

Structure-mechanical property relationship in Hot-Dip Galvanized S355K2+N steel plates

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Abstract. The aim of this study is the characterization of hot-dip galvanized S355K2+N steel plates used as components for engineering civil structures. Two thin zinc coatings with a thickness of 145±14 μm and 329±23 μm, were developed at the surface of the plates. Several experimental techniques were performed to study the microstructure, the chemical composition at the surface of the galvanized plates. The residual stress field was also evaluated in the coatings and the top surface of the plates using the incremental hole drilling method, in the rolling and the transverse directions. The results show the presence of tensile stresses and compressive stresses respectively in the coating and the substrate.

Introduction

Corrosion protection is an important step in the manufacturing of steel structures such as thermal spraying, electroplating and Hot-Dip Galvanizing (HDG). HDG treatment is one of the protection techniques of greater importance which generates a coating of an iron-zinc alloy by immersion in a bath of molten zinc at 450°C. Four intermetallic layers: zeta, delta, gamma and eta are formed. The kinetics phase formation and the thickness of the coating are influenced by the content of the silicon and the phosphorus in the substrate [1] as well as the temperature and the time of the immersion in the bath [2]. The hardness of each phase decreases from the Fe/coating interface to the surface with the decreasing of the Fe proportion.

Most galvannealing research focuses on the identification of the chemical composition, the influence of the hold time [3], the alloying elements [4], the resistance of the coating to the corrosion or to the fatigue [5]. However, residual stresses, generated by Hot-dip Galvanizing treatment and their influence on mechanical behavior are seldom studied. Most coatings obtained by deposition techniques (electroplating, DLC, etc) are usually under high compressive stresses [6]. Tensile stresses generated in the HDG coating are generally due to the superposition of intrinsic and thermal stresses [7]. Many techniques can lead to the evaluation of the residual stress such as the incremental hole drilling technique. This method, involves the drilling in a series of small steps, is able to determine stress profiles and gradients in different directions. Thus, quantitative approximation of residual stresses is necessary for the safe performance of steel structures.

Experimental methods

The specific composition of the as-received S355K2+N steel plate (400x300x10 mm³) and the zinc bath are respectively given in Table 1 and Table 2. The plate was cut in three sheet samples (350x100x10 mm³). Two samples, A and B, were considered in order to be galvanized according to standard NF EN ISO 1461, at 450°C with a holding time of 3 min for specimen A and 10 min for specimen B. The coating thickness obtained was, respectively, 145±14 μm and 329±23 μm for A and B. These thickness values correspond to an average of 45 measurements using an Elcomter Device used for the estimation of the coating thickness.

Table 1. Chemical composition of steel substrate [wt.%].

S355K2+N_NF EN 10025- 2/2004	C	Si	Mn	P	S	Cu	Fe
	0,2	0,55	1,6	0,025	0,025	0,55	98,8

Table 2. Chemical composition of zinc bath [wt.%].

Al	Cu	Fe	Pb	Sn	Zn
0,004	0,008	0,02	0,906	0,013	99,049

Optical and scanning electron microscopes were used for metallographic study on the top surface and along the cross-section of the coating and the substrate. Samples were mechanically polished with successively 600, 800, 1200, 2400 SiC papers and finished with 6 μm and 1 μm diamond suspension. The polishing with SiC paper was carried out under ethanol because of the fragility of the zinc towards water. Finally, the samples were etched with an ethanolic 3wt% nitric acid solution (Nital). It was then possible to determine the composition of both coatings using energy dispersive X-ray spectrometry (EDX).

Evaluation of the residual stress was carried out using the hole drilling method with a 2 mm diameter drill. Increments adapted to the thickness of the different intermetallic layers of the coating have been selected. The deformations were measured after each depth increment using CEA-06-062UL-120 strain gage rosettes. The elastic properties (E , $\nu=0,3$) of the different layers [8] and the substrate have been taken into account for the evaluation of the residual stress field employing the finite elements method [9], see Table 3. Gamma layer was neglected in this study because of its very low thickness.

Table 3. Young Modulus of intermetallic layers [8].

