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# Dendritic zinc growth on the edges of flat steel strip during electro galvanizing

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**Abstract**

Dendritic growth on strip edges during continuous zinc electroplating of flat steel strip for the automotive industry is a well-known problem. They produce surface defects during the stamping process. In this work the effect of the electrolytic process variables on dendrites formation is studied. Zinc was electrodeposited on rotating steel discs. This new experimental configuration reproduces the hydrodynamic conditions and the current distribution found on the strip edge in an industrial zinc electroplating line. The tangential velocity of the outer edge of the discs was adjusted to a value equal to the relative speed between strip and fluid used in the industry. The effect of current density, temperature and edge roughness was evaluated. All these variables have a great influence on the size and morphology of dendrites.


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*Keywords:* Electroplating; Dendritic growth; Zinc; Galvanization

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## 1. Introduction

In the last decades, increasingly demanding quality standards in the automotive industry have led to the replacement of flat steel strips with galvanized steel for manufacturing the exposed automotive-body panels. Currently, galvanized steel makes up over 90% of the construction of mid-range models. In this sense, electro galvanized steel strip is the most frequently used product for exposed automotive-body panels in Argentina. Ternium manufactures this product at the Florencio Varela plant by the continuous electroplating process in acid sulfate based electrolyte.

Zinc deposits known as dendrites tend to grow on the edges of the steel strip when it passes through the different electrolytic cells. Zinc is a highly fragile material; for this reason during the process of strip cutting, the dendrites become detached, swept along the strip surface and adhered to the surface during the oiling process and subsequent processing. When steel strip is formed during the stamping process to manufacture automotive body panels, zinc particles are embedded on the surface of the material, producing a defect called dent. This defect originates a defective piece, which cannot be used and provokes quality claims and in some extreme cases a stop in the production line due to the lack of raw material. The electro galvanizing production line has been improved to minimize formation of zinc dendrite with good results through the installation of automatic edge masks designed to avoid this problem. However, this defect occasionally occurs and the causes that produce it cannot be clearly determined.

General literature provides considerable information on dendritic growth and its origin, though they are all based on the basic and formal point of view [Popov et al. (1996); Popov et al. (2002); Despic and Popov (1972); Kardos and Foulke (1962); Popov and Pavlovic (1993); Wranglén (1960)]. The aim of the present work is to study, at laboratory scale, the influence of the variables in the electro galvanizing process on the formation of dendrites along the edge of the steel strip to elucidate their formation mechanisms and be able to control the variables in the industrial process to avoid dendrite formation.

## 2. Experimental

A novel rotating system was designed, with the geometry indicated in Fig 1, to simulate the fluid dynamic conditions and the current distribution at the steel strip edge during the continuous electro galvanizing industrial process of flat steel strips. Based on this system, an electrochemical cell was built (Fig 2a).SAE 1010 steel strips (0.7 mm thickness) cut in the form of disks (internal diameter: 8 mm and external diameter: 40 mm) with a laser were used as cathode (Fig 2 b)). The disks were mounted on a steel rod isolated with a Teflon cylinder, leaving an exposed area of 0.194 dm2. A ring of pure zinc ingot was used as anode (Fig 2c)).

