Structure and hardness of intermetallic compounds obtained by galvanization

Benarioua Younes

Département de Génie Mécanique, Faculté de Technologie, Université de M'sila
BP 166 Ichbilia 28000 M'sila – Algérie
benariouayounes@yahoo.fr

Abstract— **Zinc and some of its alloys have a number of characteristics that make it well suited for use as a protective coating against the corrosion of steel substrates under severe atmospheric conditions. The metal of zinc, which represents the main galvanization element offer then a cathodic protection to the ferrous materials. Because of these excellent characteristics, galvanization coatings are expected to be used for different protective applications fields. The aim of this research work is to study the intermetallic compounds of galvanization coatings deposited on three type steels and obtained at four different immersion times. Steels substrates to be coated in this case are used in agriculture field as tube and irrigation elements in pivot. After a best preparation of there surfaces by different process, various steel of substrates were galvanized in a molten zinc bath maintained at 450°C. During the galvanization process, the chemical reactions that take place between the steel and the liquid zinc give rise to the formation of different intermetallic. Thus, three phases of Γ (Gamma), σ(Delta) and ξ(Zeta) are produced on the steel substrate. Theses metallic compounds have been coated then by a solid solution of iron in zinc η(Eta). The structure of coating was identified by X ray diffraction. The morphology and thickness of phases formed the coatings at different parameters took place with scanning optical microscope. Finally the hardness of coatings was measured with a Vickers hardness tester with different loads.**

Keywords— **Steel, Zinc, galvanization, iron**

I. INTRODUCTION

The generation of zinc and zinc alloy coatings on steel is one of the commercially most important processing techniques used to protect steel components exposed to corrosive environments. From a technological standpoint, the principles of galvanizing have remained unchanged since this coating came into use over 200 years ago [1-9]. 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 [9-14]. The galvanization process is known as one of the techniques frequently used for protecting steels against corrosion [1]. The procedure of galvanization consists in applying a Zn layer to the steel surface, by immersion in a molten Zn bath at 450°C.

The Zn protective coating structure consists of intermetallic Fe–Zn compound layers, which have been identified as gamma, delta, zeta and an outer eta layer, rich in Zn. The gamma phase which appears as a layer located close to the steel material, is only seen when the immersion time is relatively long. Delta and zeta phases are immediately seen and present an important thickness. The eta phase is the outermost phase found on these coatings, and it is basically made of pure zinc, and formed on the surface at the moment of the coating solidification. However, these intermetallic layers which composed of Γ, δ and ζ phases are developed in accord with a Fe-Zn binary phase diagram [3-7].

The purpose of this work is to study the structure, the morphology, and the hardness of phases presented as intermetallic compounds. Hot-dip galvanizing samples of three different steel were obtained at temperature of 460°C at four various immersion times. The samples were characterized point of view, structure, morphology and hardness by using respectively X-ray diffraction, optical microscopy and hardness tester.

II. IRON- ZINC PHASE FORMATION

When iron is immersed in molten zinc at the typical galvanizing temperatures and according to the Fe-Zn system, Horstmann [1,7] proposed that the following layers should form: zinc saturated α -iron, Γ-phase layer, δ-phase layer, ξ-phase layer and η-phase layer. Fe-Zn phase diagram which modified at several times, has been the subject of a number of research papers [1,2]. Zinc rich corner of this binary phase diagram is presented in figure 1.

The zeta phase (ξ - $FeZn_{13}$) has an iron content of approximately 5-6 wt% [2]. This phase is formed from the peritectic reaction between the delta (δ) phase and eta (η) phase which present a liquid of zinc contained iron solute. η-Zn phase which present a solid solution at lower iron concentration is not represented in this system. The phases and characteristics of intermetallic compounds found in the diagram of Fe-Zn are outlined in table 1.
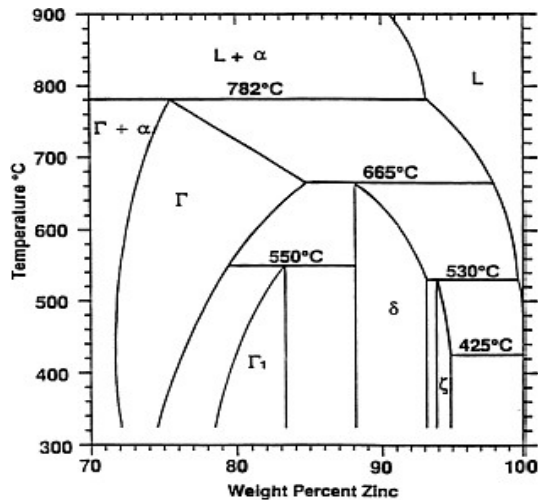
Fig.1. Zinc rich corner of the Fe-Zn binary phase diagram [2].

