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Bath chemical composition influence on intermetallic phases damage in hot dip galvanizing

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Abstract

The aim of this work is the analysis of the hot dip zinc coated steel plates mechanical properties by means of a traditional four-point bending test, performed on coated specimens at three different bending angles.
Results are analysed both in terms of mechanical behaviour and phase damages of coatings. The influence of the chemical composition of zinc baths is correlated to intermetallic phase formation and their damages. It is found that, depending on the bath composition, the different phases can form in different amounts, influencing the mechanical behaviour of the coating.

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Keywords: Hot dip galvanizing; bath chemical composition; damage.

1. Introduction

Hot-dip galvanising is one of the most widely used corrosion protection techniques in the world today because it provides effective protection against corrosion in a wide range of aggressive environments, as well as it is easy and economical to produce, as stated by Marder (2000) and Sjoukes (1990). Zinc-based coatings offer high resistance against corrosion due to their dual protective effect:

- a barrier effect that guarantees the insulation of the metal substrate from the aggressive environment:
- a galvanic protection due to the electrochemical potential of the zinc-based coating, which is lower than that of steel, as reported by Proskurkin and Gorbunov (1972) and Mackowiak and Short (1979).

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The coatings are realised thanks to the phenomena of interdiffusion of zinc and iron atoms on the steel surface, generating zones with different chemical composition, as in D'Agostino et al. (2017), Iacoviello et al. (2006), Natali et al. (2014), and Vantadori et al. (2017). In particular, the parts close to the substrate are richer in iron, while the outermost zones are characterised by a chemical composition similar to that of the melting bath. This means that the thickness is characterised by the presence of different stable phases.

There are four main intermetallic phases in zinc coatings (Marder (2000)), as visible in Fig. 1. The inner phase is a Γ phase, which is generally identified with all phases containing quantities of iron between 17% and 28%. Generally, in coatings, this phase is characterised by high fragility and a thickness that is sometimes negligible compared to the thicknesses of the other phases. The next phase is the δ phase, characterised by an iron content between 7% and 11.5% by weight. Its morphology is compact, and its behaviour is brittle. Moreover, its hardness is sometimes greater than the hardness of the steel used as a substrate to be protected, especially if it is made of steels with low carbon content. Then the coatings are characterized by the presence of a ζ phase, whose iron content is between 5% and 6% and is characterised by a typically columnar morphology which, with longer permanence and high temperature (e.g. in baths at 460 °C for times longer than 360 s) can degenerate into a non-oriented morphology. On the external part of coating, there is the presence of a η phase characterised by low iron content, whose chemical composition is similar to that of the galvanising bath. It is characterised by low hardness values and higher toughness than the other intermetallic phases. It represents the outermost part of the coating and its formation is mainly due to the wettability of the iron-based alloy used to form the coatings.

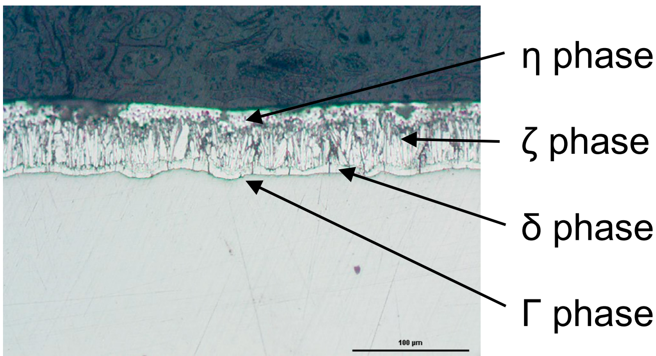

Fig. 1. Intermetallic phases which characterize the traditional hot dip galvanized coatings.

This type of coating is typical of traditional baths, in which additions of alloying elements are sometimes made to improve wettability and fluidity, as observed by Nairin et al. (1992), Kim et al. (2000), and Lin et al. (1997). The presence of alloying elements can change both the kinetics of intermetallic phase formation and the nature of the phases. In particular, some alloying elements, which do not change the nature of the Zn-Fe intermetallic phases, can act on the fluidity of the bath (lead additions were generally made for this) in order to have more homogeneous and defect-free coatings. These elements essentially act on the formation of the external phase η, as it essentially results from the solidification of the alloy present in the bath drags during the extraction operation, as indicated in Volpe et al. (2015), Di Cocco V. (2012), and Duncan et al. (1999). The addition of elements that interfere with the interdiffusion phenomena between Fe and Zn, such as titanium, leads to the formation of both phases similar to those found in traditional coatings, and to the formation of different phases.