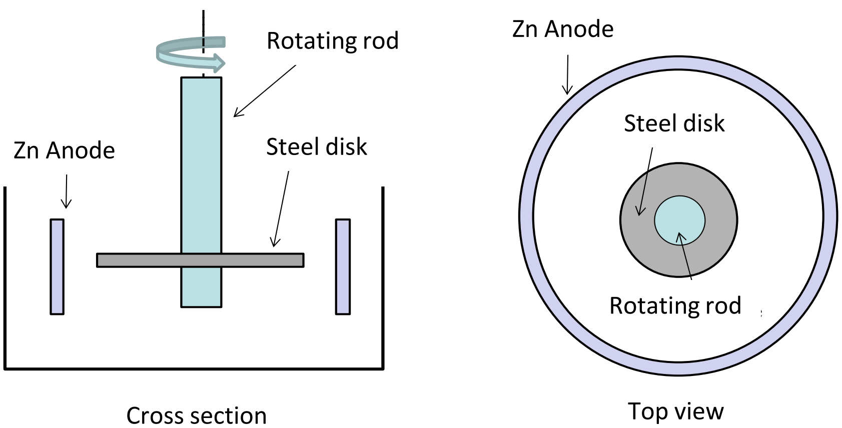


Fig. 1. Cell scheme for strip edge simulation

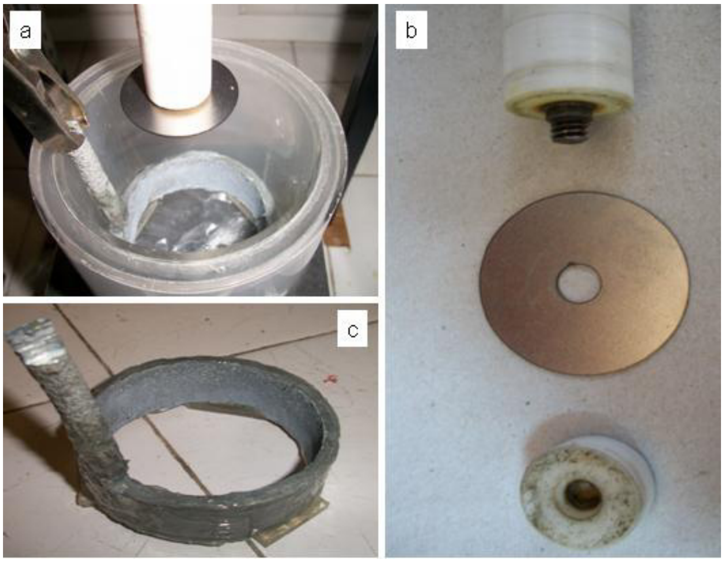


Fig. 2. a) Photograph of cell layout, b) Detail of cathode and holder, c) Detail of Zn anode.

Speed rotation was kept constant at 800 rpm throughout the tests. This value was obtained from considering that the electrolyte in the industrial process has a countercurrent flow, with respect to the way in which the strip advances, at a speed of 1m/s and the average line speed is 0.67 m/s. Hence, tangential speed of the disk in rotation was adjusted with the addition of the electrolyte speed plus the advance speed of the steel strip: 1 m/s + 0.67 m/s = 1.67 m/s which equals to 800 rpm. Although this is only an approach, configuration is similar to that of the industrial process.

The electrolyte used was a zinc sulfate solution with a $Zn^{+2}$concentration of 90 g/l. The pH was adjusted to 2 by adding sulfuric acid. Temperature of the solution was kept between 40 and 70 ºC using a Frigomix 1495 thermostatic bath. Current applied ranged between 4 and 12 A (20.6 A/dm$^2$ and 61.8 A/dm$^2$). In some cases 18 g/l de $Na^+$ was incorporated to evaluate its influence on dendrite formation, since $Na^+$ is frequently used in the production line. Zn deposits were evaluated using a light microscope (OM) and scanning electron microscopy (SEM). The size of the dendrites was measured by statistical treatment using an image analysis program (Piximetre5.4). As mentioned above, the disks were cut with a laser. This process produces a characteristic edge (Fig 3 a)) which does not represent the typical edge found along the production line (Fig 4). For this reason, the samples were smoothened by a systematic reproducible procedure using 80-grit (G80) and 600-grit (G600) sandpapers to obtain two roughnesses similar to those obtained in the industrial process (Fig 3 b) and c)).