The primary phases formed during time immersion galvanizing are gamma (Γ), delta (δ), zeta (ξ) and eta (η). According to the phase diagram part and at low temperature treatment, double layers of gamma (Γ-Fe_5Zn_{21} and Γ-Fe_3Zn_{10}) phases can form at the interface between the iron and the delta δ-phase layer. Between 550 and 665C, only the gamma (Γ) phase layer is stable along with the constant thickness delta (δ-$FeZn_{10}$) phase layer. Above 665C, the delta (δ) phase layer is no longer stable and only a gamma (Γ) phase layer forms. Since there is no evidence for flaking of the gamma (Γ) phase layer, this layer probably grows in the linear region just as it grows in both the lower parabolic and upper parabolic regions [6].

Table 1. Fe-Zn phase characteristics.

Phase	Formula	structure	HVN
α- Fe	Fe(Zn)	BCC	104
Γ	Fe3Zn10	BCC	336[2]
Γ1	Fe5Zn21	FCC	505[2]
δk	FeZn7	Hexagonal	280-258 [10]
δp	FeZn10		200 [10]
ξ	FeZn13	Monoclinic	140[2]
η-Zn	(Fe)Zn	HCP	52 [2]

The Γ phase appears as a layer located close to the base material, and it is only seen when the immersion time is relatively long. On the other hand, δ and ξ phases are immediately seen between the inner and outer layer. The phase of δ present two superposed layers ($δ_k$ and $δ_p$) witch present a same physical characteristics but different at point of view metallographic structure.

The phase of $δ_k$ compact and palisade $δ_p$ present respectively a thin continuous strip film side Γ and a thicker strip microcrack side ζ. Adjacent to the delta (δ) phase layer, the zeta (ξ) phase grows in a columnar morphology that is super-saturated in Fe. The zeta (ξ) phase has two layers depending upon the supersaturation of Fe in the melt. The η phase is the outer most phases found on these coatings, and it is basically made of pure zinc, and formed on the surface at the moment of the coating solidification.

III. EXPERIMENTAL DETAILS

Three steels material to be galvanized was used in the field of agriculture. The chemical compositions of these steels were shown in Table 2. Prior to galvanizing, the steel samples were initially prepared by three various steeps. The steel specimens, 30 mm long, 20 mm wide and 3 mm thick, were initially degreased, picked in an aqueous solution containing 16% H_2SO_4 and fluxed in an aqueous solution containing of ZnCl2 and 2NH4Cl. Finally, they were dipped into the galvanizing bath containing the chemical composition of 0.20%Cd, 1.4%Pb, 0.05%Fe, 0.01%Cu and 0.5%Al. The molten zinc was heated in furnace by an electric resistance.

For four different immersion times ranging from 15min to 60 min with a pace of 15 min, the coating of galvanization was carried out in the galvanizing bath at a temperature of about 460°C. The control of the temperature was ensured by a thermocouple. The samples of steel were then quenched immediately in water upon removal from the bath in order to preserve the structure existing at the end of the galvanizing reaction.

The structures of coating galvanization were observed using a Philips MPD diffractometer with a monochromatic Co (Kα) radiation. For the examination of the microstructure, cross-sections from the galvanized coupons have been cut and polished down to 200 Å alumina emulsion. The specimens were etched in a 2% of Nital solution and observations were made by using Nikon optical microscopy.

The thickness of different galvanization layers formed on steel substrate was measured then by optical microscopy. Surface and profile hardness were measured using a Leco microhardness tester. At least three Vickers indentations were performed for each load in order to obtain a significant statistical value.

Table 2. Chemical composition of steels substrates

Element	C	Si	Mn	Mo	Ni	Al
S1	0.25	0.32	1.10	0.01	0.03	0.07
S2	0.17	0.02	1.40	0.01	0.01	0.01
S3	0.1	0.00	0.35	0.01	0.01	0.06