The objective of this work is to study the effects that some alloying elements, present in the molten zinc bath, exert on the kinetics of intermetallic phase formation by analysing different immersion times.

2. Materials and methods

In this work, specimens of hypersandelin steel were used, the chemical composition of which is given in Tab. 1. These specimens, rectangular in shape 80x25 mm, were obtained by machining a 3mm thick hot rolled steel sheet.

Tab. 1. Chemical composition of galvanized plates.

C	Si	Mn	P	S	N
0,090	0,167	0,540	0,010	0,004	---

The specimens were subjected to pre-galvanising preparation by cleaning the surfaces both with solutions, containing surfactants to eliminate impurities of greasy nature, and acid baths, obtained by diluting hydrochloric acid at room temperature, capable of eliminating iron oxides and other compounds present on the surface deriving from corrosion phenomena. Finally, the surfaces to be galvanised were subjected to fluxing by immersion in a 500 gr/l solution of double salt of zinc chloride and ammonium chloride, in order to obtain a thin surface layer which is able to protect the steel during galvanising, thanks to the sublimation of the salt which forms, near the steel-zinc bath contact, an atmosphere based on ammoniacal fumes, which are strongly reducing. The baths used for galvanising were:

- Pure zinc bath;
- Zinc bath with 3% tin added;
- Zinc bath with the addition of 0.5% copper;
- Zinc bath with the addition of 0.5% titanium.

All the baths were used after 24 hours of homogenisation at 480°C and raised to 460°C for galvanising. Zinc plating was then carried out by immersing three specimens for 15 s, 60 s, 180 s, 360 s and 900 s in order to obtain detailed kinetics of the coating formation.

All specimens were subjected to bending tests using a tool that allows four-point bending tests. Three different bending angles were investigated to ensure an elastic recovery angle of 30°, 20°, and 10° on each head (for a total of 60°, 40°, and 20° of residual total deformation angle between the two clamping zones).

Conventional metallographic preparation, with Nital 2 etching for 15 s, allowed LOM (light optical microscope) analysis of the intermetallic phases present in the coating section, and image analysis in order to investigate the presence of cracks and their path in the coating section in the tensile side of specimens. A damage parameter has been calculated as the number of radial cracks per deformed arc length. This parameter is not able to quantify all the damages because longitudinal cracks and intergranular cracks are seldom observed, but the radial cracks are the main damage which characterize the failure of the tensile zone in bending tests.

3. Results and discussion

In order to highlight the effect of immersion time and chemical composition on the galvanising coatings, a number of galvanisations were first carried out using a zinc bath without any alloying elements. The results of bending tests of these specimens are shown in Fig. 2, where the differences of maximum values of bending moment are due to thicknesses of coatings. In general, the maximum values are observed for higher dipping time.

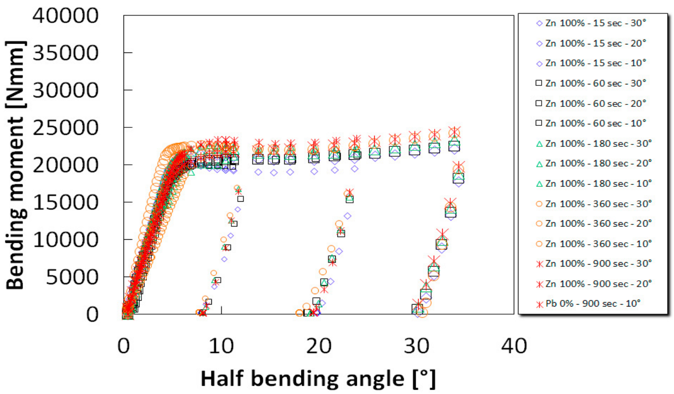

Fig. 2. Bending tests performed on specimens obtained by pure Zn bath.