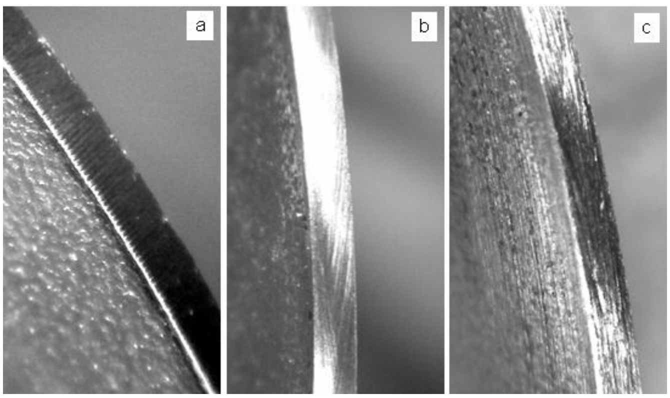


Fig. 3. Edges of the disks, a) Laser cut, b) G600 finish, c) G80 finish.

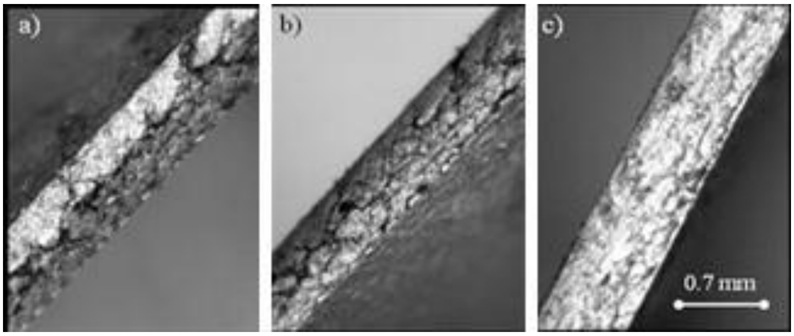


Fig. 4. Edges of steel strip (industrial samples).

## 3. Results

### *3.1. Current Density (CD)*

The influence of the current density on dendritic growth was evaluated for a coating thickness of 7 µm, which is representative of the galvanized materials for the automotive industry. To keep this value constant throughout all the tests, the time required for electrolysis was calculated for each experiment by Faraday's law (Table 1). A 100% Faradaic efficiency was verified by the change in disk's weight due to the electrodeposition process for all de CD and temperature range studied.

Table 1. Current density and electrolysis time for 7 µm coating.

| Current density (A/dm$^2$) | Time (s) |
|---|---|
| 24.7 | 60 |
| 37.1 | 40 |
| 48.9 | 30 |
| 60.8 | 24 |

Fig. 5 shows the evolution of the average length of the dendrites and its standard deviation for the G80 finished disks at 60 ºC. It can be seen that both the dendrite size and the standard deviation increase with current density, indicating that the dendrites are longer and less homogeneous for higher CD. The dendrite length standard deviation was calculated as:

$$\sigma = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(X_i - \bar{X}\right)^2} \quad (1)$$

Where ***N*** is the number of measured data, $\bar{X}$ is the average y $X_i$ is the *i* measured value.

Fig 6 shows the same dependence for the disk edges with G600 finish. It is clearly seen that roughness of the strip edge strongly affects dendrite growth. Images of Fig 7 show an example of the aspect of dendrites for 60.8 A/dm$^2$, 30 s, for the two types of finishes.

Fig 8 shows the cross section of one of the disk edges included in an epoxy resin. This image corroborates that the greatest accumulation of Zn occurs in the right angles of the disk edge.

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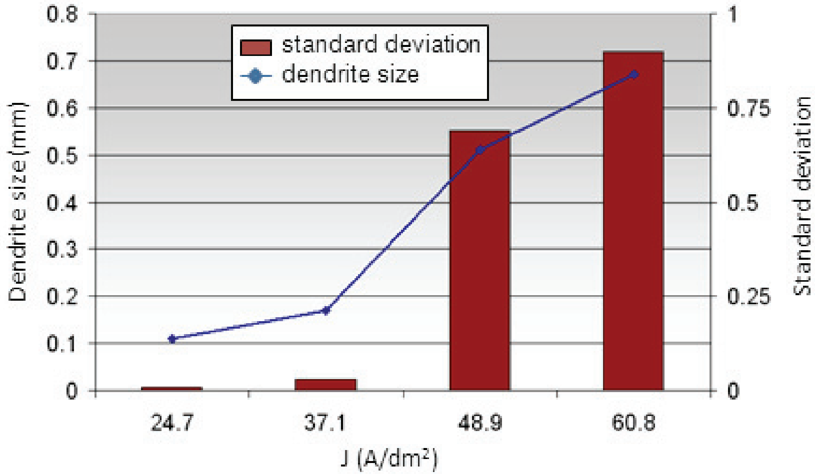


Fig. 5. Influence of CD on dendrite size and dispersion. G80 finish, 7 µm coating, 60 ºC.