	Iron	Gamma	Delta	Zeta	Eta
Young Modulus [GPa]	210	-	140	117	75

Results and discussion

Structural, morphological properties of intermetallic layers. Optical images of the surface of the HDG samples are shown in Fig.1 and display bright and dark areas. Some studies have related these areas to the solidification of the zinc [10]; the solutes are rejected to the grain boundaries leaving the surface relatively pure and bright when dendrites grow parallel to the plate plane. However, when the basal plane is inclined, the growth direction and the rejection of the solutes are towards the coating surface, leading then to dark areas.

Large grains called spangles or flowery patterns have been observed, as shown in Fig. 1. M. Dutta et al [11] have mentioned that lead (Pb), in the bath, is known to contribute to spangle formation.

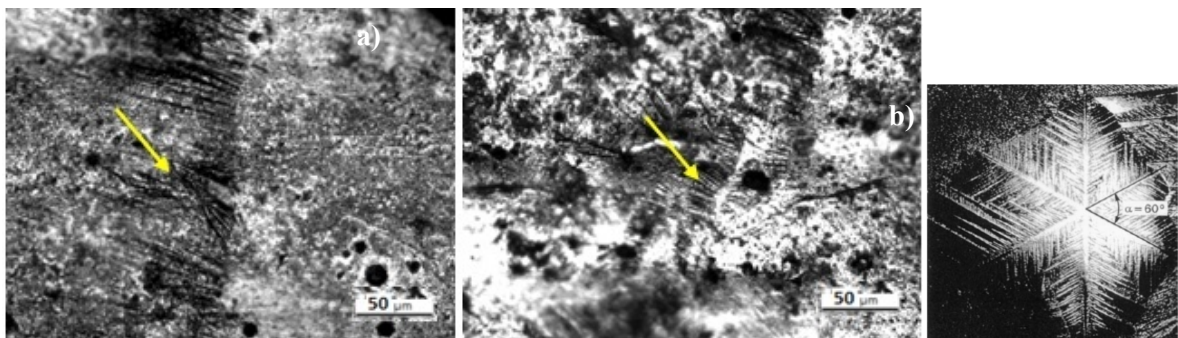


Fig.1. Spangle structure at the surface, a) samples A and B, b) clear spangle structure from literature [13].

Metallographic observations of the cross-sections of the two samples A and B are shown in Fig. 2 and illustrate the presence of different layers due to different diffusion kinetics of iron in the zinc layer: gamma, delta, zeta and eta layers can be distinguished.

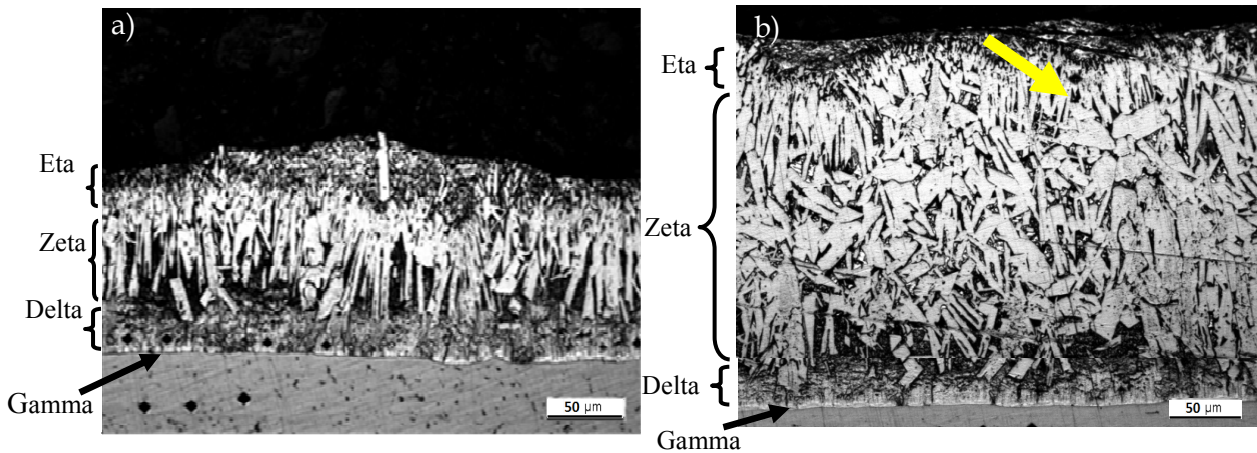


Fig. 2. Metallographic observations of iron-zinc alloy layers: a) sample A, b) sample B. (An arrow, in Fig.2-b, to indicate the presence of fine grains).

