NOVEL ZINC-BASED ALLOYS USED TO IMPROVE THE CORROSION PROTECTION OF METALLIC SUBSTRATES

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ABSTRACT

The protection of metallic structural components against corrosion is fundamental to preserve their mechanical properties in aggressive environments. Zn-based coating represents one of the most used techniques to make protective coatings for metallic substrates. In the present paper, two types of novel zinc-based coating are proposed, by employing either a tin addition or an aluminium-tin-copper addition to the traditional zinc bath. The behaviour of steel-coated specimens under bending is experimentally and numerically investigated by considering different bath dipping times. A quite satisfactory agreement

between experimental and numerical results is observed, especially under plastic behaviour regime.

Keywords: bending resistance, experimental test, intermetallic phase, numerical model, zinc coating.

1. INTRODUCTION

The Hot-Dip Galvanizing (HDG) process represents one of the most common techniques used to protect metallic structural components against corrosion, in particular those made of iron-based alloys.

Such coatings are employed, for example, in applications such as automobiles, sun-power plants and offshore platforms and, in general, in all the applications where time to mission is much more significant than life of coatings. Their large diffusion is due to both low production costs and high resistance to corrosion in many aggressive environments, also in presence of zones not-well galvanized (uncoated zones or black spot defects) [1-3].

The HDG process consists in creating a zinc-based coating over the components to be protected [4,5]. The interdiffusion phenomenon between iron-atoms of the support and zinc-atoms of melting bath generates multilayer coatings, named intermetallic phases, which are characterised by different thickness, chemical and mechanical properties. Such a phenomenon is mainly influenced by melting bath temperature and immersion time.

The inner zone of coating is characterized by high contents of iron. The content of zinc is predominant in outer zone, being the surface composition closes to the chemical composition of the bath: as a matter of fact, its formation is due to the solidification of the wet layer after extraction from the bath.

Between inner and outer zones, there is the stability of intermetallic phases according to the equilibrium diagram [5]. The inner phase, named δ phase, is a hexagonal phase, characterized by iron content equal to about 7-12% by weight (7-12 wt%). The ζ phase has an iron content equal to about 5-6 wt%. The external phase, named η phase, is characterized by a low value of iron content. Usually all phases with an iron content greater than 12wt% are named Γ phase.

In order to optimise both mechanical and chemical properties of coating, alloys of metallic elements may be added to the galvanizing bath.

Influence of copper, cadmium and tin additions on both morphology and thickness of galvanized coatings was studied by Katiforis and Papadimitriou [6]. They observed that copper, being characterized by a similar atomic diameter of iron, formed a ternary Fe-Zn-Cu intermetallic compound, which crystallised as δ phase. The ζ phase growth was hindered. Cadmium promoted both ζ phase and Γ phase, whereas δ phase was hindered. No change in both morphology and thickness of galvanized coatings occurred with the addition of tin, up to 3% in the galvanizing bath. They

concluded that δ phase growth was responsible of nucleation and propagation of transverse cracks, parallel to the steel substrate, causing the flaking of the coating.

Shibli et al. [7] analysed the addition of a 0.1% mixed oxides (Aluminum oxide and Titanium dioxide) to galvanized coatings, which was found to improve both the metallurgical structure of the coating and the effectiveness against corrosion protection in highly aggressive environments.

More recently, Di Cocco [8] have investigated tin and titanium additions to galvanized coatings, by observing that the presence of tin does not change intermetallic phases characteristics of traditional galvanized coatings, whereas a titanium addition leads to the presence of an outer zone formed by a double-phase ductile matrix and a brittle dispersed phase. A tin addition causes high bending strength and good elastic recovery properties, unlike of a titanium addition.

Di Cocco et al. [9] have analysed the influence of copper, lead, tin and titanium additions to galvanized coatings. The brittle behaviour of δ phase is emphasised by the presence of lead (not observed in coating with tin addition). The presence of copper leads to lower coating thicknesses and low values of radial damage (radial cracks density). Tin seems to be a good substitute of lead. The presence of titanium causes high reactivity to the bath and higher values of thicknesses with respect to the other investigated additions.

