zinc sulphate solution of  $1.3 \text{ M ZnSO}_4\cdot 7\text{H}_2\text{O}$ ,  $0.18 \text{ M NaCl}$  and  $0.16 \text{ M H}_3\text{BO}_3$ , at a pH of 4.5, on low-carbon steel (316 L) under pulse current plating conditions imposed by a galvano-potentiostat system (Wenking PGS95) coupled to a double pulse generator (Wenking DPC72) in a single compartment, thermostat-controlled three-electrode cell, at  $50 \pm 1^\circ\text{C}$ . A rotating disc cathode was employed (800 rpm) in order to control mass transfer in the bath.

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The electrodeposits were prepared at pulse (peak) current densities ( $j_p$ ) of 2, 10 and 20  $\text{A}\cdot\text{dm}^{-2}$ . A rectangular pulse waveform with zero current as a basis was used, the frequency ranging between 0.01 and 100 Hz, and the duty cycle from 10 to 90%. The steel cathodes were cylinders of 2.5 cm diameter and 1.5 cm thickness and the anode was a 99.9% pure zinc foil,  $7 \times 29$  cm in dimensions. Before use the steel substrates were sonicated in acetone, water and trichloroethylene, subjected to anodic dissolution in 2 M NaOH at a current density of  $6 \text{ A}\cdot\text{dm}^{-2}$ , rinsed with hot water and etched in 10%  $\text{H}_2\text{SO}_4$ .

Samples were examined by X-ray Diffraction (XRD; Siemens D5000,  $\text{CuK}_\alpha$  radiation), with a scanning rate of  $1 \text{ deg}\cdot\text{min}^{-1}$  and  $2\theta$  ranging from  $30$  to  $140^\circ$ . Microscopic imaging was performed by a XTL-1 Stereophotomicroscope outfit by a CCD camera. Scanning Electron Microscopy (SEM) images were taken by a JEOL JSM 6100 and a Phillips XL 30 FEG apparatus.

The crystallographic texture of the deposits was identified by means of the relative texture coefficient (RTC) of a given  $(hk.l)$  reflection among the (fifteen) first-order reflections that were monitored by XRD, namely the (00.2), (10.0), (10.1), (10.2), (10.3), (11.2), (11.0), (20.1), (10.4), (20.3), (10.5), (11.4), (21.0), (21.1), (21.2) indexed lines. The RTC is a weighed measure of the relative intensity of a given orientation, normalized against a randomly oriented zinc powder sample [5, 6]. An orientation having RTC value greater than 6.7% (100/15%) can be characterized as preferred. Since usually this happened for more than one diffraction peaks of a certain sample, the one with the highest RTC value was taken as the predominant one.

### 3. Results and discussion

For a kinetically controlled growth system, the texture and morphology of the deposit result from a competition between the directional components of growth with respect to the surface of the substrate. The obtained crystal configuration may be correlated in general to the mode and rate of nucleation and the type of crystal growth leading to different polycrystalline forms. The local supersaturation at the solution/electrode interface depends on the applied cathodic overvoltage, the electrode material and surface details, as well as possible physicochemical inhibition of electrocrystallization (e.g. adsorption of species from the solution). In the absence of organic additives, the electrodeposition of zinc from the present sulphate solution is a low inhibition process since the acidic pH precludes intense auto-inhibition caused by the formation of colloidal zinc hydroxide on the cathode [7]. Accordingly, applying a low to moderate deposition current density it is expected that there is sufficient time for lateral growth, leading to well formed zinc crystallites.

Different combinations of the specified electrodeposition parameters lead to polycrystalline layers of varying character. The texture dependence of galvanostatically DC-plated zinc electrodeposits on deposition

