

# THE EFFECT OF SILVER ADDITION ON THE REACTION Fe-Zn IN HOT DIP GALVANIZING

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## الملخص

تعتبر الجلفنة من أهم طرق حماية المشغولات الحديدية من التآكل، ومن أجل تحسين خواص الطبقة الواقية يتم إضافة عناصر معدنية أخرى مثل: الألمونيوم والنحاس والنيكل وغيرها بنسب صغيرة إلى معدن الزنك (المعدن الأساسي في عمليات الجلفنة). وبالرغم من أن هذه الإضافات تؤدي دورا مهما في تحديد بنية الطبقة المتكونة وكذلك معدل نموها، إلا أن ظروف التشغيل مثل درجة حرارة مصهور الزنك وزمن الغمر وكذلك سرعة سحب المشغولات من المصهور لها دورا أساسيا في طبيعة وكفاءة الطبقة الواقية.

يتناول هذا البحث تأثير إضافة الفضة إلى مصهور الزنك في جلفنة عينات من الحديد المحتوي على السيلكون ولأجل التركيز على هذا المتغير أقيمت متغيرات التشغيل ثابتة تقريبا. أظهرت نتائج هذا البحث أن مكونات (أطوار) الطبقة الواقية لم تتأثر بإضافة الفضة إلى مصهور الزنك لجميع التركيزات المختبرة. وظلت هذه الأطوار بدون تغيير حسب ظهورها في منحني الاتزان الحراري للحديد والزنك. أيضا بإضافة الفضة أمكن الحصول على سطح مجلفن وناعم وبراق فضلا على أن زيادة نسبة الفضة قد تساعد في زيادة مقاومة التآكل للصلب. تجدر الإشارة إلى أنه رغم ضآلة كمية الفضة المضافة يجب أن يتم تقييم النتائج المتحصل عليها تقييما اقتصاديا وذلك لارتفاع سعر الفضة نسبيا.

## ABSTRACT

The addition of silver to a bath of molten zinc in hot dip galvanisation process, affects the morphology and the microstructure of the resulted coatings on the surface of the given steel. The effectiveness of the obtained coatings was investigated by: (i) chemical analysis, (ii) thickness measurements, (iii) corrosion salt spray test and (iv) by metallographic observation. It was found that galvanization of reactive steel with molten zinc and silver produces coatings having four phases (Gamma, Delta, zeta and eta) and characterized by bright and smooth surface with visible, numerous and small sized spangles. On the other hand, the corrosion resistance of the galvanized steel was found to increase with the ratio of silver. The experimental results indicate that this behaviour may be related to the microstructural refinement induced by the addition of silver.

**KEYWORDS:** Hot dip galvanization; Silver; Zinc coatings; characterization.

## INTRODUCTION

Hot-dip galvanizing is one of the most effective methods used in the protection of ferrous metals from corrosion. It was established that this method can be improved by the addition of different metallic elements in zinc [1-4]. During the last decades, it has

been established that, depending on the steel geometries and composition, the growth of the alloy layer may be controlled by playing on both the chemical composition of the molten zinc and the physical operating parameters [1,5]. On the one hand, it was shown that the addition of low amounts of certain elements such as Al [6-11], Pb [12], Ge [13], Ti [14], Ni, Bi [15-17] and Cu, Cd, Sn [18] can contribute problem by inhibiting the zinc-steel reactivity and/or increasing the bath fluidity. On the other hand, it was found that, besides the additives, obtaining an acceptable product requires a suitable adjustment of the physical parameters of galvanization [4,5,19], in particular the immersion time [15] which controls the thickness of the alloy layer, the withdrawal speed [5] that controls the amount of unalloyed adhering zinc and the temperature [20] which affects both the alloy (Gamma, Delta and zeta) and the free zinc layers (eta). The effect of some elements such as Al, Ni, Pb, on the steel galvanization was reported by many authors. However, the effect of silver on such process is rarely investigated; therefore the purpose of this paper is to study the effect of adding silver on the behaviour of the formed layer on the surface of the silicon steel as a result of hot dip galvanization.

## EXPERIMENTAL PROCEDURE

The galvanizing tests were conducted into a furnace operating with Special High Grade (SHG) 99.99% of zinc. The molten zinc was contained in a low carbon steel kettle heated by an electric resistance. The control of the temperature was ensured by a K-type thermocouple and a digital temperature regulator. The immersion of the sample in the bath was guaranteed by a pneumatic jack who controls both the duration of immersion and the withdrawal speed.