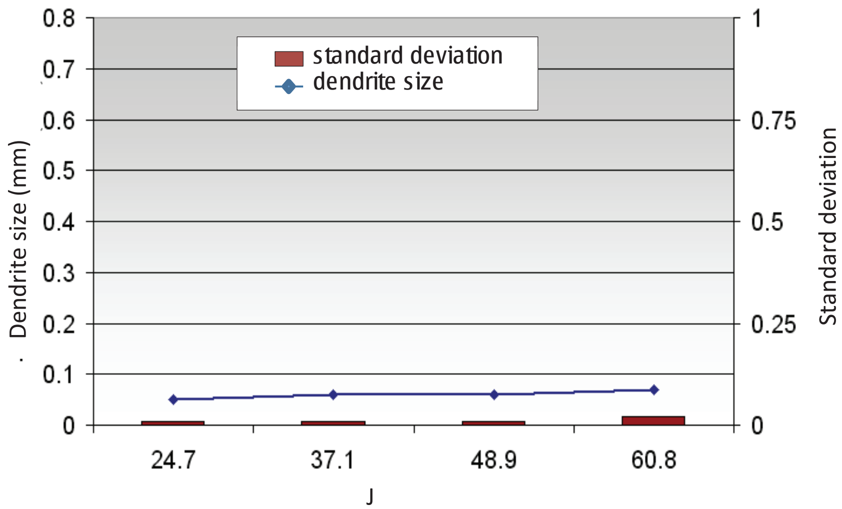


Fig. 6. Influence of CD on dendrite size and dispersion. G600 finish, 7 µm coating, 60 ºC.

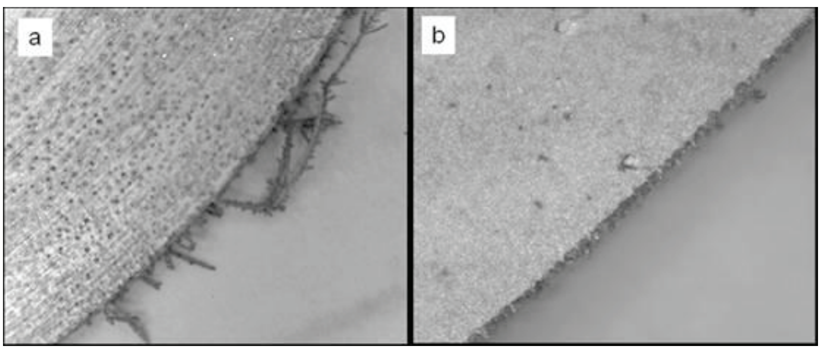


Fig. 7. Galvanized samples at 60.8A/dm2, a) G80 and b) G600 finish (30X)

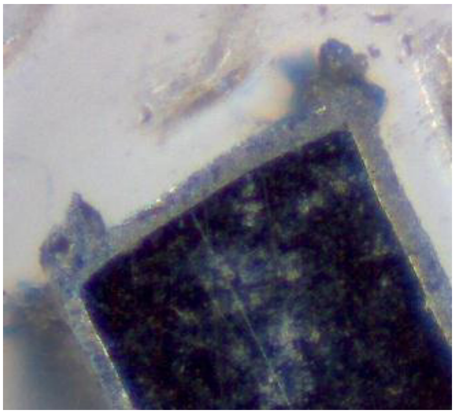

Fig. 8. Cross section of disk edge galvanized at 60.8A/dm$^2$, 7 µm, G80 finish, 60 ºC.