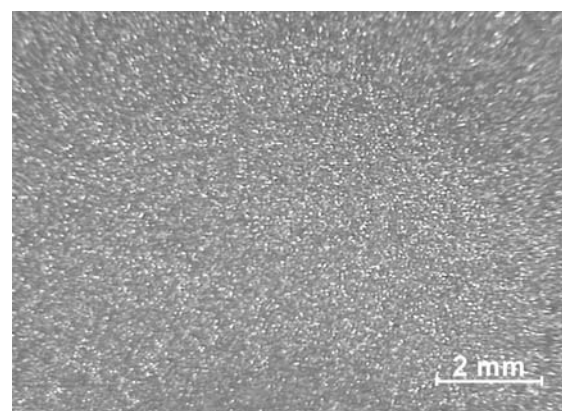
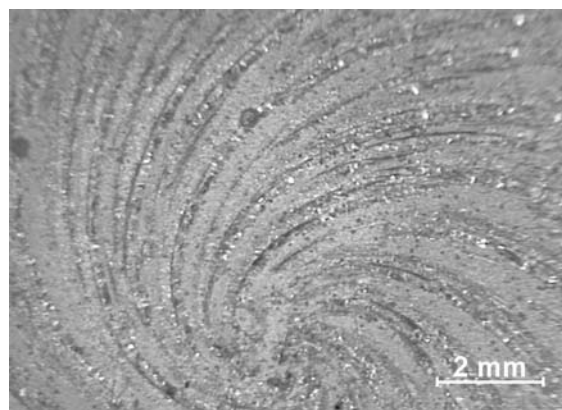
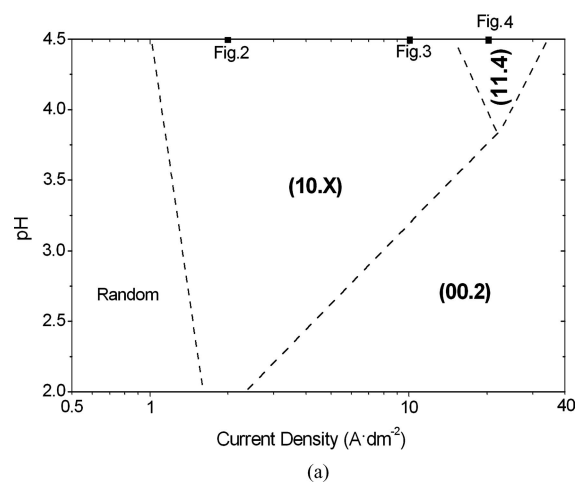


Figure 1 (1a) Simplified diagram of textures determined by the RTC method as a function of deposition current density and bath pH, for 25- $\mu\text{m}$  thick zinc coatings electrodeposited from sulphate solution on steel RDE under DC conditions. The square marks designate the preparation conditions chosen for pulse plating investigation. (1b,c) Stereoscopic images of a striated Zn coating sample having a random microstructure, deposited at DC  $1 \text{ A}\cdot\text{dm}^{-2}$  and pH = 3 (b), and a smooth (00.2)-textured Zn coating sample deposited at DC  $20 \text{ A}\cdot\text{dm}^{-2}$  and pH = 2 (c).

current and sulphate bath pH was investigated in a previous work [4]. It was found that in the major range of the current density magnitude, i.e. from 10 to  $40 \text{ A}\cdot\text{dm}^{-2}$ , and for the whole range of employed bath pH (2.0 to 4.5), a basal (00.2) texture is obtained. Pyramidal high index (10.X) ( $X = 3, 4, 5$ ) and (11.4) orientations were