IV. RESULTS AND DISCUSSION

A. Morphology and Structure

X-ray diffraction spectra of coating galvanization obtained for higher immersion time is also shown in Fig. 2. In this case, XRD measurements have revealed the phases of η-Zn, ξ - $FeZn_{13}$, δ_k-$FeZn_7$, and δ_p- $FeZn_{10}$. In this case, no inner phase of Γ is visible.
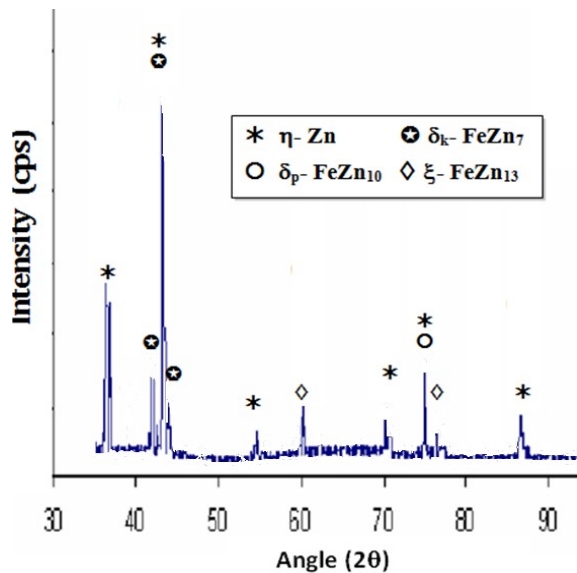
Fig. 2. X-ray diffraction spectra of galvanization coating obtained at immersion time of 300 min

In figure 3, we present typical microstructures of the coatings obtained by two immersion times of galvanization (15 and 60 min). The gamma phase (Γ) appear as a thin layer with a planar interface between the steel substrate and the delta (δ) phase layer. The delta phase (δ) present a columnar morphology as a result of a preferred growth perpendicular to the interface in a direction along the basal plan of coating structure.

It has then two distinct zones which the first is compact δ_p-$FeZn_7$ layer a neighborhood of Γ-Fe_3Zn_{10} layer and the second is δ_k-$FeZn_{10}$ layer palisade nearly of inter-metallic compound ζ-$FeZn_{13}$. Adjacent to the delta (δ_k) phase layer, ζ-$FeZn_{13}$ phase appears and grows in a columnar morphology.

Continued growth of these inter layers occurs rather than the formation of new outer layer of η-Zn phase is formed.

The variation of thickness for different phase forming the galvanization coating as a function of immersion time has been presented in figure 4. We notice that the total thickness of the galvanization coatings increases with increasing of immersion time. The thickness of zeta and eta phases increase with immersion time as parabolic function. However, the growth of the gamma phase with immesrion time present an exponentiel function. When immersion time is above 35 min as shown figure 4, the thickness of the ξ−layer is much thicker than that of η−layers.

The variation of thickness phases can be explained by the kinetics growth of these different solid solutions in galvanization bath. Horstmann [1,6] reported that there is an overall inward movement of the Γ-phase layer towards the steel, whereas the ξ - phase layer is displaced towards the zinc melt.
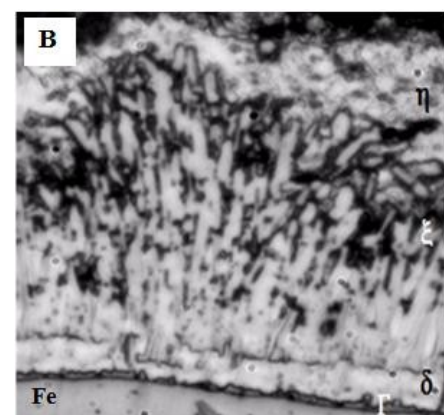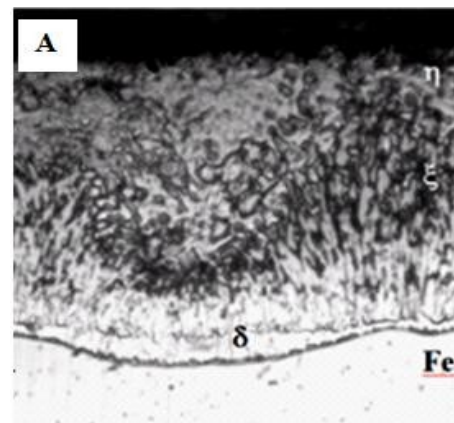

Fig.3. optical micrographs of galvanization coatings obtained by immersion time(a) 15min and (b) 60 min

The δ-phase layer expands in both directions, but generally towards the zinc melt. For three different steel, the thickness of galvanisation increased continuously with immersion time as indicated in fig. 5.
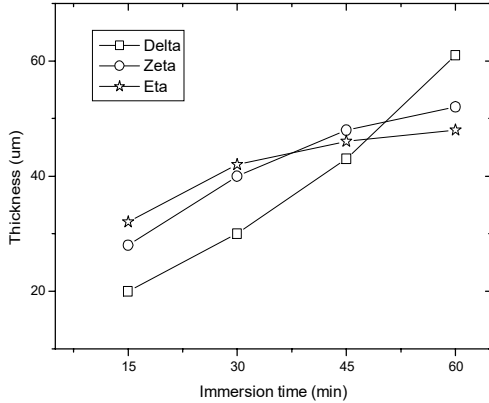