### *3.2. Temperature*

To evaluate the effect of the electrolyte temperature on dendrite formation and growth, the experiments were conducted at a CD of 48.9 A/dm$^2$ and the electrolysis time was set to 30 s (7 µm coating).The temperature was controlled between 40 ºC and 70 ºC. Fig. 9 shows the evolution of dendrite length and dispersion as a function of the electrolyte temperature for G80 finished discs, while the effect of temperature for G600 finished discs can be seen in Fig 10. A comparison of these corroborates the important effect that the substrate’s surface roughness has on dendritic formation and growth; smaller and more homogeneous dendrites are obtained for smoother substrates.

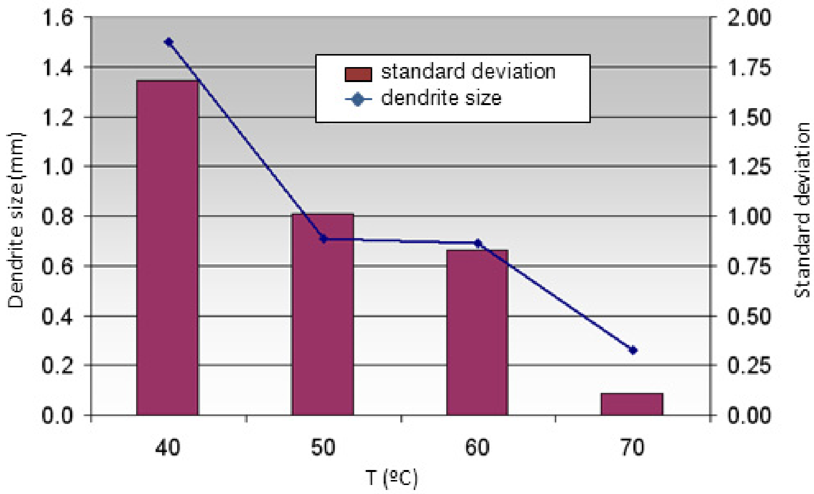


Fig. 9. Influence of temperature on dendrite size and dispersion, G80 finish, 48.9 A/dm$^2$, 30 s.

An important influence of the temperature on dendritic growth on the disk edge can be observed. When temperature increases, the size of the dendrites decreases and they become more homogeneous. SEM images in Fig 11 show that the bigger crystals are located in the corners of the disk edges. Dendritic formation and growth is a process governed by mass transfer and for this reason, temperature strongly affects its behavior. This arises from the dependence of the diffusion coefficient, which follows the Arrhenius equation type [Schaffer (2000)].

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \tag{2}$$

Where $D$ is the diffusion coefficient, $D_0$ is a constant that considers the size and form of the molecule of the diffusing species, the resistance that the medium imposes when it is passed through and the energy required to move the molecule in the medium; $Q$ is the activation energy of the process, $R$ is the universal constant of the gases and $T$ is the absolute temperature.

The SEM images of the edges of the G600 finished samples (Fig. 12) confirm the strong effect that temperature has on dendrite growth. It is clearly seen that at higher temperature the Zn dendrites do not formed (Fig. 12 b)), and in general, the size of the Zn crystals deposited in the right corners of the disk edges are smaller compared with samples treated withG80-grit sandpaper (Fig.11).