The bending test performed on specimens galvanized in baths with Sn and Cu addition are shown in Fig. 3. As confirmed by results, the maximum bending resistance is observed in Zn-Sn3% coatings, probably due to the effect of Sn which is the optimizing element of bath used in more commercial applications.

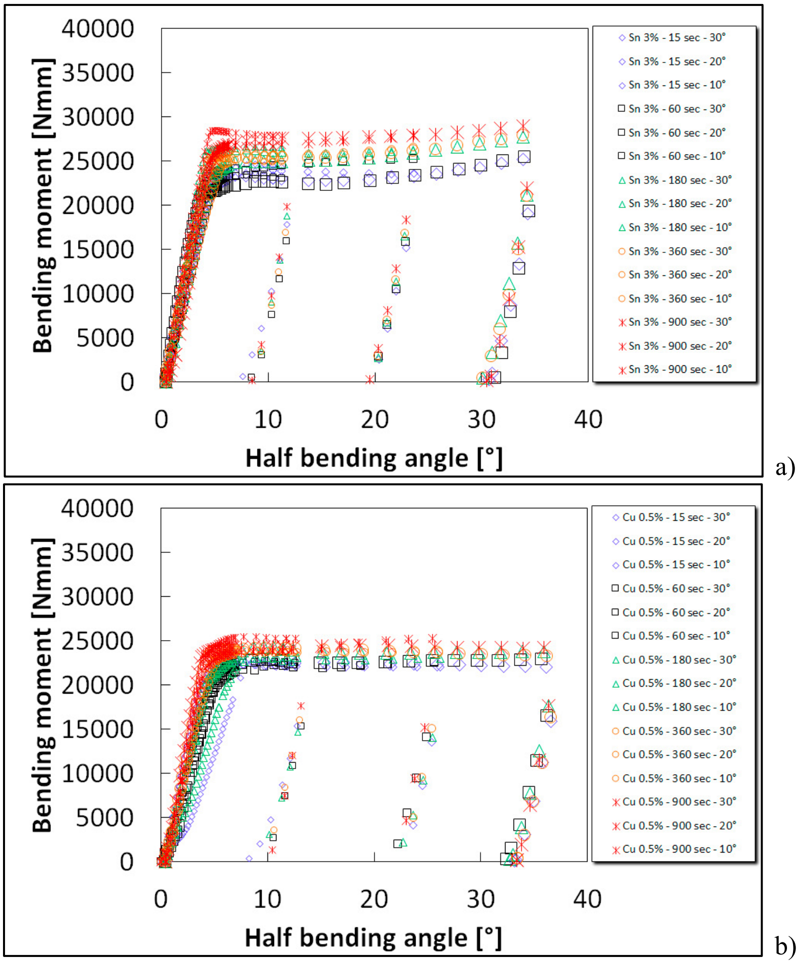

Fig. 3. Bending tests results of specimens galvanized in: a) Zn-Sn3% bath, b) Zn-Cu0.5% bath.

The addition of Ti in the bath leads to non-optimized coatings but is characterized by the ability to change the surface colour, controlling the state of surface oxidation at high temperatures.

In terms of bending performances, as shown in Fig. 4, the presence of Ti shows a wide range of bending resistance, due to the high difference of phase formation kinetics.

The analysis with the optical microscope revealed the presence of three intermetallic phases: the first phase, closest to the surface of the steel sample, is the δ phase. As can be seen from the metallographs in Fig. 5 (similar to phases observed in Fig. 1), the δ phase is damaged by radial cracks due to the different thermal expansion during cooling. In addition, ζ phases with well-developed columnar morphology are present in all the immersion times investigated. Cracks of any kind are absent in these phases, demonstrating less brittle behaviour than in the δ phase. An even more ductile phase, called the η phase, can be observed on the outside. Its presence is due to the reduced fluidity of the pure zinc bath.