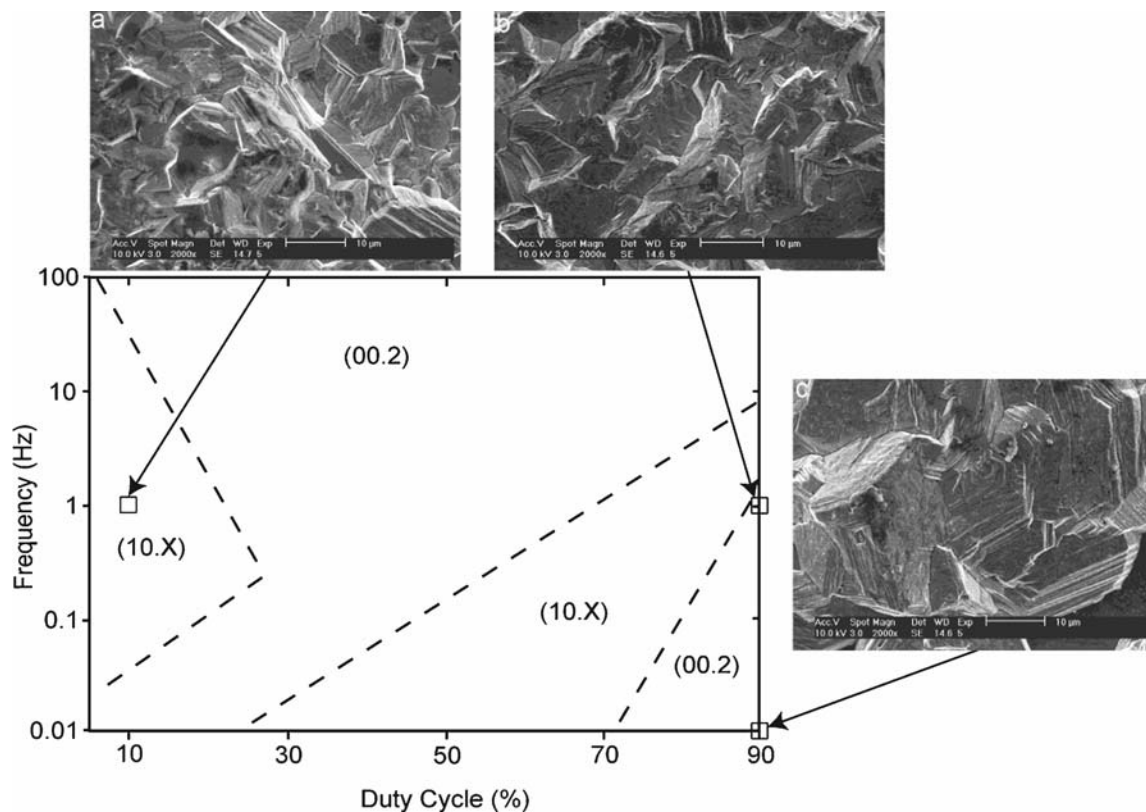


Figure 2 Textures of Zn coatings pulse plated at a peak current density of  $2 \text{ A} \cdot \text{dm}^{-2}$  as a function of pulse frequency and duty cycle. SEM images are shown for representative samples in the (00.2) and (10.X) regions.

dominant at relatively high pH ( $>3.5$ ) and medium to low currents ( $1\text{--}10 \text{ A} \cdot \text{dm}^{-2}$ ), while coatings with randomly distributed crystallites were obtained at deposition currents lower than about  $1 \text{ A} \cdot \text{dm}^{-2}$ . The preceding results are reproduced in Fig. 1a. A microstructural feature of the random layers is the striated morphology, i.e. a specific helical pattern due to hydrodynamic flux, associated to the charge transfer control near the redox potential of zinc. Optical images of a striated-random and a (00.2)-textured samples, deposited within the relevant areas of occurrence, are shown in Fig. 1b and c.

Pulse plating took place at a bath pH of 4.5 (approximately the as-prepared bath acidity), a compromising value between the requirement of an acidic agent capable for preparing well-crystallized coatings (low auto-inhibition, well formed crystallites, compact layers), and the need for environmentally proper electrochemistry with near neutral solutions. Series of deposits were prepared with various cycle profiles at three selected pulse peak-current densities corresponding to the points shown in Fig. 1a. The findings from XRD characterization of the deposits are illustrated in terms of preferred RTC orientation in the texture diagrams of Figs. 2–4. The dashed lines in these diagrams outline various sets of loci, each set regarding a specific orientation having the highest RTC value.

We assume that the basal crystal growth in the [00.1] direction is typically normal for the electrodeposition ex-

periment from the acidic bath, as arising from an unrestricted, fast development of the dense hcp (00.2) atomic layers of Zn parallel to the substrate, and a slow layer by layer growth to the [00.1] direction. Then, any other texture arises when growth at glancing angles, vertically to inclined (pyramidal) planes become slower than or comparable with the growth at [00.1]. The normally fast two dimensional growth of the (00.2) layers may be confined because either a) the rate of the  $\text{Zn}^{2+}$  ions reduction is not sufficient in order to sustain the “normal” deposition process; this happens near equilibrium conditions when the applied current is low, or b) an adsorbent or a compound formation decelerates the process.