Natali et al. [10] have evaluated the influence of titanium addition to galvanized coatings. They have observed that, under suitable conditions of both bath temperature and cooling rate, it is possible to obtain colored coatings. Regarding mechanical properties, such a coating shows more fragile behavior than a traditional galvanized coating.

The problem of improved zinc-based coatings of metallic materials is very challenging, still open and worthy of investigation [11-23].

In the present paper, two different types of improved zinc-based coatings are analysed, with the coating obtained employing either a tin addition or an aluminium-tin-copper addition. Firstly, the mechanical behaviour of the two aforementioned coatings is experimentally analysed by performing bending tests on galvanized ipersandelin steel plate specimens. In particular, five different dipping times of the support into the bath are examined and, for each of them, the intermetallic phase thicknesses are measured in order to evaluate the kinetic formation. Then, a 2D Finite Element (FE) model is implemented in order to simulate the above experimental tests. The bending behaviour (in terms of bending moment against half-bending angle) is numerically investigated by implementing into the model both intermetallic phase thicknesses (experimentally measured) and loading and boundary conditions applied during tests. A numerical non-linear static analysis is performed.

A quite satisfactory agreement between experimental and numerical results is noticed, especially under plastic behaviour regime. The present study can be considered of direct relevance to the practice of engineering failure analysis.

2. EXPERIMENTAL CAMPAIGN

2.1 Specimens

Two series of rectangular 80x25x3mm specimens are obtained from two hot-rolled ipersandelin plates (named Support 1 and Support 2 in the following). The mechanical properties of Supports 1 and 2 are reported in Table 1 and Table 2, respectively.

Table 1.

Table 2.

Samples are polished by degreasing and cleaning of oxides and hydroxides compounds [9]. Then, specimens are washed in fresh water, and fluxed in an aqueous solution [9]. A warm air current is used to dry the fluxing wet solution in order to generate a layer of double salt, which produces a reducing atmosphere around the surface during dipping operations. The reducing atmosphere is characterized by ammonia vapor, which inhibits oxidizing process

of steel at high temperature at contact of the bath surface (bath temperature equal to $460 \pm 2^\circ\text{C}$) [9].

Two different types of improved zinc-based coated specimens are analysed, with a coating obtained employing either a 3% in weight tin addition (named Series 1 specimens), or a 5% in weight aluminium, 1% in weight tin, 0.5% in weight copper addition (named Series 2 specimens).

For each of the above series, five dipping times, Δt , equal to 15, 60, 180, 360, and 900s, are examined. It has experimentally been observed that dipping time influences both coatings in terms of phase thicknesses (Fig.1) and intermetallic phases formation (Figs 2, 3). In particular, there are two common phases in each galvanized series, that is:

- δ phase, characterized by high content of iron (equal to about 7-12% in weight), located in the inner zone of the coating;
- η phase, characterized by low content of iron (lower than 5-6% in weight), located in the outer zone of the coating.

Figure 1.

The measurement of intermetallic phase thicknesses for both series is performed by means of an Optical Light Microscope (OLM), and the corresponding values are shown in Figure 1. OLM analysis on both series specimens shows the presence of a third phase which is

ζ for Series 1 specimens (Fig.2) and lamellar for Series 2 (Fig.3), each of them situated between δ and η phase (Figs 2,3).

Figure 2.

Figure 3.

2.2 Experimental tests

On each Series of specimens, three experimental bending tests were performed for the five values of dipping time examined, by employing an electromechanical non-standard device, shown in Figure 4. Such a device does not allow specimens to roll, minimizing their interaction with the supports, and ensures a constant bending moment in all the sections of the specimen.

Figure 4.

2.3 Results

The experimental results related to the above bending tests, in terms of bending moment against half bending angle of specimen, are shown in Figure 5 for each considered dipping time.

As can be noted, the increasing dipping time leads to higher bending moment values, and this effect is more pronounced for Series 2 specimens due to their higher bath reactivity.

Figure 5.

Tension and compression sides of the tested specimens are characterized by different damage morphology. In the compression side, the main damage morphology is the formation of longitudinal cracks, as is shown in Figure 2 and 3 for Series 1 and Series 2 specimens, respectively. In the tensile side, the main damage morphology is given by radial cracks in many of the investigated conditions. Assuming the ratio 'number of radial cracks/deformed arc length' as damage parameter, the different coatings behaviour of Series 1 and Series 2 specimens is shown in Figures 6 and 7, respectively.