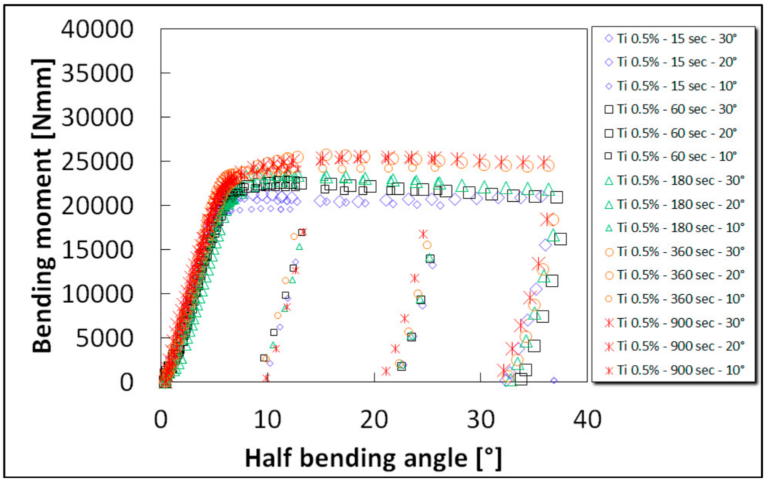

Fig. 4. Bending tests performed on specimens obtained by Zn-Ti0.5 % bath.

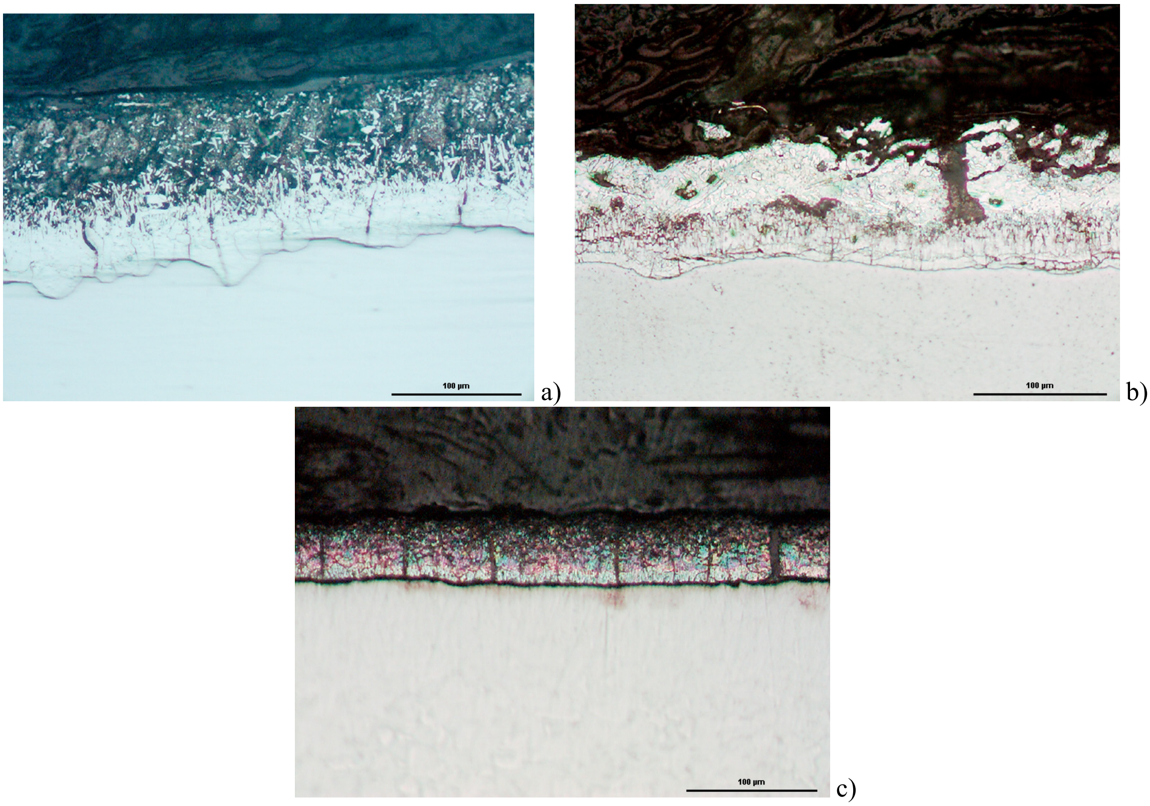

Fig. 5. Metallographic analyses of coatings sections and their damage: a) Pure Zn - 60s, b) Zn-Sn3% - 60s and c) Zn-Cu0.5% - 60s

The same effect has been observed for coatings obtained from baths containing Sn and Cu because these coatings are characterized by the same intermetallic phases. Differences are due only to the different chemical activities of the baths, which leads to different formation kinetics and different thicknesses of both coatings and intermetallic phase layers.