Chemical composition and the thickness of intermetallic-layers are presented in Table 4.

Table 4. Characteristics of intermetallic layers of samples A and B.

Fe-Zn layers	Structure	Thickness [μm]		%Zn [wt.%]		%Zn [wt.%] from literature [2]
		A (145 +/-14)	B (329 +/- 23)	A	B	
Eta (Zn(Fe))	Hexagonal close packed	20-35	30-40	-	94,31	98-100
Zeta (FeZn_{13})	Monoclinic (columnar)	70-90	200-270	92,84	93,03	92-96
Delta (FeZn_7)/(FeZn_{10})	Hexagonal (columnar)	20-35	30-40	91,7	90,97	90-94
Gamma ($\text{Fe}_3\text{Zn}_{10}$)/($\text{Fe}_5\text{Zn}_{21}$)	Base centered cubic	1-2	1-2	77,46	54,48	≈ 71

Fe content decreases as a function of the distance towards the substrate-coating interface. The chronological order of the layers nucleation has been explained by Marder [2]. The zeta layer is first formed, after 5s, and is characterized by a columnar grain structure (columnar dendritic structure) with axes perpendicular to the surface. The columnar grain structure is well developed in sample A (Fig. 2-a) as well as in sample B (Fig. 2-b).

At the same time, solidification rate increases and fine grains appear in the top surface, as indicated by the arrow in Fig.2-b. Fine grains ensure the blocking of zinc liquid after its passage between grain boundaries and as a consequence, the crystallographic growth directions and the growth rate of grains change in zeta [12]. Generally, this residual solidified liquid has not the same composition as the liquid in the bath.

The zeta layer nucleation is immediately followed by delta-phase formation. Delta is also characterized by columnar grains. Zeta or delta phases were found to form a continuous layer at the lowest reaction times, i.e. after 5s. The third thin phase formed, after an incubation time of 30 s, is gamma. The last eta-phase just forms at the surface of zeta when the plate is removed from the bath. It is composed of equiaxed grains.

After attack with 3%Nital, some grains have been degraded (black contrast in Fig.3. Typically, they present the eutectic Zn-Pb formed during the crystallization of the solid zinc; they can be enriched

with alloying elements sensitive to the attack and especially with lead. But, Fig. 3 presents the eutectic in other structures (see the arrow and the circle). Grains are not totally degraded, the residual solute was rejected or absorbed during the solidification of the liquid zinc. This phenomenon is called the supercooling; the liquid zinc is "supercooled" under to its crystal homogeneous nucleation without solidifying.