Fig.4. Variation of thickness of phases galvanized S1 steel in function of immersion time

The growth total coatings present then three curve parabolic type. We notice that as indicated in fig. The steel which has element allows present relatively a higher thickness galvanization coating at different immersion times. The presence of silicon element, promotes the formation of Fe–Zn alloys, and produces thicker coatings.
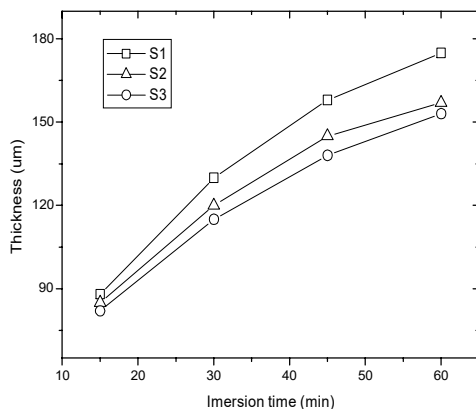

Fig.5. Variation of total thickness of galvanization coated three steels in function of immersion time

B. Kinetics growth

To evaluate the kinetics growth of different inter-metallic layer, a power-law growth equation is generally used to interpret the growth rate data [1], as follows:

$$Y = Kt^n$$

Where Y is growth layer thickness, K is growth rate constant, t is reaction time, and n is growth rate time constant.

Kinetic growth of phase galvanization are presented in table 3. The growth rate time constant, n, is an indication of the type of kinetics controlling the growth of the layer under study.

Tab. 3. Growth rate of phases and total layer of S1

Growth rate	δ-FeZn$_7$	ξ -FeZn$_{13}$	η-Zn	Total layer
n	0.49	0.23	0.19	0.41

An n value of 0.5 is indicative of parabolic diffusion controlled growth, while an n value of 1.0 is representative of linear kinetics in which growth is interface controlled. In our research work, the values of growth rate time constant n tend to be around 0.5 for delta δ phase layer growth and total layer growth.

The kinetics controlling the growth of δ -layer and total coating under different immersion time is parabolic. Values of n for the ξ-phase layer and η-phase layer growth were lower, around 0.25 and 0.19, respectively. In this case, the kinetics which controlled the growth of these layers is linear.

C. Hardness

In order to study the hardness of galvanization coatings, we perform first Vickers indentation for a load of 0.25N and at least three indentations using a LECO microhardness tester. To determine the evolution of intrinsic hardness from coating and substrate, a hardness profile has been applied. A series of microhardness indentations at load of 0.25 N was performed on polished sections of three specimen galvanized at immersion time of 15 and 60 min.

Hardness profiles obtained for the galvanized samples are shown in figure 6. For two chosen immersion period of galvanization, it is shown then that the profil hardness present four zones. For the first zone corresponding to the steel substrate, no hardness variation was found after different treatment time.

The hardness reaches maximum values corresponding to delta phase. This properties was successively decreased and take respectively the value that of zeta and eta phases. This type of characterization allows for confirming the thickness of different galvanization phases observed optically.

Figure 7 present the hardness measurements from indentation performed on cross-section of the sample galvanized at

immersion time of 60 min. We notice that the δ-phase present an elevated hardness compared to the substrate and the other phases of ζ- FeZn13 and η-Zn.
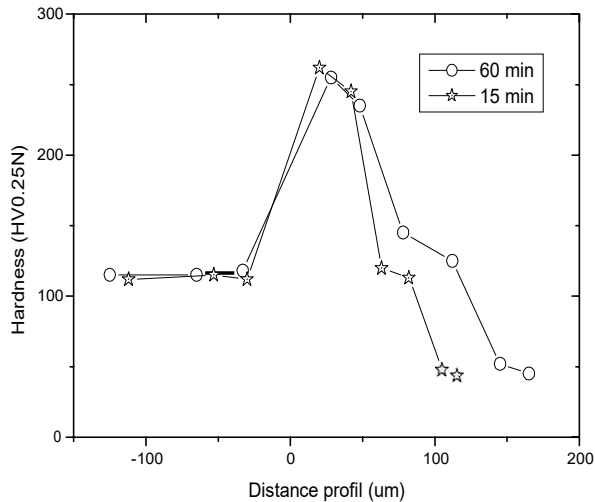