More specifically, the application of a low DC  $2 \text{ A} \cdot \text{dm}^{-2}$  current at high pH (4.5) leads to the obtaining of deposits with pyramidal (10.X) dominant orientations, and this might be considered as an electrochemically inhibited process leading to a modification of the typical basal growth. Interestingly, respective conditions under a pulse-plating regime, i.e. a pulse peak current of  $2 \text{ A} \cdot \text{dm}^{-2}$  and similar electrochemical charge, reinstate the (00.2) texture in the major part of the applied parameters’ range (Fig. 2). This is valid in particular for relatively high pulse frequencies ( $>1 \text{ Hz}$ ) within the whole range of duty cycles, while at lower frequencies ( $<1 \text{ Hz}$ ), regions of (00.2) texture appear at the d.c. intervals 10–30% and 70–90%. A DC current of  $10 \text{ A} \cdot \text{dm}^{-2}$  (pH = 4.5) similarly leads to (10.X) deposits while pulse plating with the same peak current

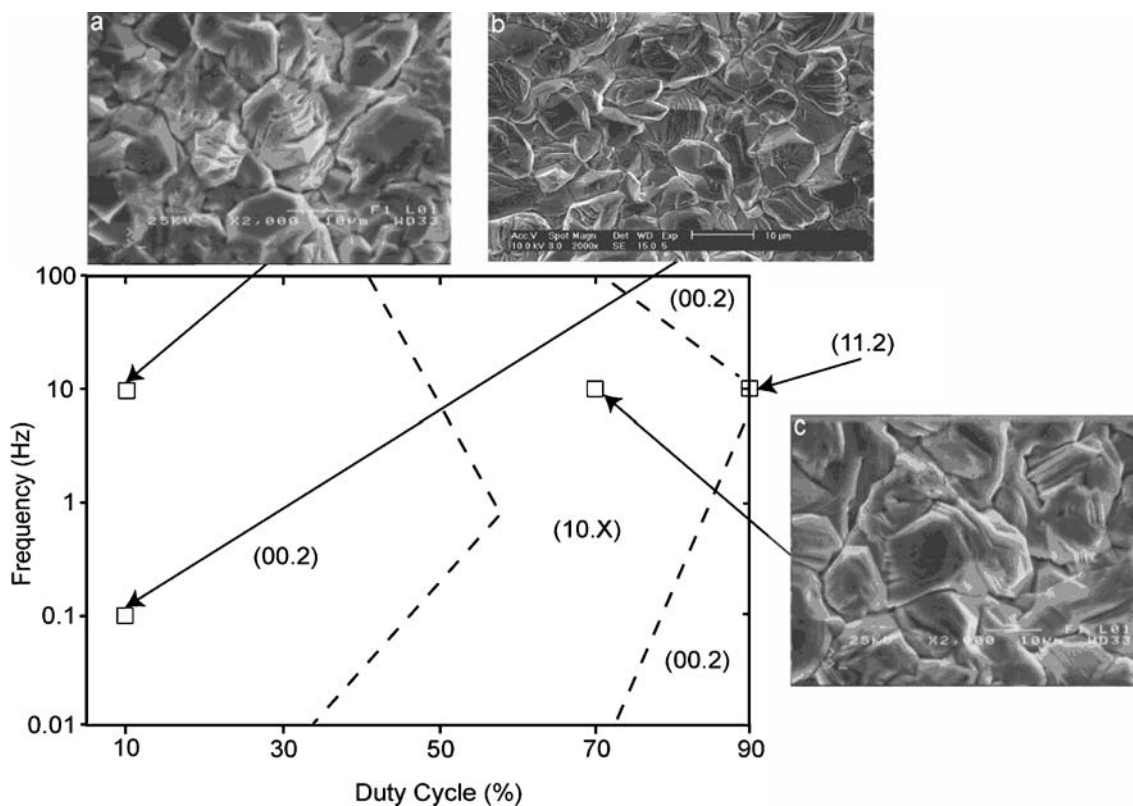


Figure 3 Textures of Zn coatings pulse plated at a peak current density of  $10 \text{ A}\cdot\text{dm}^{-2}$  as a function of pulse frequency and duty cycle. SEM images are shown for samples in the (00.2) and (10.X) regions.

results again in a basal (00.2) texture wherever the on time is less than 50% of a pulse (Fig. 3). Increasing further the current density (Fig. 4;  $20 \text{ A}\cdot\text{dm}^{-2}$ ), the former DC (11.4) texture (Fig. 1a) effectively disappears (actually contracts to a small area by d.c. >85%), and (00.2) establishes over duty cycles lower than 50%.

