Morphology of a zinc layer electrodeposited on steel using an Electroplating Cell

F. Silva Filho[1]; M.S. Andrade[2] and V.F.C. Lins[3]
[1]*Research and Development Center of USIMINAS Industry*
[2]*Technological Center of Minas Gerais Foundation –CETEC*
[3]*Chemical Engineering Department, Federal University of Minas Gerais, Rua Espirito Santo 35, 6° floor, tel 55 031 32381773, fax 55 031 32381789, 30160-030, Belo Horizonte, Minas Gerais, Brazil, vlins@deq.ufmg.br*

Abstract

The USIMINAS company that provides steel for the automotive industry decided to acquire an electroplating process able to alternate coating on both faces of steel plates, and to start an intense electrolytic flux and a high deposition rate. The objective of this work is to construct an electroplating cell in order to study the main process variables such as current density and electrolyte flow rate. The influence of current density and electrolyte flow velocity on the morphology of zinc coating was observed. Through the AFM technique, three different crystallization forms were observed. Using the atomic force microscopy it was possible to observe the zinc layer at the early stages of deposition. It could be clearly seen that morphology of the deposited film is correlated to the substrate grains.

Keywords: Electroplating process, zinc coating, morphology, atomic force microscopy (AFM)

Introduction

The Brazilian automotive industries started to electroplate steel in order to increase the corrosion resistance of their cars and to compete successfully with international industries. USIMINAS that provides steel for the automotive industry decided to acquire an electroplating process. A process, which was able to alternate coating on both faces of steel plates, originated a great electrolytic flux and a high deposition rate.

The objective of this work is the construction of an electroplating cell to study the effect of the main process variables such as current density and electrolyte rate on the coating morphology. This study makes possible a new product development and increases the quality of the present products. The cell also makes possible the study of mass transfer phenomena and laminar and turbulent flow related to electric field effects in the deposition process.

This research is relevant to the automotive industry and the university. In recent years, there has been significant progress in the study of electrodeposit composition and microstructure. Surface Engineering deals with the surface alteration in order to reach adequate properties such as corrosion resistance, magnetic and tribological properties.

All these properties depend on the chemical composition and structure of the coating and the original metal surface (3).

The Electroplating Process

The main characteristic of this process is the manner in which high deposition rates are obtained through the application of high current density and high electrolyte flow.

The electroplating line of USIMINAS consists of an entrance section where the bobbins are welded. Then, there is a chemical and electrolytic cleaning and pickling with H_2SO_4 in order to remove oxide layers. The deposition section contains 20 vertical cells. Each cell has 4 boxes with insoluble anodes. Connections and the withdrawal of the anode box are easily done. Therefore it is possible to deposit the zinc layer on one face or both steel faces. The electrolyte flows from the anode box top and drains away between the anode and the sample. The distance between the sample and the anode is 6.5 mm. The anode is titanium coated with iridium oxide. The flow rate of the electrolyte in the lower region reaches 4 m/s. The electrolyte drains away through holes in the anode box in order to distribute the pressure. Gravitational force is used to accelerate the electrolyte in cells. The application of high current densities (13.000 A/m^2 or higher) is possible because of the high flow rate. The energy consumption is 140 kwh/t. The zinc concentration is maintained through

two dissolution stations and the zinc electrolyte is fed into the stations through a by-pass system. The concentration control is done through the flux control in the dissolution stations. The electrolyte pH is a control variable and is measured continuously. The other important variables are temperature and electrolyte drainage flow.

Materials and Methods

The standard procedure for the cell operation (Figure 1) is described. The samples were taken from the production after the hardening rolling and were cut and covered with oil for the storage period.