Figure 6.

Figure 7.

3. NUMERICAL SIMULATION OF EXPERIMENTAL TESTING

3.1 Finite element model

A Finite Element (FE) model is developed to simulate the bending behaviour of the tested coated specimens, for all galvanizing dipping times experimentally examined. A commercial finite element modeling software package (Straus 7, G+D Computing, Sydney, Australia) is used.

By assuming plain strain condition, a 2D model with 4-nodes plates finite elements is employed. Due to the symmetry, only one half of the specimen is modeled (Fig.8). The specimen has a length of 50mm, being such a value equal to the calibrated length of the bent specimen (Fig.4).

Figure 8.

Three layers are piled up for meshing the thicknesses of coating corresponding to the experimentally observed δ , ζ and η phases for Series 1 specimens, whereas δ , lamellar and η phases for Series 2 specimens, whose thicknesses are plotted in Figure 1. A layer of a thickness equal to 3mm is used for meshing the substrate. The bonds between the phases and between the δ phase and the support are perfect.

In order to numerically simulate the experimental boundary condition, the following conditions are modeled:

- for nodes along x_2 -axis (Fig.8), displacements along x_1 -axis and rotation around x_3 -axis are taken equal to zero;

- for nodes along the opposite extreme, rotation around x_3 -axis is applied (Fig.8), by increasing the half bending angle from 0 to 35 degrees, degrees with an increment equal to 1 degree at a time.

For Series 1 specimens, the following stress-strain relationships are assumed:

(i) for Support 1, a constitutive law typical for ductile steels, with the mechanical properties listed in Table 1;

(ii) for both δ and η phase, constitutive laws typical of elastic-plastic materials, with the mechanical properties listed in Table 1 (properties independent of the dipping time);

(iii) for ζ phase, a constitutive law that changes by varying the dipping time, according to Figure 9.

Figure 9.

The assumption (iii) is justified by the fact that, for dipping time equal to 180, 360, and 900 s, the ζ phase experimentally shows a large region characterized by a nonoriented morphology, that strongly modifies the mechanical behaviour of such a phase, while columnar crystals are predominant for lower dipping times.

For Series 2 specimens, the following stress-strain relationships are assumed:

(i) for Support 2, a constitutive law typical for cast irons, with the mechanical properties listed in Table 2;

(ii) for both δ and η phase, constitutive laws typical of elastic-plastic materials, with the mechanical properties listed in Table 2 (properties independent of the dipping time);

(iii) for lamellar phase, a constitutive law that changes by varying the dipping time, according to Figure 10.

The assumption (iii) is justified by the fact that, for dipping time equal to 180, 360, and 900 s, the lamellar phase changes its morphology. On the other hand, the lamella is characterized by a different chemical composition than the matrix, and its formation is probably due to presence of an eutectic liquid during the coating formation in the beginning stages (up to 60s). Exposing the lamella and its matrix at high temperature for more time (180, 360 and 900s) implies the activation of diffusion phenomena which lead to a better homogenization of the chemical composition, changing the lamellar phase morphology and its mechanical properties.

Figure 10.

A numerical nonlinear static analysis is performed.

In Figures 11 and 12, the numerical results in terms of bending moment against half-bending angle are shown for each Series specimens and dipping time examined. The dashed lines represent a scatter band equal to $\pm 1^\circ$, corresponding to the accuracy of the

testing machine. Such results are compared with the experimental ones.

Figure 11.

Figure 12.

A satisfactory agreement between the above results can be observed for Series 1 specimens in Figure 11, especially in plastic region (that is, for half-bending angle higher than 7 degrees). The phase thickness increasing with dipping time leads to appreciably higher bending moment bearing.

However, a satisfactory agreement between numerical and experimental results can be also noted for Series 2 specimens (Fig. 12), except for a dipping time equal to 15s. Figure 12 shows a stronger influence of phase thickness on mechanical behaviour in the case of Series 2 specimens with respect to the Series 1 specimens but, in such a case, a decrease in bending strength is observed for high values of bending angle.

