

A COMBINED CHARACTERIZATION OF ZINC HOT-DIP GALVANIZED WIRES WITH DSC, XRD AND SEM*

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The effect of Pb and Sn on the structure of zinc hot-dip galvanized coatings on steel wires is examined. The coating quality is often low because of the Sandelin effect. An improvement could be expected if 1.0 mass% Pb is added to the Zn bath. In this case the η phase formation is enhanced, while the coating thickness is reduced. The Sn addition at the same concentration promotes the formation of the η phase but it does not affect the thickness.

Keywords: corrosion protection, DSC characterization, hot-dip galvanizing, metallic coatings

Introduction

Hot-dip galvanizing is one of the most effective methods for the corrosion protection of steel and iron substrates [1–3]. It is accomplished through the immersion of the ferrous substrate in a bath of molten zinc, resulting to the formation of a zinc coating on the substrate with an average thickness of a few tens of microns.

Concerning the continuous wire galvanizing lines, three defects were reported: the formation of very thick zinc coating [4], the uncompleted zinc deposition [4] and the Sandelin effect [5]. The thick coatings are brittle and poorly adherent. Consequently it is possible to be separated from the substrate (flaking) during the deformation of the wire. The uncompleted deposition leads to the formation of areas of uncoated steel, while the Sandelin effect consists of very rapid reactions between zinc and iron, thus a very hard and brittle coating is formed with high content of iron in the outer layer.

In order to overcome these problems Al is added to the zinc kettle [1]. However this method does not seem to be always effective concerning the above-mentioned problems. As it was mentioned elsewhere [4], several defects were detected during the microscopic examination of industrially hot-dip galvanized wires in a zinc kettle containing 0.14 mass% Al.

These phenomena could probably be overcome by the replacement of Al with other alloying elements. For this purpose samples with Pb and Sn were examined. The aim of this paper is to evaluate these alternative solutions, after re-examining the industrially galvanized wires because their initial examina-

tion was only microscopic. The examination of that kind offers reliable results when localized phenomena are studied. However, it is not possible to offer any information about the extend of a phenomenon, especially in the case of an industrial product, such as the galvanized wires. Therefore wire samples were examined with X-ray diffraction (XRD) and differential scanning calorimetry (DSC), since these methods, by contrast to microscopy, allow quick data acquisition for a large number of specimens [6–9].

Experimental

Two groups of samples were examined during this project. The first one includes pieces of industrially galvanized wire, which were collected from a galvanized wire mill for a period of time of about six months. The galvanizing process used for the production of these samples is outlined in Fig. 1.

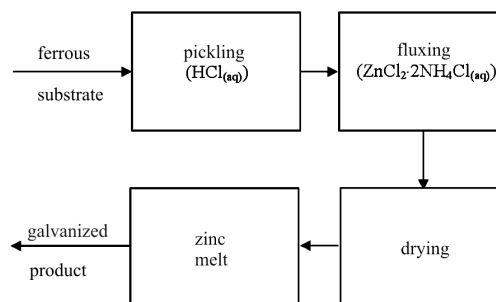


Fig. 1 Schematic diagram of a typical wire hot-dip galvanizing line. The chemicals used in every step are presented in the brackets. The index (aq) implies aqueous solution

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The second group includes samples, which were galvanized in a laboratory scale facility. For that purpose rectangular specimens of steel (3 mm thick, 60 mm long and 7 mm wide) with the same composition to the wire steel were used. The galvanization took place in a Thermolyne 1400 electric furnace inside a graphite crucible. The dipping time was set at 1 min. The specimens were degreased in a solution of a non-ionic tenside containing H_3PO_4 , pickled in an aqueous solution containing 16% HCl and fluxed in an aqueous solution containing 50% $ZnCl_2 \cdot 2NH_4Cl$, before their dipping in the galvanizing bath at a temperature of 450–460°C. The bath was prepared using industrial grade zinc (99.9861% Zn, 0.01% Pb, 0.001% Cd, 0.0012% Fe, 0.0007% Cu and 0.001% Sn). Inside this bath Pb was dissolved at a concentration of 1.0 mass%, while inside another Zn bath Sn was dissolved at the same concentration. Both these metals (Sn and Pb) were of laboratory grade. A few samples were also galvanized in pure zinc, under the same conditions, in order to be compared with the industrially galvanized wires and the coupons which were galvanized in baths containing Pb and Sn.