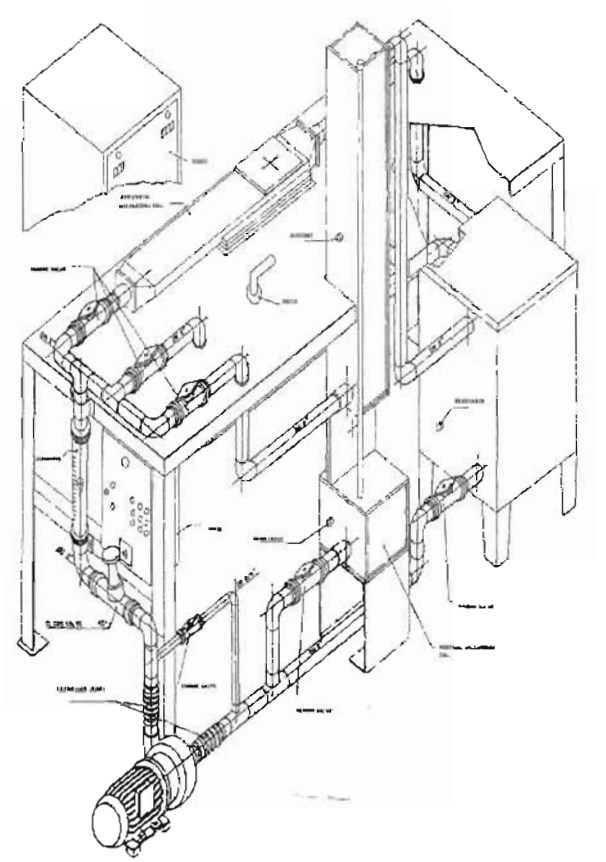

Figure 1 – Electroplating cell

The general reservoir was filled with an electrolyte (60 litters) and the fluid was heated to 55°C. The high purity electrolyte was obtained by the dissolution of zinc oxide. The electrolyte pH was 1.45, and the Fe content of the electrolyte was 0.06 g/L, and the Zn concentration of the electrolyte was 126.6 g/L. The experimental equipment was mounted vertically taking advantage of the gravitational flow. The tanks at the bottom and at the top of the equipment were also filled. The samples were cleaned with the product "Parco Cleaner" in the concentration of 60 g/l at a temperature of 60°C. Then, the samples were treated with H_2SO_4, at the temperature of 50°C. The distance between the sample and the anode was 6.5 mm at the tank bottom and 7.5 mm at the top. The electrolyte temperature was controlled through a pair of electrical heaters in the vertical cell controlled by a thermostat. In this test, the electrolyte temperature was maintained at 55°C by water circulating through a coil in the upper tank. In the industrial plant, only the gravitational force accelerates the electrolyte. In the laboratory scale, a pump was introduced in the circuit in order to reach the adequate flow rate. The flow rate was 3 m/s. The anode is the same as in the industrial plant and is of titanium coated with iridium oxide.

A voltage of 21.2 V was applied and the samples were introduced into the electroplating cell. The voltage was increased up to a current value of 180 A, and the time deposition was 40 seconds. After the deposition, the samples were immersed in a sulfuric solution for dissolution of the zinc sulfate that was deposited in a pure form. The samples were then cleaned and dried.

Three initial tests were done and the results were evaluated statistically. In the first stage, the equipment efficiency was calculated through the relation of deposited mass compared with the theoretic mass. The theoretic mass was obtained applying the Faraday law and the experimental mass was obtained by the zinc layer dissolution using the Coulometric method. The efficiency of 95% was obtained using the values of 154.3 g/m^2 for the deposited mass, and 163 g/m^2 for the theoretic mass. The deposition time was 40 s and the current was 180 A.

After the optimization of the electroplating cell, the influence of current density and electrolyte rate on the morphology of zinc coating was studied by atomic force microscopy (AFM). Atomic force microscopy images were obtained with a Dimension 3000, from Digital Instruments Inc., operating in contact mode. Silicon nitride probes were used.

Tests with the cell using the values of 1,500, 6,000, 10,000 and 15,000 A/m^2 for current density and electrolyte rates of 0, 3 and 4.3 m/s were done.

Results and Discussion

The steel used for the deposition process showed a homogeneous surface in relation to crystallographic texture, carbon residue and roughness. The carbon residue in the steel surface varied between the values 2.8 and 4.7 mg/m^2, and the average value being 3.6 mg/m^2. The average roughness was 0.59 µm.

The optimization of the electroplating cell was done with the objective of obtaining a product similar to industrial steel. The final analysis of the electroplating

steel considered the morphology, roughness and crystallographic texture of the coating. The final operation characteristics of the cell are:

- Storage electrolyte tank
  length: 360 mm
  height: 360 mm
  width: 560 mm
  heating system: 3,000 W, 220 V
  thermostat: 0 to 100°C
- Pump
  material: glass fibber
  motor: 3cv
  3,440 rpm
- Rotameter (flow meter)
  fluid: H_2SO_4 (10%)
  outlet: 0 to 18 m^3/h
- Lower tank
  dimensions: 180 mm x 180 mm x 180 mm
  resistance: 1,000 W, 220 V
  thermostat: 0 to 250°C
- Upper tank
  height: 900 mm
  width: 90 mm
  length, 122 mm
  resistance: 1,000 W, 220 V
- Electrical source
  entry: 220 V
  exit: 30 V, 350 A
  constant current

The main variables of the process are concentration and type of cleaning product, current density, deposition time, electrolyte speed, electrolyte temperature, chemical composition electrolyte, and distance between the anode and plate.