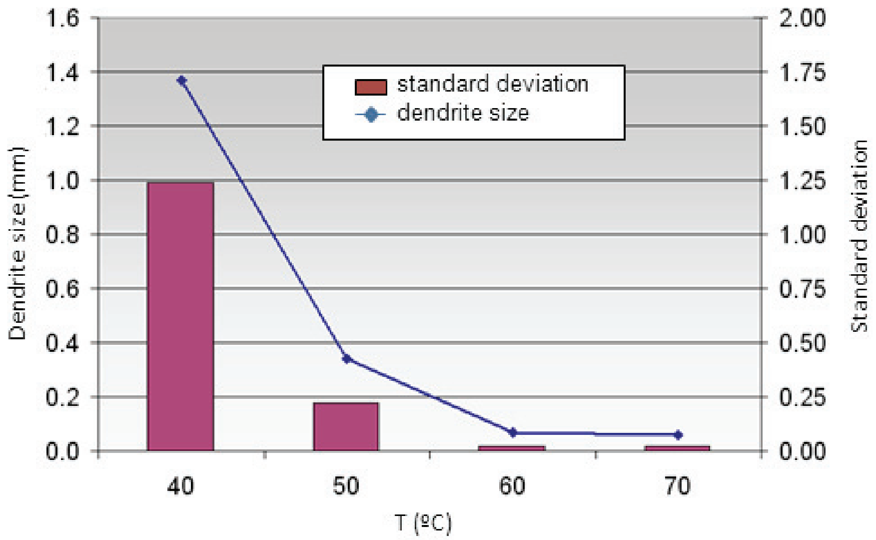


Fig. 10. Influence of temperature on dendrite size and dispersion, G600 finish, 48.9 A/dm$^2$, 30 s.

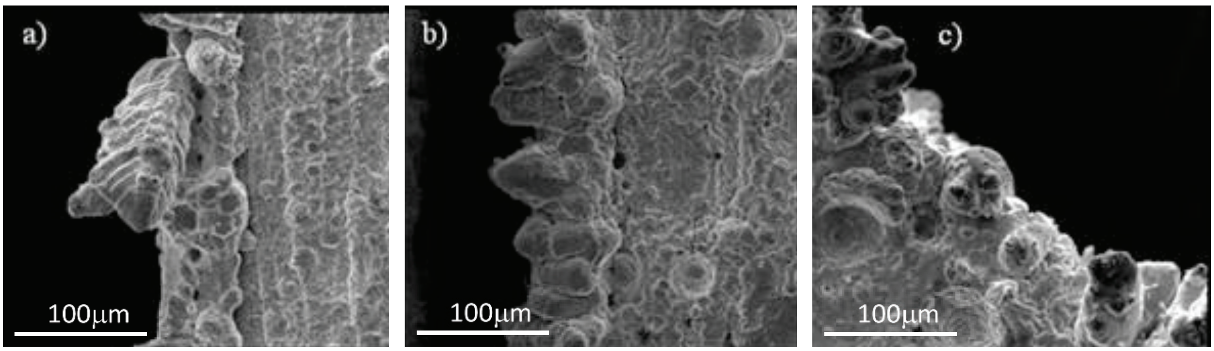


Fig. 11. SEM images of 7 µm deposits obtained at a) 40 ºC, b) 60 ºC and c) 70 ºC, 48.9 A/dm$^2$, 30 s, G80 finish.

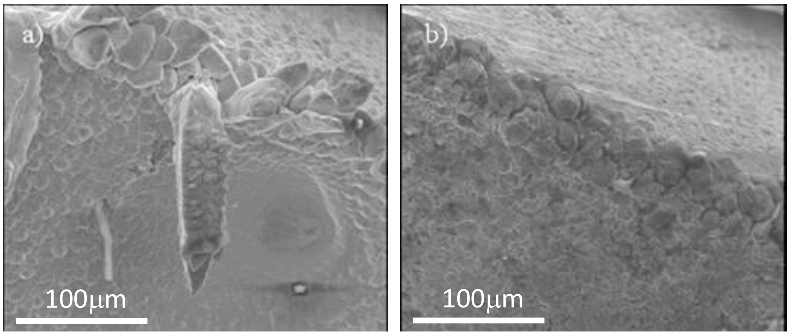


Fig. 12. SEM images of 7 μm deposits for disks with G600 finish at a) 40 ºC, b) 60 ºC. 48.9 A/dm$^2$ and 30 s.

OM images of the electro galvanized disks in Fig 13 show the general morphology of dendrites for different temperatures and finishes. It is clear from this analysis that both variables have an important effect on the onset of dendrite birth and growth at the edges of the steel strip.