Generally, when increasing the on-time the pulse-induced disturbance to the system is weaker and the “inclined” (DC) texture is preserved (Figs. 3, 4 and 1a). This is true for all pulse frequencies employed; increasing the duty cycle leads to a decrease in the cathodic surface concentration of the reducing agent until the DC condition is reached. Now, increasing the frequency, for constant duty cycle, might result again in a decreasing surface concentration of  $\text{Zn}^{2+}$  due to small relaxation time if the supply from the bulk solution was ample. However, mass transfer is not controlling (i.e. the current is a fraction of its limiting value), so the system has a fast response to the changes in overpotential, even by 100 cycles per sec; the diffusion layer is depleted of  $\text{Zn}^{2+}$  at each off pulse and replenished at each on pulse.

It is inferred from Fig. 1a that the EC conditions cause preferential orientation. For constant, low current densities ( $0.5$  to  $3.0 \text{ A}\cdot\text{dm}^{-2}$ ), the texture is independent on pH because the hydrogen overpotential is not yet surmounted and hydrogen reduction is limited. At moderate DC currents ( $3$  to  $30 \text{ A}\cdot\text{dm}^{-2}$ ) the hydrogen-related reactions become more influential as the alkalinity of the bath increases, and seriously affect the electrocrystalliza-

tion process. Finally, even higher DC deposition currents yield similarly oriented texture for all pH although the degree of texture depends weakly on the bath acidity—the intensity of preferred (00.2) varies, namely decreases with increasing pH. The influence of the bath pH has been analyzed in terms of hydrogen cations’ effect on the cathodic process kinetics [2]. The reduction of hydrogen during electrolysis in an acidic sulphate bath brings on a progressive alkalization of the cathodic layer, so that colloidal  $\text{Zn}(\text{OH})_2$  may finally form and selectively influence the growth rates of the various crystal planes through changes in their crystallization overpotential [8]. Therefore, at the working pH of the present experiments (4.5) an auto-inhibition effect from hydroxide formation is to be expected. However, according to XRD there is no indication for the formation of a second phase at the cathode, so the general PC growth is not considered to be inhibited by hydroxide formation at  $\text{pH} = 4.5$ ; this is rather due to the periodic replenishment of the diffusion layer by  $\text{H}^+$  from the bulk solution. At the DC conditions the crystallites generally maintain their size at different pH, so neither increased nucleation is involved at DC  $\text{pH} = 4.5$ . It has been verified though, that the application of a current or potential pulse increases nucleation more than it increases growth of the already established crystallites [9]. Hence, the observed results, namely the changes induced by pulse plating, can be explained by considering that the pulse current application periodically increases nucleation and confines growth so that the growth-dependent

