# Damaging and cracks path in bended galvanized specimens: influence of Pb and Sn contents

# V. Di Cocco<sup>1</sup>, F. Iacoviello<sup>1</sup> and S. Natali<sup>2</sup>

<sup>1</sup> Di.M.S.A.T. - Università di Cassino, via G. Di Biasio, 43 03043, Cassino (FR), Italy <sup>2</sup> Dip.I.C.M.A. - Università di Roma "Sapienza", Via Eudossiana 18, Roma

**ABSTRACT.** Hot-dip galvanizing is one of most important protection technique against corrosion in many environments. In this work damage and crack propagation in intermetallic zinc based coating phases was investigated in order to evaluate chemical influence of Pb and Sn in the bath, comparing not-alloyed zinc bath. Hot dip zinc coated ipersandelin steel specimens were investigated in order to identify the main damaging micromechanisms during bending tests, considering both chemical composition and intermetallic phases distribution influence. Longitudinal sections of bended specimens were observed by means of a LOM (Light Optical Microscope) and main damage micromechanisms were identified as longitudinal and radial cracks. Experimetal results obtained with Zn-Pb and Zn-Sn baths were compared with coatings obtained using Zn bath.

## **INTRODUCTION**

Hot dip galvanizing is one of most important processing technique to protect metallic components in many corrosive environments [1]. From a technological standpoint, the principles of galvanizing have remained unchanged since this coating came into use over 200 years ago. However, because of new applications in the automotive and construction industry, a considerable amount of research has recently occurred on all aspects of the galvanizing process and on new types of Zn coatings [2]. New applications investigations on bath composition were oriented to obtained coating mechanical behaviour oriented to use in high plastic deformations [1-4].

Zn and Zn-based coating formation is a diffusion driving phenomenon, where Zn and Fe atoms are characterized by interdiffusion at high temperature [5]. Different Zn contents from external surface of coating to substrate boundary, generate some intermetallic phases [3]. The influence of alloying components and their concentrations in the bath on intermetallic phases formations are very important to generate a brittle or a ductile coating, due to different phases behaviours and thicknesses.

Four intermetallic layers are usually observed in classical Zn, Zn-Pb and Zn-Sn coatings, characterized by with different Fe contents (decreasing from steel substrate to surface [5]). The inner layer, namely  $\Gamma$  phase (generally BCC), is characterized by high Fe content (17-28 wt%), with a very low thickness, often negligible [3].  $\delta$  phase is

characterized by a Fe content ranging between 7.0 and 11.5 wt%, with HPC unit cell and a brittle behaviour.  $\xi$  phase, located between  $\delta$  and outer phase, is characterized by a radial oriented morphology, due to growth mechanisms. It is possible to obtain a notoriented morphology due to different diffusion coefficients of Fe atoms in Zn matrix [6]. External surface is characterized by the presence of  $\eta$  phase, that is characterized by a ductile behaviour and a chemical composition near to bath composition (with a very low Fe content).

In this work damage and crack propagation in intermetallic zinc based coating phases was investigated in order to evaluate chemical influence of Pb and Sn in the bath, comparing not-alloyed zinc bath.



Figure 1. Section of Zn-based coating with intermetallic phases.

# MATERIAL AND EXPERIMENTAL PROCEDURES

In this work seven different bath compositions were used to generate zinc-based coating on the specimen. For all investigated Zn coatings procedures, 3 mm thick commercial carbon steel plates were considered. Table 1 shows the steel chemical composition. All Zn and Zn-based baths were Fe saturated.

Prior to galvanizing, steels samples were degreased and rinsed with alcohol. Subsequently they were pickled in an aqueous solution 20%  $H_2SO_4$  at 50°C for 10 minutes, washed in fresh water, fluxed in an aqueous solution containing 280 g/l ZnCl<sub>2</sub> and 220 g/l NH<sub>4</sub>Cl at environment temperature for 2 minutes and then they were dried for 10 minutes at 100°C. After this procedure, they were immediately dipped into the galvanizing bath, that is held at 460 ± 2 °C, for 60 seconds. Finally, they were cooled in air.

С	Si	Mn	Р	S	Al	Fe
0.090	0.167	0.540	0.010	0.004	0.051	Bal.

Table 1: Chemical composition of the steel used as substrate (wt%).

Bending tests were performed by means of a non-standard device (Fig. 2a,) and repeated at least three times for each considered condition. An electromechanical 100kN testing machine was used, considering a crosshead displacement equal to 35 mm, that corresponds to a bending angle equal to  $30^{\circ}$  (Fig. 2c) [7-10].