The experiments were carried out using high-silicon steel samples prepared by cutting thin rectangular slices (30 x 100 mm) of about 1.5 mm in thickness. The composition of the steel is given in Table (1).

**Table 1: Chemical composition of the steel (wt. %)**

C	Si	P	Al	Ni	S	Cu	Cr	Fe
0.104	0.074	0.012	0.057	0.037	0.020	0.067	0.030	bal

Prior to galvanizing, the steel samples were initially prepared in the appropriate solutions. The samples were degreased with a 15% NaOH solution, rinsed with water and then pickled for 30 min with a 16% HCl solution containing 3 g/l of hexamethylenetetramine ( $C_6H_{12}N_4$ ) as inhibitor. They were pre-fluxed at room temperature in a solution containing 550 g/l of  $ZnCl_2 \cdot 2NH_4Cl$ , then dried in an oven at 120°C for 15 min. The galvanizing process conditions are shown in Table (2). Finally, they were dipped into the galvanizing bath, and then quenched immediately in water upon removal from the bath in order to preserve the structure existing at the end of the galvanizing reaction.

**Table 2: Galvanization process conditions**

Bath	Temperature (°C)	Immersion time (min)	Withdrawal speed (m min <sup>-1</sup> )	Ag wt (%)
1	450	2.5	3.5	0.03
2	450	2.5	3.5	0.06
3	450	2.5	3.5	0.09

The thickness of the formed coating layer was measured using an electromagnetic thickness gauge (Elcometer 345). Ten measurements were taken at different locations for each specimen and the average is reported.

For the examination of the microstructure, cross-sections from the galvanized samples have been cut, mounted in bakelite and polished down to 200 Å alumina emulsion. The specimens were etched in a 2% Nital solution and observations were made by using scanning electron microscopy (SEM) associated with an EDS analyzer.

The coulometric dissolution studies were conducted in an electrolytical solution containing 2.8 mol l<sup>-1</sup> NH<sub>4</sub>Cl at a current density of 5mA cm<sup>-2</sup>. The revolution of the disc is 500 rev min<sup>-1</sup>. The pH of the electrolyte was 4. These conditions were adopted by Besseyrias, et al. [21]. Ascott type salt spray test was carried out on specimens of galvanized steel having the dimensions of (30 x 100 x 1.5 mm).

## RESULTS AND DISCUSSION

Using Zn- Ag equilibrium phase diagram (Figure 1) is helpful in understanding the overlay cast structure, as was previously reported. The solid phases present in the Zn- Ag system are β, ξ, γ and ε. The Zn terminal solid solution (η) is hexagonal close packed with maximum Ag. The solubility of silver in the zinc, at the eutectoid temperature (431°C), is 8 wt. % Ag. This solubility decreases to 2.6 wt. % Ag at room temperature [22].

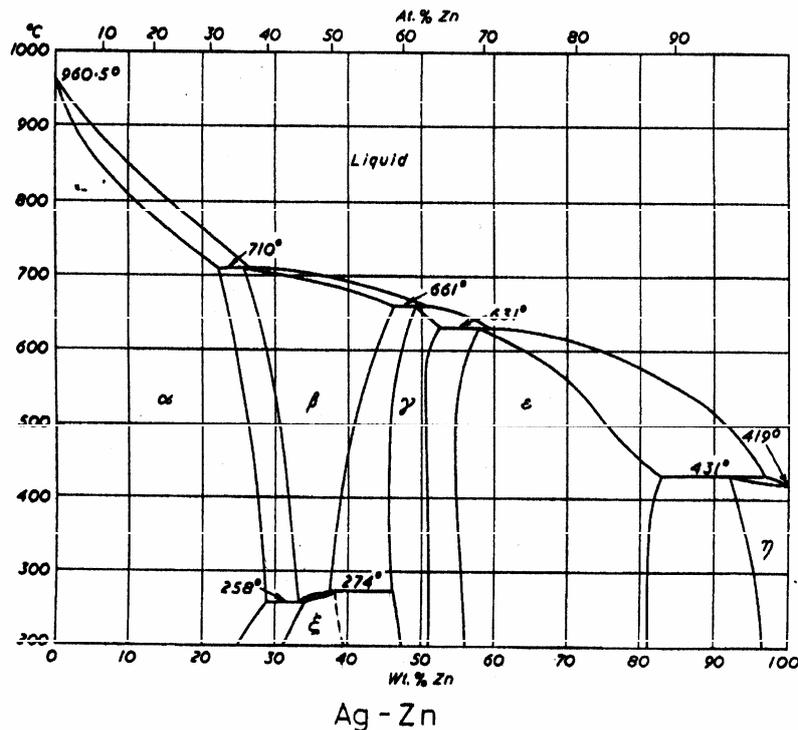


Figure 1: Ag-Zn equilibrium phase diagram [22]