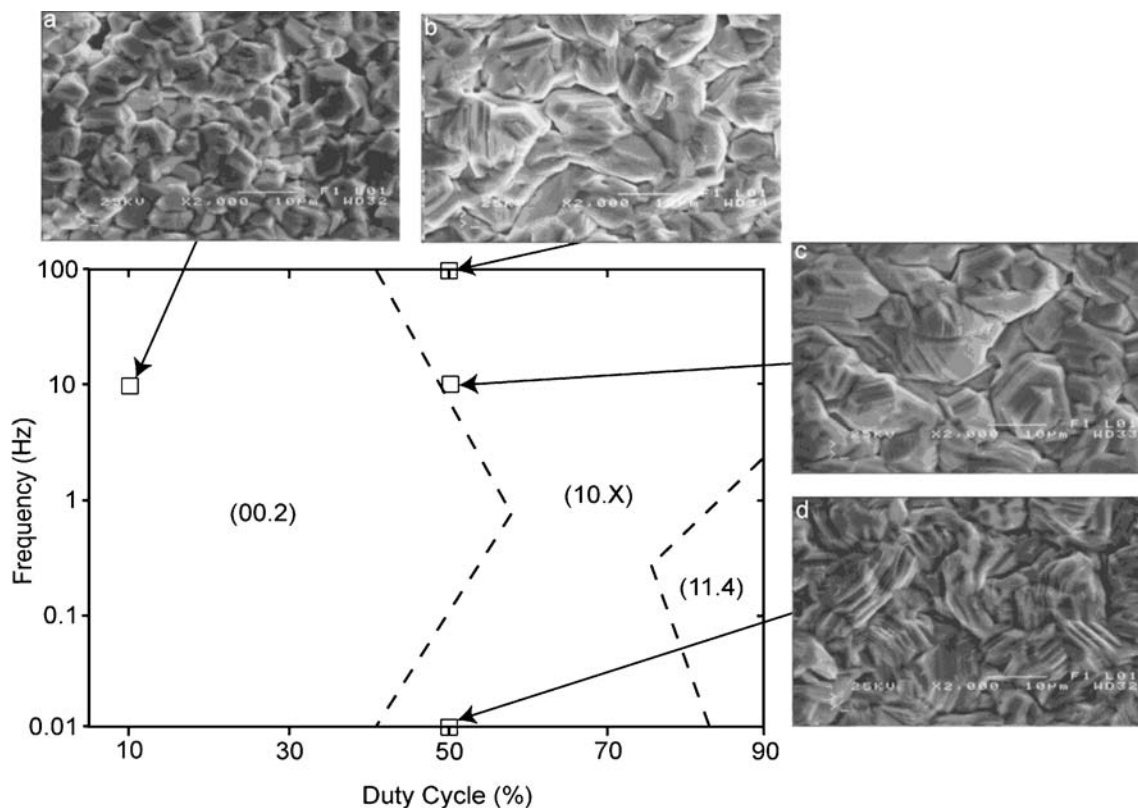


Figure 4 Textures of Zn coatings pulse plated at a peak current density of  $20 \text{ A} \cdot \text{dm}^{-2}$  as a function of pulse frequency and duty cycle. SEM images are shown for samples in the (00.2) and (10.X) regions.

orientations are not obtained any more. Even when the deposition proceeds by a quasi steady ion-to-ion reduction and incorporation into a lattice, as is the case for zinc deposition at continuous plating conditions, a crystal might stop growing (e.g. due to impurity adsorption) and further growth occurs only by nucleation of a new crystal on the previous one. The pulse mode itself induces a serious perturbation in the crystallization process, completely modifying the kinetics of crystal growth and nucleation. Therefore, it is quite reasonable that a change in texture is observed from DC to PC at similar electrochemical conditions.

As an explanation of the fact that no “secondary” growth of the already existing crystallites takes place during the intermittent PC process, it has been suggested that the adsorption of sulphate anions blocks the growth centers during the off-time, and as a consequence the system is forced to create new nuclei with each new pulse [10, 11]. The sizeable sulphate anions are periodically expelled and re-entering the interface between the working electrode and solution and might indeed influence the crystallization procedure. However, in the absence of any experimental verification for the nature and action of blocking species, the energetic activation of the normally inhibited substrate sites during each pulse is sufficient to account for augmented nucleation and less regenerative growth. Actually, an exact description of the phenomena involved is more complicated in that the current distribu-

tion on the cathodic electrode during PC plating is different from that during DC plating. It has been shown [12] that when the applied (peak) current density is a fraction of its limiting value, as is the case here, its distribution on the cathodic electrode is not uniform, due to the non uniform ohmic potential drop in the solution neighboring the cathode. The variance of the current with respect to the electrode radial dimension introduces an additional perturbation which tends to diminish the homogeneity of the deposit, regarding both the thickness of the coating and the surface density of crystallites at various points. Note that the results presented here concern properties averaged over the surface area of the deposits.

SEM micrographs of several samples are shown at the relevant points of the texture diagrams. A strict layer-by-layer flat platelet construction can be seen in Figs. 2a, c and 4d. This feature is common for (00.2) samples but it is observed at the inclined forms of pyramidal layers as well. A distinction between *texturally* different samples based on their SEM imaging is not straightforward since most deposits are deprived of a highly intense eminent orientation of crystallites with respect to the vertical axis. Even the RTC (00.2) samples include prismatically oriented platelets, e.g. the (10.0) can be clearly seen in Fig. 2c. On the average, the various inclinations of grains for each sample result the XRD-determined texture, the percentage of each kind of grain being related to the RTC value.