Fig. 6. Hardness profil of S2 steel /coating obtained at immersion time of 15 and 60 min

For delta phase, the hardness reported by several literatures, take generally values of 240 to 280Hv. The elevation of this properties can be explained by residual stress of layer. The hardness of delta zone in our case, take the value of 200 to 250Hv. The galvanization for high time of immersion plays the role of annealing treatment which permits to reduce any residual stress. Fig. 8 shows the deformation of the impressions due to the phase of gamma which presented as thin layer and has a higher hardness.
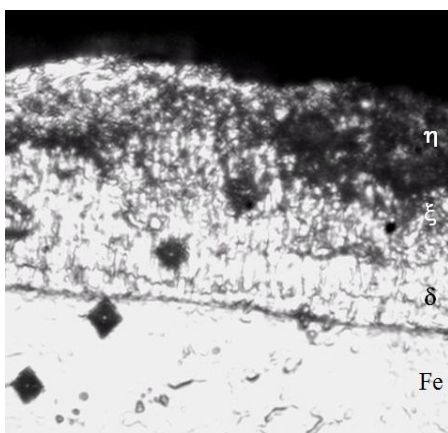

Fig. 7. Micrographic and profil hardness performed on cross-section of steel S1 galvanized at 60 min
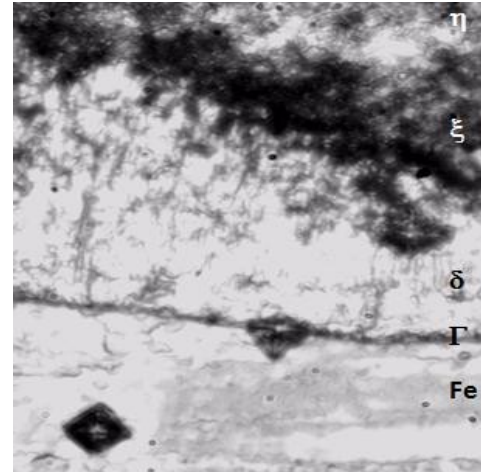

Fig. 8. Impression state obtained on cross-section of steel and phases of galvanization (60 min)

V. Conclusions

The galvanization coatings are used as treatment to improve chemical and mechanical behaviour of steel. The coating obtained for short immersion time, present heterogeneous layer of δ, ξ and η- phase. For average and long immersion time the total coating of galvanization contained the different solid solution produced in galvanization process. In this case, it was found, that the formation of Γ- phase was occur. Among of these inter-metallic compounds, the δ-phase layer was precipitates by kinetic growth parabolic occupy important volume of total coating. The solid solution of δ-phase present then a important mechanical behaviour. The long immersion time produce m higher coating thickness and provide the effect role on of annealing treatment.

References

[1]   D. Horstmann, Zinc Development Association, London 1978
[2]   A.R. Marder, Mater. Sci. 45 (2000) 191.
[3]   P.Bicao, W. Jianhua, S. Xuping , L. Zhi, Y. Fucheng, Surface & Coatings Technology 202 (2008) 1785–1788
[4]   D. Horstmann, F K Peters Proceeding of 9th International Hot Dip Galvanization Conference. London: Zinc Development Association, 1971
[5]   C.E. Jordan, A.R. Marder. Part I. J Mater Sci 1997;32: 55- 93.
[6]   D. Horstmann; Proceeding of 14th International Hot Dip Galvani-zation Conference. London; 1986. p. 6-1.
[7]   M. Onishi, Y. Wakamatsu, H. Miura, Trans JIM 1974
[8]   G.F. Bastin, F.J.J. van Loo, G.D. Rieck; Z Metallkde 1977.
[9]   C.E. Jordan, A.R. Marder, J. Mater. Sci. 32 (1997); 5593.
[10]   G. Vourlias, N. Pistofidis, G. Stergioudis, D. Tsipas; Cryst. Res. No. 1, 23 –29 (2004)
[11]   A.R.B. Verma, W.J. van Ooij, Surf. Coat. Technol. 89 (1997) 143
[12]   C.E. Jordon, A.K. Marder, Metall. Mater. Trans. 25 a (1994); 2101.
[13]   D. Horstmann, Proceeding of 14th International Hot Dip Galvani-zation Conference, Zinc Development Association, London, 1986.
[14]   J.H. Hong , S.J. Oh S. J. Kwon, Intermetallics 11 (2003) 207.