The addition of titanium in the pure zinc bath, up to a value of 0.5%, determines not only a greater reactivity of the zinc bath on the surface of the steel, with a consequent increase in the thickness of the coatings, but also a different formation of the intermetallic phases. As can be seen in Fig. 6, the coatings obtained from this bath present not only a highly developed iron-rich δ phase (high reactivity of the bath), but also a matrix characterised by the presence of a compact but ductile phase, similar to the η phase, with the presence of a lamellar phase.

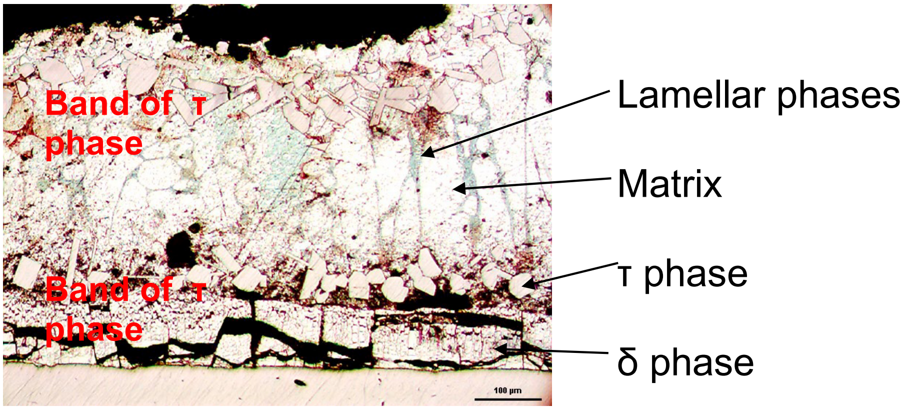

Fig. 6. Microstructure of coatings obtained from Zn-Ti 0.5%.

In addition, within this matrix it is possible to observe the presence of a compact phase, rich in iron and titanium, called the τ phase. This phase develops from the δ phase due to titanium enrichment and detaches from it, migrating into the compact matrix to form different layers, especially at high immersion times. This phase, especially in the outermost parts, can be dispersed in the bath if it reaches the surface or it releases titanium to the compact matrix, forming the lamellar phase. The main characteristic of the τ phase is its high hardness.

In all the investigated coatings the radial crack of δ phases is the main damage of coatings in the tensile side of specimens, and for this reason the number of radial cracks for deformed arc length has been chosen as damage parameter. In figure 7, the damages of δ phases of coatings obtained for 180 s of dipping time for each investigated bath is shown.It is possible to understand as the bending damage sharply increases in the case of coatings obtained from pure Zn baths. The presence of Sn smooths the increment of damage at a higher bending angle, improving the ductility of the coating. The minimum damage is obtained in the coatings with Cu addition. This is due to the increase of toughness as an effect of Cu addition. The coatings containing Ti are characterized by an increment of damage at a high value of deformation similar to the damage observed in coatings containing Sn.

4. Conclusion

In this work, four different bath chemical compositions have been used to obtain galvanized coatings. Specimens have been tested by traditional bending tests and sections of coatings have been analysed by means of a light optical microscope in order to evaluate the presence of cracks and their paths. The results can be summarized as follows:

- The chemical composition of the bath strongly influences the zinc coating phases formation;
- Bending tests confirm that the phases influence the resistance of specimens mainly at high values of deformation;
- In the traditional coatings the crack starts at the iron-coating interface, propagates through the δ phase, and arrests in the ζ phase;
- In coating characterized by Ti addition, the radial cracks are present in the δ phase. Sometimes delamination between δ and three phases zone is present;
- τ phase is characterized by intergranular cracks.