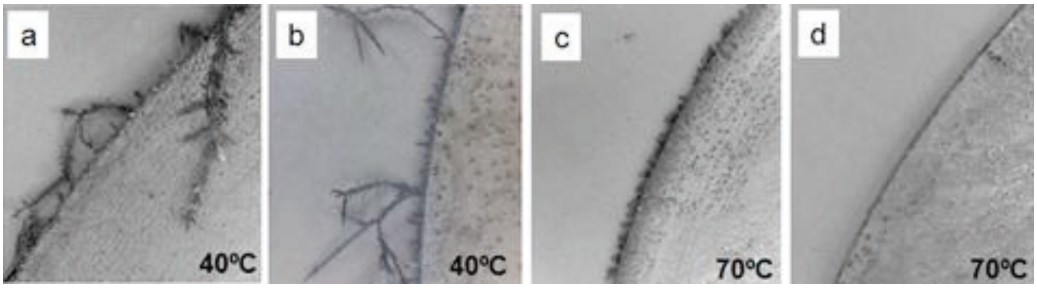


Fig. 13. OM images of samples galvanized at different temperatures and surface finishes, a) and b) G80, c) and d) G600. 30 X, 48.9 A/dm$^2$, 30 s.

### 3.3. Sodium addition to the electrolyte

To evaluate the influence of the addition of sodium to the electrolyte, sodium sulfate was added up to a concentration of 18 g/l $Na^+$. The CD was kept constant throughout all the tests at 48.9 A/dm$^2$ and the electrolysis time was 30 s, in order to obtain 7 μm thick deposits. The electrolyte temperature ranged between 40 ºC and 70 ºC. Comparison of Figs 14 and 11 shows the effect of the addition of sodium for disks with G600 finish at several temperatures.

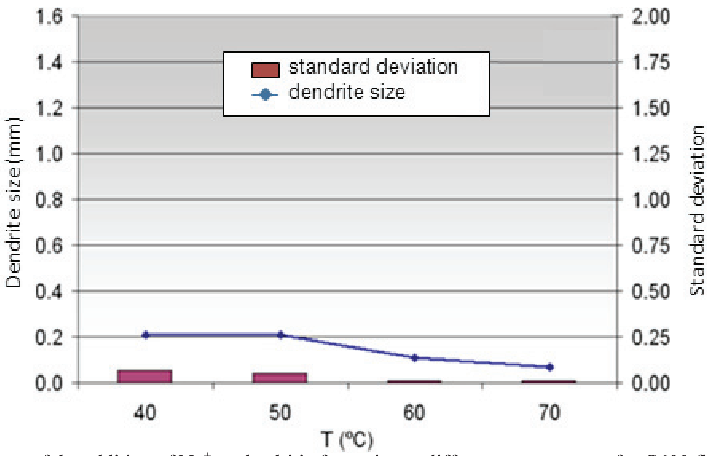


Fig. 14. Influence of the addition of $Na^+$ on dendritic formation at different temperatures for G600 finish with 18g/l of $Na^+$

It is evident from this results that the addition of sodium reduces dendrite formation, with a more pronounced effect at low temperatures. Also, dendrite morphology is affected by temperature, making them more homogeneous. This is revealed in the values of the standard deviation and in the images of Fig 15.The addition of sodium reduces the resistance of the solution, increasing the Wagner's number *Wa* (Eq3), which considerably improves primary distribution of current. Hence, zinc is deposited more homogenously on the substrate surface.

$$Wa = \frac{d\eta_a}{dj}\frac{\kappa}{l} \qquad (3)$$

Where $d\eta_a/dj$ is the resistance to polarization, $\kappa$ is the specific conductivity and $l$ a characteristic length. [Ibl (1983)].

The SEM images of Fig. 16 show that for samples with G600 finish, increasing the temperature from 40 ºC to 60 ºC produce no important changes in the morphology and size of the Zn crystals deposited at the edges of the disks. This effect is very different compared with the results obtained for the sodium free electrolyte.