The process variable limits are:

-Current density up to 23,000 A/m^2
-Deposition time from 1 to 999s
-Electrolyte speed from 1 to 5 m/s
-Electrolyte temperature up to 75°C
-Distance between the anode and plate from 5 to 10 mm
-Sample thickness up to 2 mm
- Concentration of the H_2SO_4 solution up to 10%

Three initial tests were done with the electroplating cell. In the first test, two electrical problems were observed. The source tension was stabilized but not the current. After 14 seconds, the tension and current reached the appropriate values of 150 A. Then, alterations were made to the source in order to provide a continuous current source with the desired value of 150 A in t = 0. In the first test, it was observed that a high-tension value (24 V) was necessary to reach a high current density. The electrical resistance of the circuit verified that the high value of tension was related to the excessive distance between the anode and the plate (12 mm). This distance was reduced to about 7 mm.

After the process optimization, the effect of the current density and the electrolyte flow rate in the coating morphology was studied. It was observed that the coating morphology tends toward a homogeneous form with small crystals, when the current density is increased.

The effect of current density on the zinc morphology was found to be more significant than the influence of the electrolyte rate.

Through the AFM technique, three different crystallization forms were observed:

- Type 1 : large crystals showed the hexagonal edges and were parallel to each other (2)
- Type 2: smaller crystals, than in type 1, appeared in series perpendicular to each other
- Type 3: hexagonal crystals parallel to each other showed more surface area than the crystals in types 1 and 2 (Figure 2).

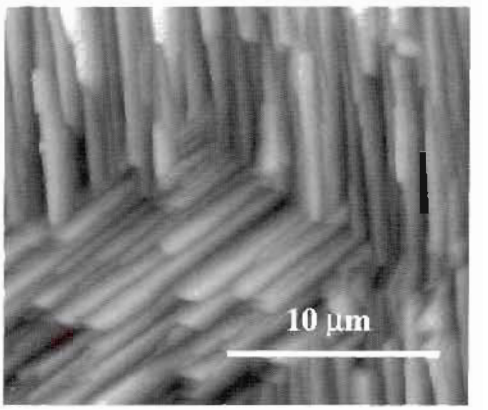

Figure 2 – AFM image of zinc electrodeposit, current density of 100 A/dm^2, electrolyte flow rate of 4.3 m/s.

Types 2 and 3 were found in zinc coating deposited with current densities of 6,000, 10,000 and 15,000 A/m^2, and type 1 was seen in coating deposited with a current density of 1,500 A/m^2. This result is similar to the literature data (6). According to Winand (6), the nuclei number decrease with the decrease in current density. Weymeersch et al (5) studied the zinc electrodeposition for high current densities up to 35000 A/m^2 and identified five coating types that depend on the electrolyte rate and current density. Ting et al (4), in their work, verified that the effect of current density and electrolyte rate on the morphology coating is relevant. As the current density increases, the electrodeposits change to a more compact form with hexagonal crystal (1).

Using Atomic Force Microscopy, it was possible to observe zinc layers at the early stages of deposition (Fig. 3). It could be clearly seen that morphology of the deposited film is correlated to the substrate grains.

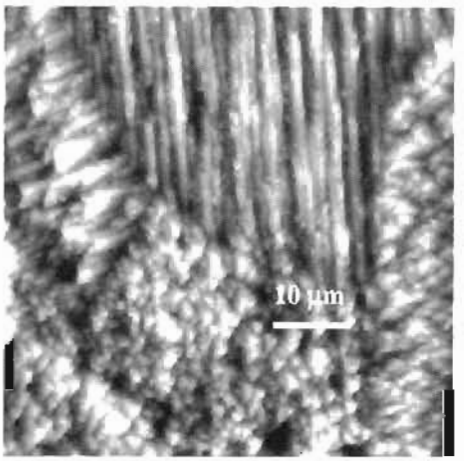

Figure 3 – Atomic force microscopy images of the zinc layer at the early stages of deposition

Acknowledgment

The authors knowledge the financial support of USIMINAS industry.

References

1. Epelboin, I., Kasouri, M. and Wiart, R., J. Electrochem. Soc., p 1206 (1979).

2. Kamei, K., Ohmori, Y. Galvatech ISIJ., p. 449-464 (1989).

3. Ludwig, R.S. Corrosão e Tratamentos Superficiais dos Metais Associação Brasileira de Metais (1971).

4. Ting, J. M., Guzzeta, F. H. Galvatech ISIJ. p. 179-184 (1989).

5. Weymeersch, A., Winand, R. and Renard, L. Plating and Surface Finishing. p. 118 (1981).

6. Winand, R. Electrocrystalization. The theory and applications. p 567-98 (1992).