4. CONCLUSIONS

In the present work, the mechanical behaviour of ipersandelin steel plate specimens galvanized with two different types of improved zinc-based coatings has been analysed. In particular,

both a coating with an addition of tin and a coating with an addition of aluminium-tin-copper have been examined, by considering five different dipping times in galvanization bath.

Experimental bending tests have been carried out by means of a non-standard device, which prevents specimens to roll and ensures to have constant bending moment in all specimen sections.

Then, a Finite Element (FE) model has been developed in order to simulate bending behaviour of tested specimens, by performing a non-linear static analysis and implementing suitable boundary conditions.

The agreement between experimental and numerical results is quite satisfactory. Such results show how coating thickness can influence the mechanical behaviour of specimens due to kinetic formation and mechanical properties of intermetallic phases. In particular, this influence is more pronounced for Series 2 specimens characterized by a zinc coating improved with aluminium, tin and copper.

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CAPTIONS

Table 1. Mechanical properties of Support 1 and intermetallic phases δ and η related to Series 1 specimens.

Table 2. Mechanical properties of Support 2 and intermetallic phases δ and η related to Series 2 specimens.

Figure 1. Thicknesses of intermetallic phases for two types of improved zinc-based coating with: (a) a tin addition (3% in weight); (b) aluminium (5% in weight), tin (1% in weight) and copper (0.5% in weight) addition.

Figure 2. Intermetallic phases located at the tensile side of zinc-based coating with a tin addition, at 30° of the half-bending angle, corresponding to a dipping time equal to: (a) 15s, (b) 60s, (c) 180s, (d) 360s, (e) 900s.

Figure 3. Intermetallic phases located at the tensile side of zinc-based coating with aluminium, tin and copper addition, at 30° of the half-bending angle, corresponding to a dipping time equal to: (a) 15s, (b) 60s, (c) 180s, (d) 360s, (e) 900s.

Figure 4. Electromechanical non-standard device used to perform the experimental bending tests.

Figure 5. Experimental bending behaviour of improved zinc-based coated specimens with: (a) a tin addition; (b) aluminium, tin and copper addition, corresponding to a dipping time equal to 15, 60, 180, 360, 900s.

Figure 6. Radial cracks damage, as the number of cracks for deformed arc length, in improved zinc-based coating with a tin addition, against the half-bending angle, corresponding to a dipping time equal to: (a) 15s, (b) 60s, (c) 180s, (d) 360s, (e) 900s.

Figure 7. Radial cracks damage, as the number of cracks for deformed arc length, in improved zinc-based coating with aluminium, tin and copper additions, against the half-bending angle, corresponding to a dipping time equal to: (a) 15s, (b) 60s, (c) 180s, (d) 360s, (e) 900s.

Figure 8. Finite Element model employed to numerically simulate bending behaviour of specimens, and mesh detail.

Figure 9. The stress-strain curve for ζ phase, by varying the dipping time.

Figure 10. The stress-strain curve for lamellar phase, by varying the dipping time.

Figure 11. Numerical bending behaviour of coated specimens, characterised by improved zinc-based coating with tin addition, at dipping time equal to: (a) 15, (b) 60, (c) 180, (d) 360, (e) 900s.

Figure 12. Numerical bending behaviour of coated specimens, characterised by improved zinc-based coating with aluminium, tin and copper addition, at dipping time equal to: (a) 15, (b) 60, (c) 180, (d) 360, (e) 900s.

Table 1.

LAYER	E [MPa]	$f_{y,H}$ [MPa]	$f_{y,L}$ [MPa]	$f_{\max}$ [MPa]	f_u [MPa]
Support 1	190000	450	400	588	533
δ - phase	73000	–	–	210	210
η - phase	73000	–	–	210	210

Table 2.

LAYER	E [MPa]	$f_{y,H}$ [MPa]	$f_{y,L}$ [MPa]	$f_{\max}$ [MPa]	f_u [MPa]
Support 2	150000	–	–	450	350
δ - phase	73000	–	–	210	210
η - phase	73	–	–	0.21	0.21

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7

Figure 8.

Figure 9.

Figure 10.

Figure 11.

Figure 12.