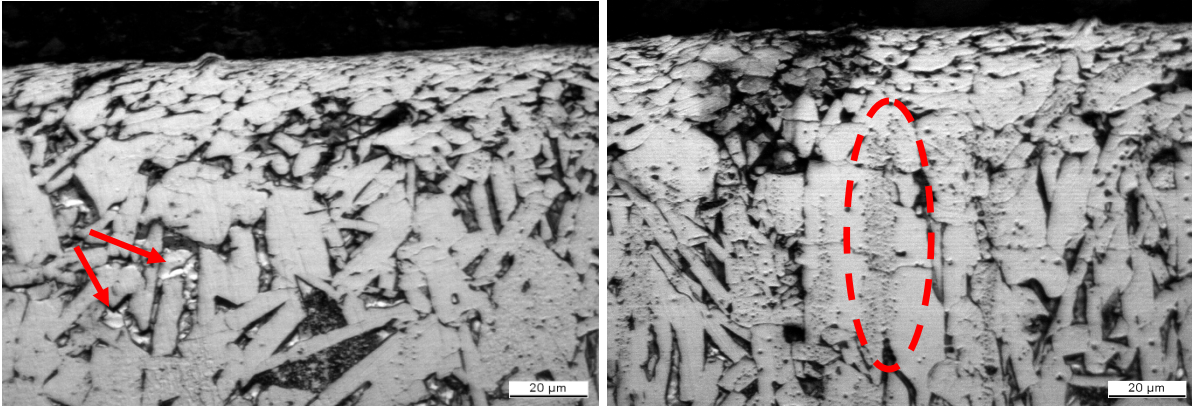


Fig. 3. Optical Micrographs of the eutectic Zn-Pb.

Evaluation of the residual stress using the hole drilling technique. The residual stress profiles were evaluated in the rolling direction (RD for σ_{yy}) and the transverse direction (TD for σ_{xx}), as shown in Fig. 4 (uncoated sample) and Fig.5 (HDG samples). Small increments (20 μm) were performed to finely evaluate the stress in the zinc coating, while bigger increments of 100 μm were selected for measurements in the substrate.

Let's focus on the residual stress profile in the rolling direction (σ_{yy}). In the uncoated sample (ref sample), the surface is affected by compressive stresses because of the effect of the rolling process (see Fig. 4). High tensile stresses can be observed in the A coating because of the holding during few minutes in the zinc bath. The maximum tensile residual stress level is observed at a subsurface depth of 50 μm for both A and B coatings. Following the sign change at the interface, the substrates present a compressive stress. This trend is caused by the high temperature in the bath and by the cooling kinetics of zinc. At the interface, the residual stresses are respectively in A and B, 50 MPa and 25 MPa, compared to -150 MPa before galvanizing. In the substrate, the compressive stresses are concentrated at a depth of 150 μm to 250 μm from the surface in A and B. The compressive stresses seem also to spread into a depth of 250 μm in the reference sample, as for the sample B.

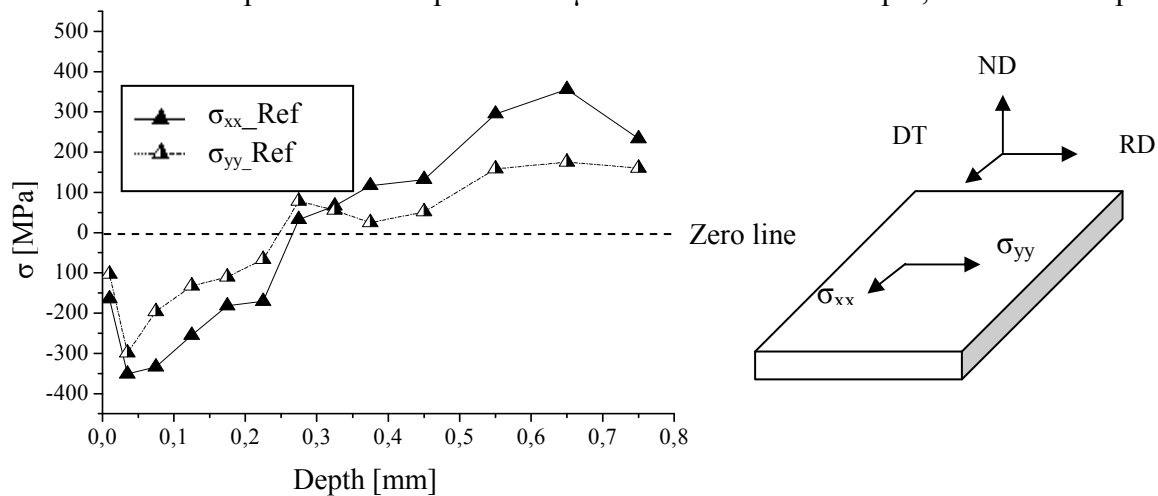


Fig. 4. The hole drilling evaluations of the residual stress along the transverse direction σ_{xx} and the rolling direction σ_{yy} of the uncoated sample (Ref sample).