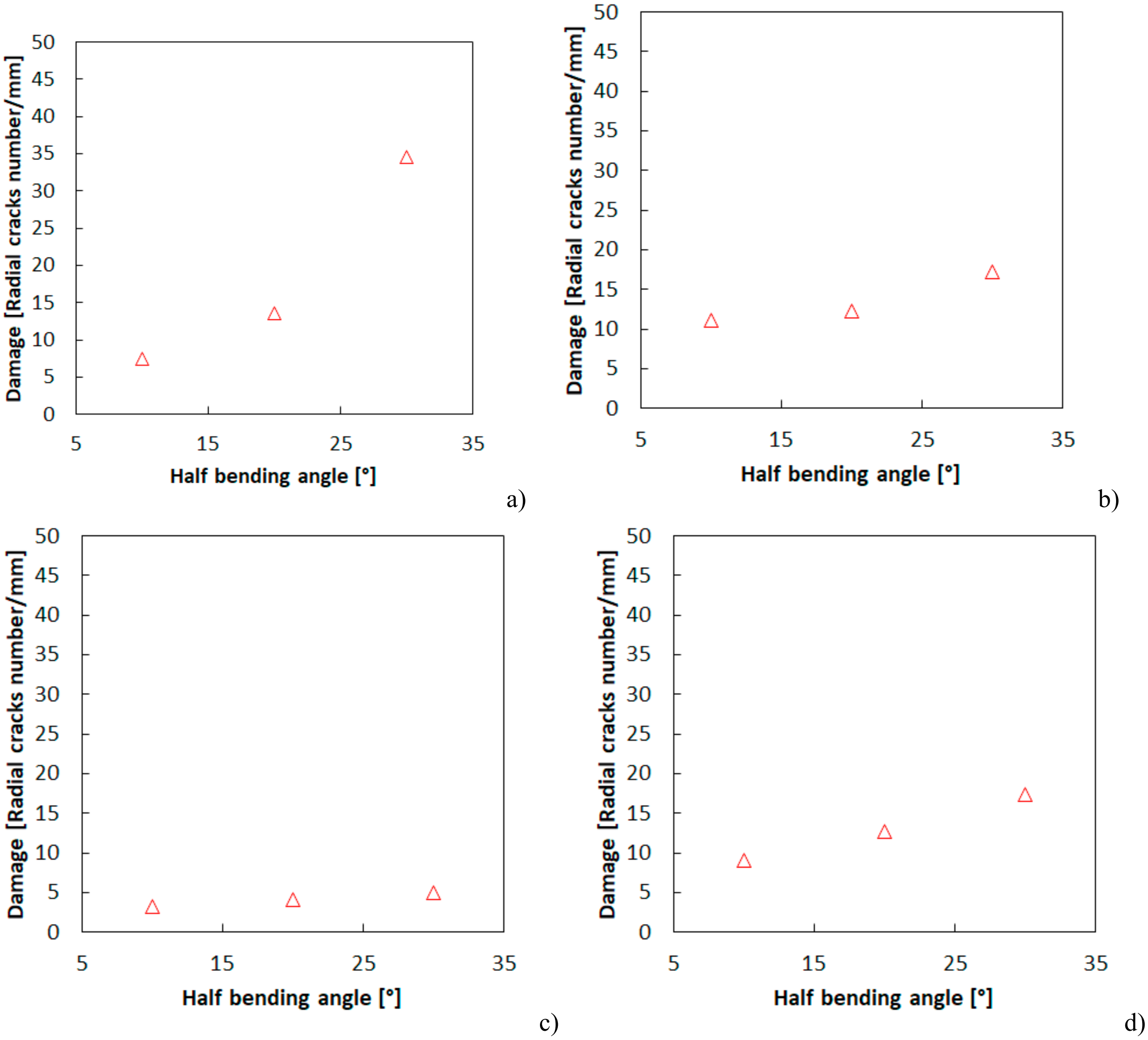

Fig. 7. Damage of some investigated coatings obtained at 180s of dipping time: a) Zn100%, b) Zn-Sn3%, c) Zn-Cu0.5% and d) Zn-Ti0.5%.

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