Figures (3a, b and c) show the SEM micrographs of these cross-sections of the coatings obtained with three zinc baths 1, 2 and 3 (Table 2). The morphology of these micrographs is typical for the hot-dip galvanized coatings. Four layers could be distinguished based on their relief. The first layer is a very thin zone, formed just on the ferrous substrate. This zone represents the gamma (Γ) phase of the Fe-Zn phase diagram (Figure 2).

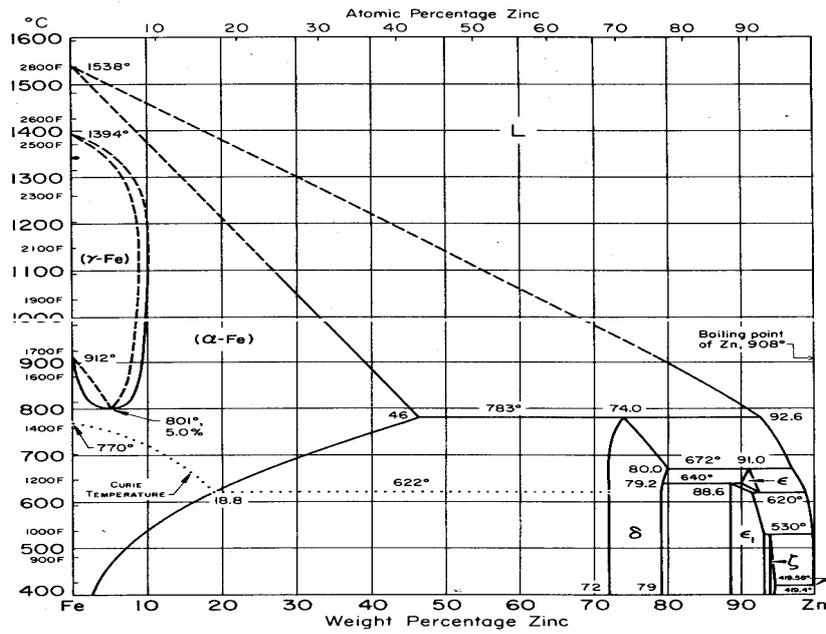


Figure 2: Fe-Zn equilibrium phase diagram [19]

A thicker layer with a large number of cracks can be observed in Figure (3) and correspond to delta ( $\delta$ ) phase. The third layer is the zeta ( $\zeta$ ) phase. It is the thickest one. It is composed from long and continuous crystals and shows an almost columnar growth. However, the outer surface of the coating is covered with a thin and even eta ( $\eta$ ) phase.