The characterization of the samples took place with MS, XRD, DSC and SEM. MS was used to perform the chemical analysis of the ferrous substrates. A Spectrolab M8 mass spectrometer was used.

The XRD study was accomplished with a one-cycle Philips diffractometer, where CuK_{α} radiation ($\lambda=1.54406 \text{ \AA}$) was used for the samples of the first group and FeK_{α} radiation ($\lambda=1.936 \text{ \AA}$) for the samples of the second group.

The thermal behaviour of the materials was investigated using a Setaram DSC 141. Temperature and energy calibrations of the instrument were performed using the well-known melting temperatures and enthalpies of high purity zinc and indium. The samples weighing about 15 mg were crimped in aluminium crucibles and an empty aluminium crucible was used as reference. This study was performed by non-isothermal DSC runs by heating the specimens from room temperature up to 550°C with heating rate 10 K min^{-1} .

The examination of the samples was accomplished with SEM. For this purpose cross sections from each sample have been cut, mounted in bakelite and polished down to 5 μm alumina emulsion. The samples have been etched in 2% Nital and the initial observations took place with an Olympus BX60 optical microscope connected with a digital camera CCD JVC TK-C1381. The SEM used was a 20 kV JEOL 840A SEM equipped with an Oxford ISIS 300 EDAX analyzer and the necessary software to perform point microanalysis, linear microanalysis or chemical mapping of the surface under examination.

Results and discussion

Industrially galvanized wires

The examination of the samples of industrially galvanized wires revealed that the quality of a large amount of the coatings was poor. Their SE micrographs present in a few cases thick coatings (Fig. 2a), while the observation of areas of uncoated steel (Fig. 2b) is not rare.

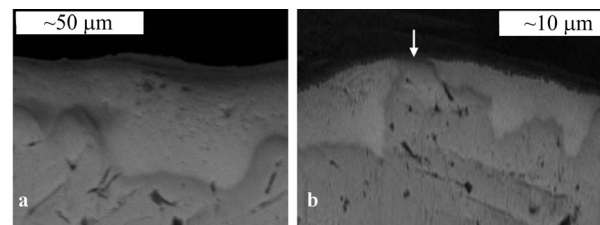


Fig. 2 SEM micrographs of a thick coating on a – galvanized wire and of b – an uncoated area of steel of a galvanized wire (the uncoated area is noted with an arrow)

Moreover XRD and DSC measurements showed that η phase (pure Zn) is completely absent from the outer layer of the coating. At the XRD pattern only the peaks referring to Fe–Zn alloys are present (PDF card#71-0399, PDF card#32-0478, PDF card#33-0697 [10]), as it could be concluded by comparing the XRD pattern of Fig. 3 with the XRD pattern of pure Zn (PDF card#04-0831 [10]). The same conclusion could be drawn by the DSC plot (Fig. 3b), which is characterized by the full absence of the peak referring to the Zn melting [11]. In this figure the curve referring to the samples cast from a pure Zn bath is also plotted, so as to be compared with the DSC plot of the industrially galvanized pieces. In this case the peak of the Zn melting point is obvious. Both these measurements verify that zinc is completely consumed during the galvanizing process forming Fe–Zn phases.

The formation of the η phase is very important because it ‘seals’ the underlying phases, which are composed by Fe–Zn alloys. Thanks to its reaction with some of the atmospheric compounds (O_2 , CO_2 and H_2O), the coating is covered by a layer of highly corrosion resistant Zn compounds [1]. Furthermore it is very ductile, while the Fe–Zn alloys are hard and brittle [1]. As a result, it improves the mechanical properties of the coating, which are of great importance especially in the case of wires, since they are unavoidably deformed during their usage. Consequently, its absence could be detrimental for the field performance of the galvanized coating, without taking in mind the fact that the commercially attractive, shiny appearance of the galvanized objects is owned to its presence.