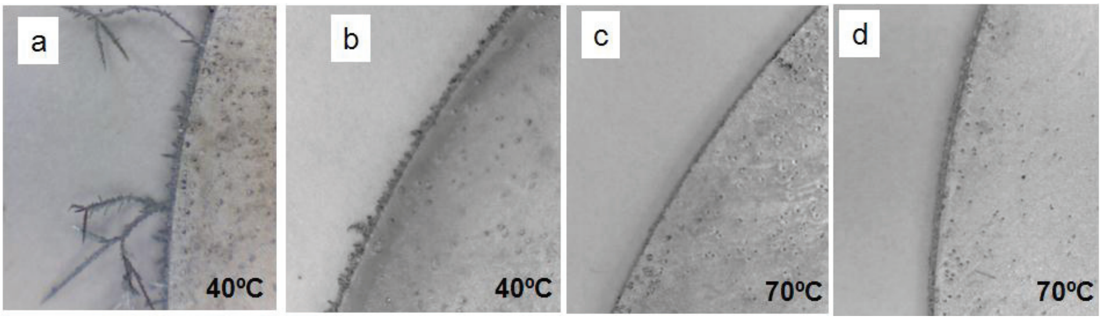


Fig. 15. OM images of the samples galvanized at different temperatures and G600 finish, a) and c) without sodium addition, b) and d) with addition of 18 g/l of $Na^+$. 30 X, 48.9 A/dm$^2$, 30 s.

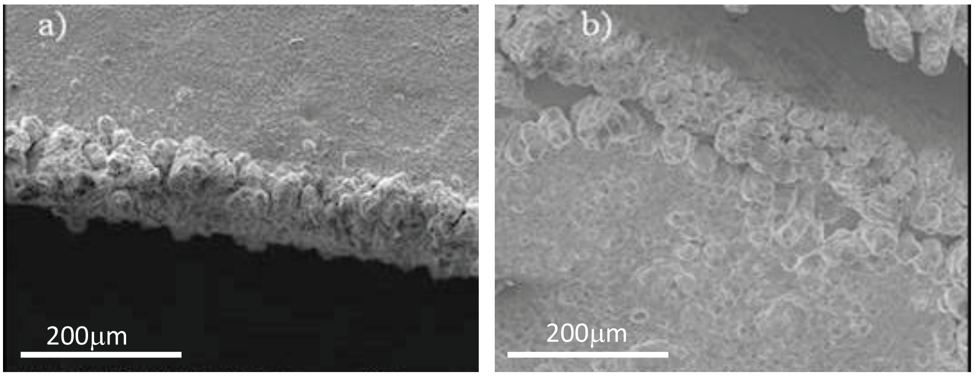


Fig. 16. SEM images of edge disks electro galvanized at two different temperatures, a) 40 ºC, b) 60 ºC with addition of 18 g/l Na+. 48.9 A/dm$^2$, 30 s, G600 finish.

## 4. Conclusions

A lab-scale electrochemical cell was designed to simulate the hydrodynamic and current density distribution conditions at the edge of the steel strip during the electro galvanizing industrial process in acid sulfate electrolyte. The results show the effect of the most important parameters of the process on the formation of Zn dendrites on the corners of the edges of the steel strip. It is clearly seen that roughness of the substrate, current density and temperature of the electrolyte are key factors for dendrite formation and growth. When roughness of the edge increases, the average length of dendrites increases and their size dispersion is higher, indicating that the dendrite growth speed is not uniform throughout the surface. In addition to this, it was found that, for an equal coating thickness, an increase in current density produces longer dendrites that also grow in a more heterogeneous state producing high size dispersion. In contrast with CD, he increase in temperature reduces the average length of the edge dendrites and their size dispersion.

The addition of $Na_2SO_4$, reduces the average length of dendrites and generates more homogeneous deposits being more efficient at low temperatures. This last behavior is mainly attributed to the modification of the conductivity of the solution and smoothening of the primary current distribution.

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