Finally, in order to identify the damaging mechanisms for each investigated loading condition, longitudinal sections of the bended specimens were metallographycally prepared and observed by means of an optical microscope (LOM).

The damage level was evaluated in term of "cracks density", that corresponds to the cracks number contained in a specimen length equal to  $1000 \ \mu m [9, 10]$ .



Figure 2. Clamping system for bending test (on the left). Different clamping configurations (on the right): a) Starting position; b) Pure applied bending moment; c) 30° position [11].

#### **RESULTS AND DISCUSSION**

Moment-curvature results of bending tests are reported in Fig. 3, where Zn-Pb and Zn-Sn coatings are compared with pure Zn coating. Both Pb and Sn additions to Zn bath influence coating bending resistance identifying an optimal value: 8% of Sn and 0.5% of Pb, respectively. Highest values are obtained with Sn additions.

Fig. 4 shows the influence of Sn and Pb bath contents on intermetallic phases thicknesses evolution. Higher bending resistance is obtained corresponding to the highest  $\xi$  phase thickness values.



Figure 3. Influence of alloy components in the bath on bending strenght: a) influence of Sn [12], b) influence of Pb [6].



Figure 4. Bath chemical composition influence on coatings thickness and on intermetallic phases: a) and b) Sn influence, c) and d) Pb influence.



Figure 5. LOM intermetallic phases damage analyses on Zn and Zn-Sn coatings (etching nital 1% - 20 seconds).

Damage evolution investigation performed by means of a LOM analysis of bended specimens transversal sections showed a different coating behaviour depending on the stress state and on the bath chemical composition (Figs 5 and 6). Considering

compression stresses, for all the investigated bath chemical compositions, no mechanical cracks were observed, but only some thermal cracks were obtained corresponding to  $\delta$  phase.



Figure 6. LOM intermetallic phases damage analyses on Zn and Zn-Pb coatings (etching nital 1% - 20 seconds).

Focusing coatings under tensile stress conditions, radial cracks in  $\delta$  and in  $\xi$  phases were observed for all the investigated conditions. These cracks initiate corresponding to  $\delta$ - $\Gamma$  interfaces and propagate in  $\delta$  phase, arresting at  $\delta$ - $\xi$  interface or propagating in  $\xi$  phase, where no cracks initiation was observed. No cracks were observed in  $\eta$  phase.

Considering coatings obtained using baths with Pb-0.5% and Pb-1%, some longitudinal cracks in  $\delta$  and at  $\delta$ - $\xi$  interface were observed, due to different mechanical behaviour of intermetallic phases (Fig. 6). Coating obtained from bath containing Sn-8% shows  $\delta$ - $\xi$  interface longitudinal cracks (Fig. 5).

Fig. 7 shows damage parameter on Sn and Pb contents compared with damage of Zn coating (defined as cracks/coating lenght).



Figure 7. Influence of alloy components in the bath on intermetallic phases damage: a) influence of Pb, b) influence of Sn.

For all the investigated coating conditions,  $\delta$  phase was more damaged than  $\xi$  phase, and presence of Pb increases damage in  $\delta$  phase. Lower damage level in  $\xi$  phase for both Pb-1% and Sn-12% coating was probably due to the not oriented morphology of this phase. Sn influences damaging level and micromechanisms: lower Sn contents (3%) implies a damage increase localized in  $\xi$  phase (probably due to its colonnar morphology); higher Sn contents (at 8 and 12 wt%) are characterized by a more and more evident damage in  $\delta$  and in  $\xi$  phases.

#### CONCLUSIONS

In this work, bending resistance and intermetallic phases damage of Zn and Zn-based coatings were investigated considering different bath chemical compositions (three different Pb contents from 0.1 up to 1.0 wt% and three Sn contents from 3 up to 12

wt%, compared with pure Zn bath), analyzing damage mechanisms by means of metallographic measurements performed on longitudinal sections of tested specimens.

Damage was identified as radial and longitudinal cracks and different damaging mechanisms were proposed considering different phases morphology and mechanical properties.

Following results can be summarized:

- no cracks were observed in investigated coatings under compression stress state (for all the observed intermetallic phases);

- no cracks were observed in ductile η phase;

- considering coatings under tensile stress state, radial cracks nucleate in  $\delta$  phase and propagate in  $\xi$  phase, depending on the Pb content; for Pb-1% and Sn-12%,  $\xi$  phase peculiar morphology implies an increase of the difficulty for the crack propagation from  $\delta$  phase, with a consequent increase of the importance of longitudinal cracks in  $\delta$  phase.

- Lowest Sn contents imply a decreases of the damage level in  $\delta$  phase.

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