The absence of the η phase could be explained taking into account the steel composition (Table 1). The data of this table averages the measurements of

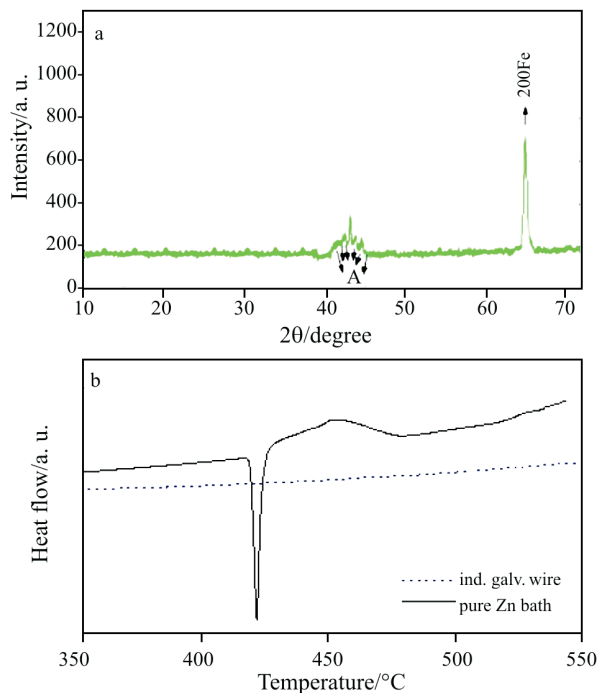


Fig. 3 a – XRD pattern of the industrially galvanized wire (the Fe–Zn phases are noted with A and b – DSC plot of the industrially galvanized wire and the coating formed from a pure Zn bath

40 samples. From this information it is obvious that both silicon (Si) and phosphorus (P) have comparatively high concentration in the substrate. Hence, the conditions strongly favour the Sandelin effect [5]. As a result the Fe–Zn reactions are rapid and consequently the coating is composed only by Fe–Zn phases as XRD and DSC showed (Fig. 3).

The addition of Al is supposed to inhibit this phenomenon because a layer of an intermetallic compound with the chemical formula $\text{Fe}_2\text{Al}_5\text{Zn}_x$ is formed at the interface of the substrate and the coating. This layer inhibits the formation of the Fe–Zn phases [1]. Consequently the as-formed coating is composed by only two phases, the first of which is $\text{Fe}_2\text{Al}_5\text{Zn}_x$ and the second is the η phase formed on the outer layer through the solidification of the liquid Zn attached to the surface of the intermetallic as a result of the surface tension. However the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ is rather unstable. After a short period of time in the Zn melt this layer is dissolved and the regular growth begins. This period of time is strongly affected by the Al concentration of the bath [1]. Concerning the Zn bath of the wire mill which provided the industrial samples Al is present at a concentration of about 0.14 mass%, as it was verified by the examination of a sample of the Zn bath with MS. This concentration is in accordance with the literature data [1]. Consequently since the Al concentration in the bath is acceptable, the failure of the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ layer could be explained only by the in-

Table 1 Average composition of the ferrous substrates

Element	Concentration/mass%
Fe	96.867
C	0.080
Mn	1.505
S	0.028
P	0.020
Si	0.900
Cr	0.130
Ni	0.150
Cu	0.320

correct dipping time of the wire. It could be supposed that the dipping time was very long and consequently the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ dissolution was allowed. However the modification of this parameter is not possible because the dipping time influences the coating thickness of the wire. As a result the final product is not conformed to the standards about hot-dip galvanizing.

From the previous analysis it is obvious that the low quality industrially galvanized wires is not something peculiar or unusual. Furthermore this problem is impossible to be solved only through the optimization of the galvanizing conditions. Consequently it is justified to undertake a research at the above topic involving the addition of different alloying elements in the Zn bath apart from Al.