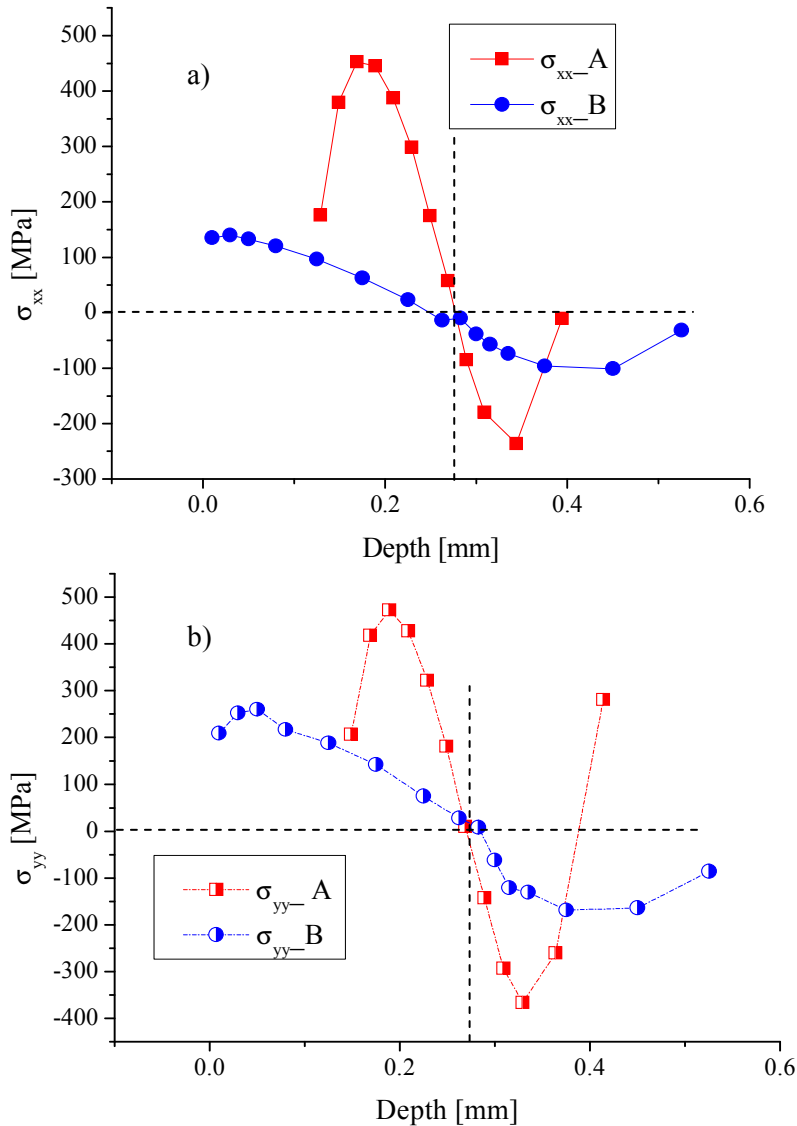


Fig. 5. The hole drilling evaluations of the residual stress along the transverse direction σ_{xx} (a) and the rolling direction σ_{yy} (b) of the HDG samples A and B.

Summary

In order to determine the influence of the holding time in the zinc bath on the stress profile as well as on the structure of the coating, an experimental investigation of two hot-dip galvanized coatings has been performed. We extract from this study the following findings:

1. The holding time increase from 3 and 10 minutes led to a thickness increase of the coating by about 50%; from $145 \pm 14 \mu\text{m}$ to $329 \pm 23 \mu\text{m}$.
2. The growing of the zinc coating led to the formation of spangles in the top surface as well as dendrites.
3. Due to the difference of the thermal expansion coefficient between the substrate and the coating, as well as different mechanisms of the interdiffusion between layers, four intermetallic phases were identified.
4. Like for many crystals during their thermal cycling, the stress changes from the compressive state during the annealing process, to the tensile state during the cooling. The thicker B coating has a lower compressive stress level than the thinner A coating. It can be attributed to the time of immersion in the zinc bath. The residual stress level in the thicker B coating represents about 44% of the residual stress level in the A coating.

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