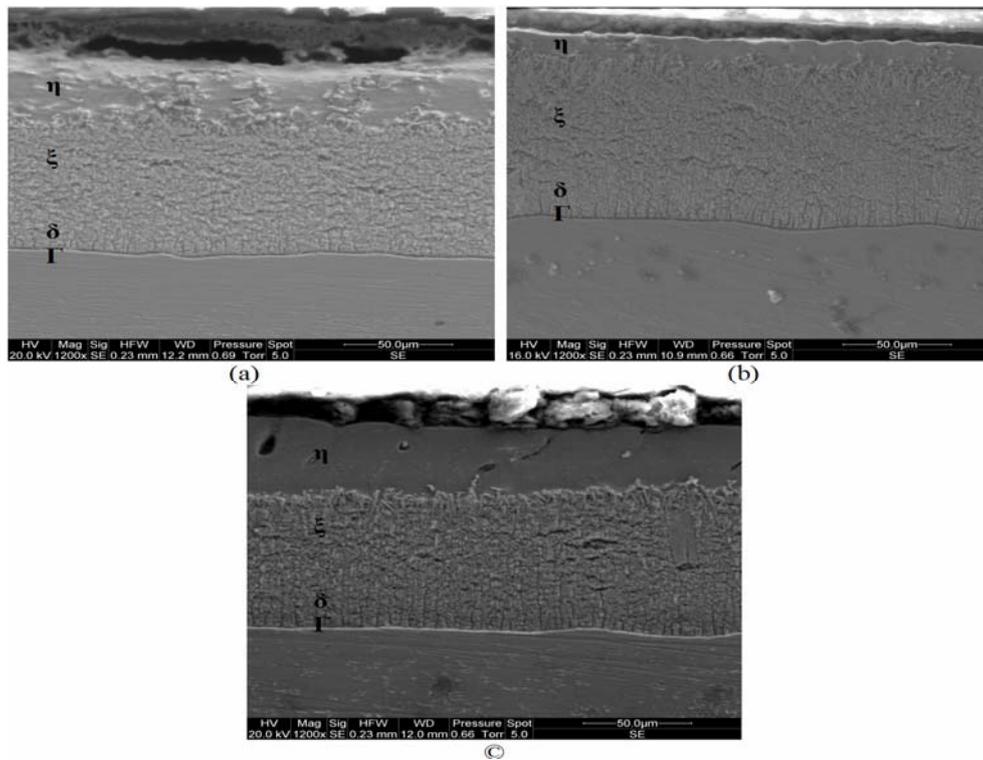


Figure 3: SEM micrographs of galvanised steel obtained with zinc bath containing: (a) 0.03, (b) 0.06 and (c) 0.09 % wt. Ag at  $T = 450^\circ\text{C}$ ,  $t = 3$  min and  $v = 3.5$  m/min.

**Table 3: Influence of Ag on the thickness of the different phases of galvanized coatings**

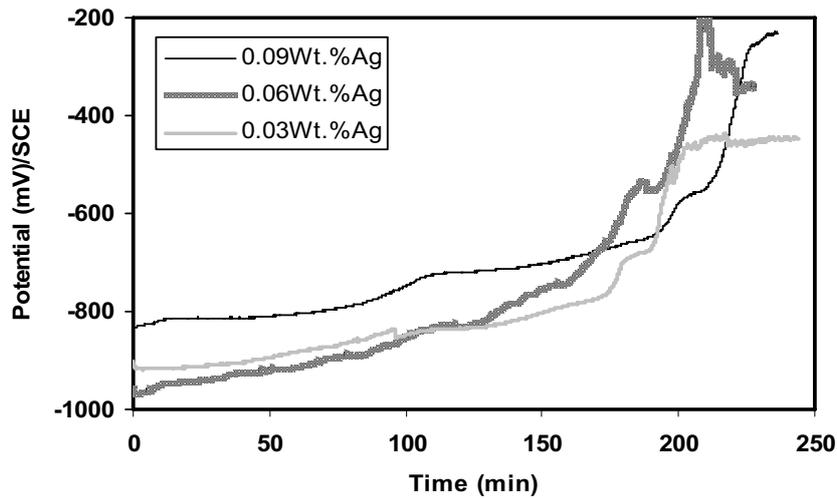
Bath containing wt.% Ag	Thickness phases ( $\mu\text{m}$ )			Total thickness ( $\mu\text{m}$ )
	Eta ( $\eta$ )	Zeta ( $\xi$ )	Delta ( $\delta$ ) and Gamma ( $\Gamma$ )	
0.03	6-9	96-99	9	114
0.06	12-18	87-93	9	114
0.09	36-45	68-77	9	122

As already noted, there is a thickness variation involved especially the phases  $\zeta$  and  $\eta$ . When the averages of the values given in Table (3) are taken as indicators, the corresponding thickness of  $\eta$  can be found as 6-9  $\mu\text{m}$  for 0.03 wt. % Ag, 12-18  $\mu\text{m}$  for 0.06 wt. % Ag and 36-45  $\mu\text{m}$  for 0.09 wt.% Ag. However, it can be noted that the thickness of  $\zeta$  phase shows an inverse relationship with the ratio of silver. Indeed,  $\zeta$  phase showed roughly 96-99  $\mu\text{m}$  for 0.03 wt. % Ag, 87-96 for 0.06 wt. % Ag, and 68-77  $\mu\text{m}$  for 0.09 wt. % Ag. This reduction represents around 30 % of thickness of  $\zeta$  phase. This can be explained by the effect of silver on kinetics of the reaction. This is consistent with Jordan who showed that additives have an effect on the  $\zeta$  phase [9].