Coatings formed from a Zn–1.0 mass% Pb bath and a Zn–1.0 mass% Sn bath

The next step was the examination of galvanized coatings from two different Zn baths containing 1.0 mass% Pb and 1.0 mass% Sn respectively. Cross-sections of the as-formed coatings were observed with SE Microscopy, while XRD measurements were taken from their lateral surface. Moreover small pieces of them were examined with DSC.

The morphology of the coatings is presented at the SEM micrographs of Fig. 4. On the outer layer of the coating the η phase is observed. The ζ phase is clearly distinguished thanks to its needle-like crystals and the δ phase appears as a thin layer at the Fe–Zn interface. The formation of the mentioned phases was verified by the microanalysis of the coatings (Table 2) and their line scan (Fig. 5). The data presented in Fig. 5 averages 15 measurements almost equally spaced around the circumference of a coating.

The short immersion time during the galvanizing process did not permit the formation of the gamma (Γ) and the gamma 1 ($\Gamma 1$) phases which are known to be formed during a prolonged immersion time [1].

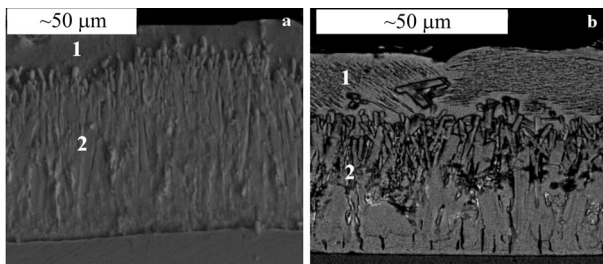


Fig. 4 SEM micrographs of the coatings formed from a – Zn–1.0 mass% Pb bath and b – Zn–1.0 mass% Sn bath. The numbers on the micrographs refer to the position numbers mentioned at Table 2

DSC plots (Figs 6a and b) provided useful information about phase formation. First of all, from this data it is obvious that both Pb and Sn are dissolved in the coating. There are no inclusions composed exclusively by these elements because none of the peaks recorded refers to their melting point (which is 327.4°C for Pb and 231.9°C for Sn). Consequently an alteration of the structure of the coating is expected. However, as SEM proved, this alteration does not affect the morphology of the coating. As a matter of fact, the presence of the η phase was also verified with DSC. Peaks referring to the melting point of Zn are present in every DSC plot. However there is a small shift of the temperature recorded for this transformation, while the initial edge of this peak is not as steep as in the case of pure Zn (Fig. 6). These phenomena could be explained by the fact that other elements are also dissolved in Zn, as it was mentioned before. The presence of Fe (up to 0.03 mass% [1]) is highly possible, while the presence of Sn and Pb is also probable. Nevertheless the same phenomenon could be caused by a small variation of the crystal structure of the η phase.

Furthermore, DSC plots imply also the presence of the ζ phase. At a temperature of about 450–500°C in every plot a wide exothermic peak was recorded. The transformation referring to this peak is irreversible, as it is not observed when the sample is cooled down and reheated. From the shape of the peak it is also possible to deduce that the crystallization of new phases takes place. It is likely that this peak is caused by the reaction between molten Zn and the ζ phase in order to form the δ phase [1].

Regarding the DSC plots of the coatings formed from a Zn–1 mass% Sn bath (Fig. 6) there is a new peak, which was absent from every other sample. This peak was recorded at the melting point of the eutectic alloy between Zn and Sn (198.5°C). Although its height is very low, it is obvious that in the coating there is a certain amount of this alloy. It is probably formed during the solidification of the coating at areas where the Sn concentration was higher. It is difficult to predict its total influence to the behavior of the coating, but it is likely that it affects the hardness of the coating. It is known that these inclusions behave as obstacles to the displacement of the dislocations, so they increase the coating hardness [12]. Furthermore, it is possible to act as corrosion nuclei because of their chemical variation with regard to their environment [13].