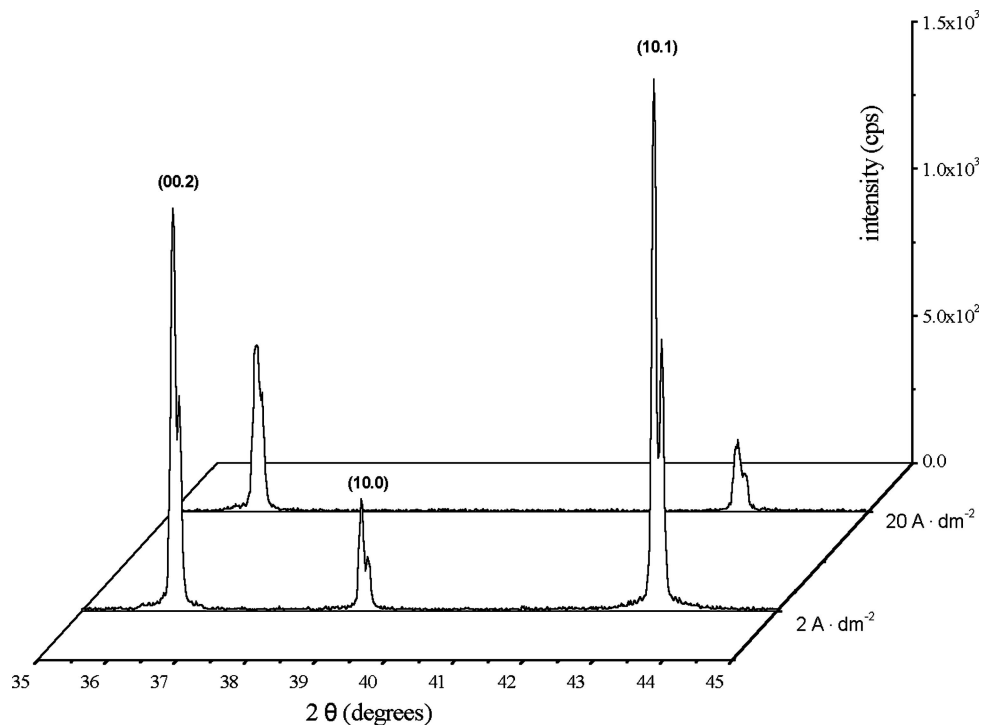


Figure 5 XRD patterns ( $2\theta$ : 35–45°) of samples deposited at pulse peak currents 2 and 20  $\text{A}\cdot\text{dm}^{-2}$  (0.01 Hz, 90%).

The microstructural characteristics of the coatings are intimately related to their properties, although the influences of texturing and grain size are not easily discernible. An intense basal texture is ideal for good paint adhesion [13] and corrosion behavior [14] while a fine grain structure is associated to a substantial increase in hardness [15]. It has been verified that the texture has remarkable influence on properties for which the grain size may have a secondary effect, e.g. *elastic* properties depend strongly on texture. According to Xingpu Ye et al. [6], the ductility of zinc coatings is directly connected to the percentage of crystallites that lie at inclined angles with respect to the (00.2) basal planes. The sum of the RTCs of the planes that satisfy the inclination condition can be selected and designated as an index for available deformability. Alternatively, the sum of the RTCs of (00.2), (10.0), (11.0) and (21.0) planes can be designated as an index for nonavailable deformability.

The deposits obtained at 10 and particularly 20  $\text{A}\cdot\text{dm}^{-2}$  are uniformly compact and macroscopically smooth. It would be possible to perceive a general trend for the grain size examining the mean size of the individual forms appearing in the SEM pictures, at least comparing the PC 2  $\text{A}\cdot\text{dm}^{-2}$  samples (Fig. 2) to those obtained at higher currents (Figs. 3, 4), whereas a less tentative measure can be attained from the features of the diffraction lines. Their broadening at half peak height (FWHM) was related to the crystallite size via the Scherrer equation [16] corrected for instrumental broadening with respect to a standard Mo powder made up of sufficiently large crystallites (average diameter 10  $\mu\text{m}$ ). It was premised that the samples are sufficiently homogeneous so that the broadening of the