Many important data are also offered by XRD. Figure 7 presents the XRD pattern of a coating formed from a bath with 1 mass% Pb. Because of the low intensity of the X-rays, the pattern of Fig. 7 refers only to the outer phase of the coating, e.g. the η phase. From this figure is obvious that there is a preferential growth of the (101) layer. This means that Pb additions strongly alter the crystallographic orientation of the η phase. Although hot-dip galvanized coatings often show a strong (0001) basal plane tex-

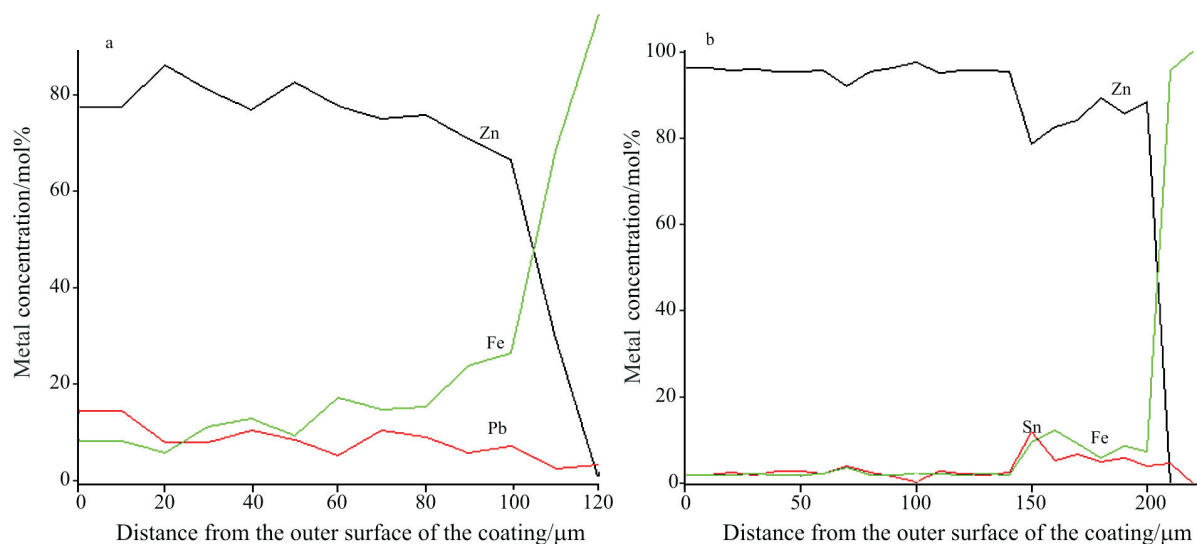
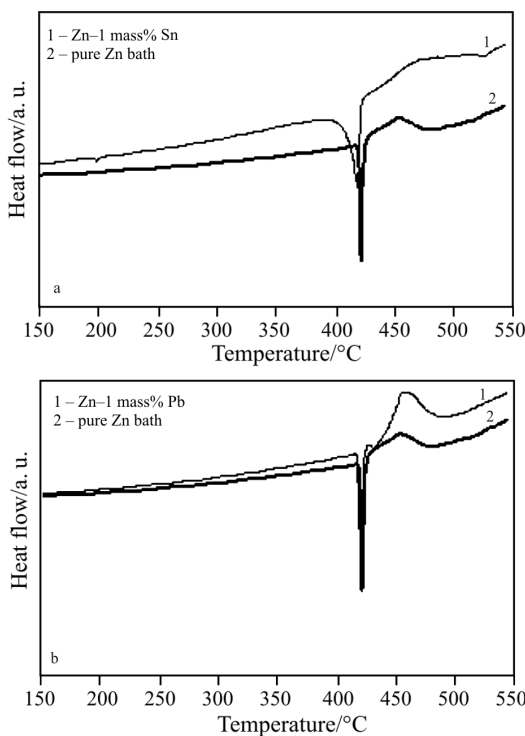


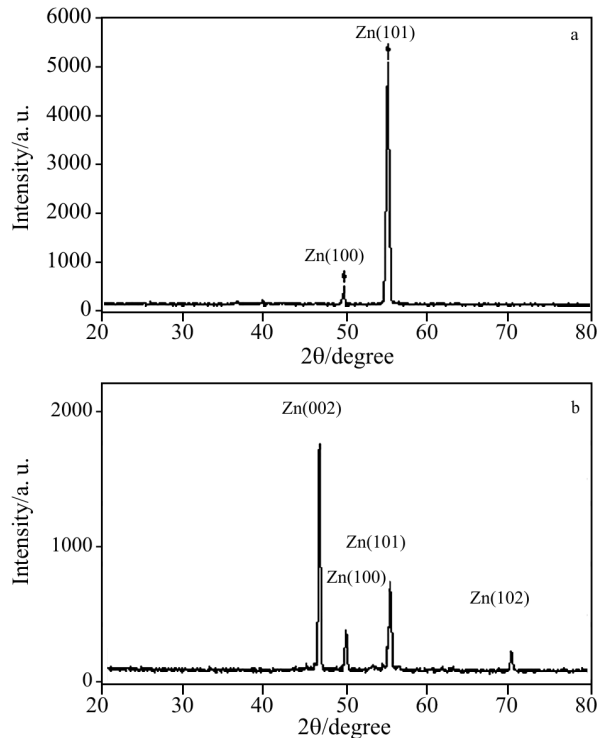
Fig. 5 Linear microanalysis of the coatings formed from a – Zn–1.0 mass% Pb bath and b – Zn–1.0 mass% Sn bath

Table 2 Results of the microanalysis of the coatings formed from a Zn–1.0 mass% Pb bath and a Zn–1.0 mass% Sn bath

Position	Bath with 1.0 mass% Pb		Bath with 1.0 mass% Sn	
	Element	Concentration/mass%	Element	Concentration/mass%
1	Zn	99.48	Zn	99.73
	Fe	0.50	Fe	0.26
	Pb	0.02	Sn	0.01
2	Zn	93.76	Zn	92.23
	Fe	5.94	Fe	6.27
	Pb	0.30	Sn	1.50

**Fig. 6** DSC plots of coatings formed in a – Zn–1.0 mass% Sn bath and b – Zn–1.0 mass% Pb bath

turing [1], in the case of Pb additions the (0001) texturing disappears. The as prepared specimens show a $(2\bar{1}\bar{1}1)$ plane texturing due to a gradual inclination of the basal plane (0001). This inclination probably results from fast growth of the grains in thermodynamically favored directions laid within the (0001) basal plane of the zinc lattice. XRD measurements clearly revealed that the $(2\bar{1}\bar{1}1)$ planes, which consist of very large grains, are almost perfectly parallel to the sheet surface (Fig. 7a). Moreover Pb additions delay the fast thickening of the solid layer, as Pb lowers the surface tension and promotes a planar growth [14, 15]. Thus Pb seems to improve the quality of the coatings and to produce thinner layer. However Sn does not seem to have the same beneficial effect as Pb. Its XRD pattern (Fig. 7b) does not show any preferential orientation of the η phase. Consequently Sn does not affect the coating thickness.

**Fig. 7** XRD pattern of the coatings formed in a bath with a – 1.0 mass% Pb and b – 1.0 mass% Sn

Conclusions

From the above analysis it is obvious that the quality of the zinc coatings cast on steel wires is often low. A very usual observation is the absence of the η phase from the coating. This phenomenon could be explained by the high Si and P content of the substrate that enhances the Sandelin effect.

A certain improvement could be expected if Pb is added in the Zn bath at low concentration (1 mass%). In this case the η phase is formed and consequently the protection offered by the coating is the highest possible. Furthermore Pb enhances the formation of thinner coatings.

Concerning the coatings with Sn, although the presence of the η phase is obvious, the thickness is not affected. Consequently, Pb in spite of the fact that it is hazardous to the human health [16] has a beneficial effect to hot-dip galvanizing, which overcomes the effect of Zn.

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