XRD peaks be a statistical feature and not due to few small crystallites. Also, the micro-stress induced broadening was disregarded on account of the rapid recrystallization reported to occur in zinc coatings deposited from sulphate solutions without inhibitors [17]. Since the application of the Scherrer formula is based on the X-ray wave coherence length in the vertical dimension, calculations for each sample were made for basal (00.2), prismatic (10.0), (11.0) and pyramidal (10.1), (10.2), (10.3), (10.5), reflections in order to cope with the various shapes of Zn crystallites. The statistical treatment of the results showed that the average value of grain size decreases when increasing deposition current density. Crystal dimensions larger than 1  $\mu\text{m}$  (roughly the limit of the determination technique) and rather in the range 5–10  $\mu\text{m}$  were found for both PC 2 and 10  $\text{A}\cdot\text{dm}^{-2}$ . The dimensions were reduced to about 100–200 nm at PC 20  $\text{A}\cdot\text{dm}^{-2}$ , at least along one and usually for most directions examined for any individual sample. The morphology trend could be related also to the extent of  $\text{Cu } K\alpha_1$  and  $K\alpha_2$  XRD resolution. Explicit doublet (00.2) and (10.2) reflections can be seen in the pattern of a PC 2  $\text{A}\cdot\text{dm}^{-2}$  sample (Fig. 5); the peaks are not so well resolved by the smaller crystallites of a PC 20  $\text{A}\cdot\text{dm}^{-2}$  coating.

The PC 2  $\text{A}\cdot\text{dm}^{-2}$  is associated with a limited availability of free energy for nucleation, so that an as-deposited layer consists of a few growing islands (Fig. 6) unlike the deposits obtained at higher current densities, for constant electrodeposition charge. These islands are nucleated at active substrate sites where the local current density is strong enough to overcome any inhibition (also [11]). With longer deposition time, growth and/or progressive

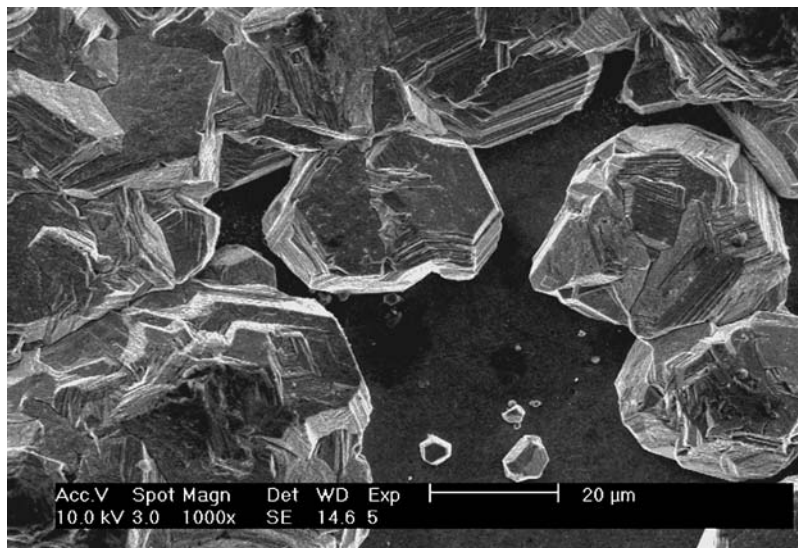


Figure 6 SEM image of a coating deposited at a pulse peak current density of  $2 \text{ A} \cdot \text{dm}^{-2}$  (0.01 Hz, 90%).

secondary nucleation fill in the voids until the crystals coalesce (Figs. 2a, b, c). At higher current densities ( $10$  and  $20 \text{ A} \cdot \text{dm}^{-2}$ ), the gain in free energy allows the instantaneous formation of numerous nuclei over the entire cathode surface (also [18]) but the potential for growth is limited as the large population of nuclei is subject to increased overlapping. Therefore, smaller grained layers are obtained in general, which then construct more compact and macroscopically smooth coatings (Figs. 3a and 4a). The trend of size variation is generally alike for both DC and PC regimes; however, pulse plating is associated to smaller absolute size of crystallites [4] due to the higher tolerance in the surface energy of the deposits.

#### 4. Conclusions

Pulse-current plated single phase zinc coatings on low-carbon steel were characterized in terms of microstructural texture and morphology, with respect to the electrodeposition parameters. Basal (00.2) and pyramidal (10.X) ( $X = 3, 4, 5$ ) oriented textures were obtained depending on current density, duty cycle and pulse frequency. The experimental results were summarized through texture diagrams for different deposition currents. The main finding of this investigation was that the present technique results in leveling off the DC growth-dependent habits and establishing mostly a (00.2) texture, as (a) removing the hydroxide auto-inhibition, (b) activating the normally inhibited sites for nucleation, and (c) hindering regenerative growth. Therefore, pulse plating served as an agent for effective grain refinement, at moderate current densities of deposition ( $20 \text{ A} \cdot \text{dm}^{-2}$ ), enabling the preparation of compact coatings of a uniform basal texture.

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