In contrast, the thickness of the  $\eta$  phase increases with the ratio of silver. This phenomenon is highly related to the fluidity of liquid zinc; this finding suggests that silver addition causes a decrease of the zinc fluidity. It is worth noting that the addition of silver in such galvanization process does not cause a considerable variation in the thickness of  $\delta$  and  $\Gamma$  phases in a way that their thickness remains almost constant (9  $\mu\text{m}$ ). Consequently the total thickness of the coating remains constant. The surface appearance of coatings obtained with the Ag alloys is brighter and smoother than results obtained with other additives [23]. Furthermore, these coatings are characterized by more numerous and small size spangles than that obtained using a traditional bath as shown in Figure (4).

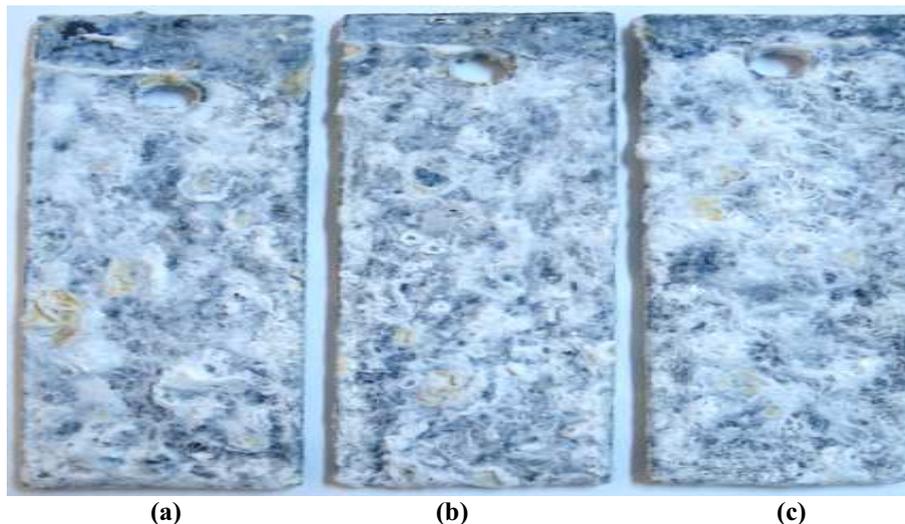
**Figure 4: Surface appearance of galvanized steel obtained at 0.09% wt. Ag, T = 450°C, t = 3 min and v = 3.5 m/min**

The coulometric dissolution test result showed that coatings using 0.09 wt. % Ag are more resistant to coating dissolution as shown in Figure (5) than coatings using 0.03 and 0.06 wt. % Ag. Furthermore, the measurement of resistance to coating dissolution serves as an indicator of resistance to corrosion. Hence, the coating using 0.09 wt. % Ag also provides a better resistance to corrosion. In  $\text{NH}_4\text{Cl}$  2.8 M electrolyte, the coulometric dissolution induces the appearance of well defined potential plateaus. These potential plateaus do not indicate the stripping of a unique phase. Every plateau represents one phase. As deduced from the anodic dissolution of pure zinc iron intermetallic phases as reported by Besseyrias [21].



**Figure 5: Potential versus time during galvanostatic stripping of galvanised steel**

Figures (6a, b and c) show dissolution of coatings in the spray test. It is obvious from this figure that coatings produced when using 0.09 wt.% Ag show better resistance against chloride attack than those obtained at 0.03 and 0.06 wt.% Ag. Table (4) and Figure (6) show evidence for this behaviour. After an exposure of 1000 h brown rust appears on samples obtained with coatings having 0.03 and 0.06 wt.% Ag. However, the coating having 0.09 wt. % Ag does not show any rust.



**Figure 6: The surface appearance of the galvanized steel after salt spray test at; (a) 0.03 wt % Ag, (b) 0.06 wt % Ag, and (c) 0.09 wt % Ag.**

**Table 4: White rust %(WR) and brown rust %(BR) in 3.5% chloride environment after different exposure times.**

Galvanising bath	24 h	120 h	360 h	600 h	960 h	1000 h	1200 h
Zn- 0.03 wt %Ag	-	2 %WR	-	100%WR	-	1%BR	-
Zn-0.06 wt %Ag	-	5 % WR	100%WR	-	-	1%BR	-
Zn-0.09 wt %Ag	-	7 %WR	100%WR	-	-	-	1%BR

## CONCLUSIONS

From the above investigation the following conclusions could be drawn:

- Silver addition did not affect the morphology of the galvanized coatings on the steel for 0.03, 0.06 and 0.09 wt. % concentrations. The coating still consists of the gamma, delta, zeta and eta as predicted in Fe–Zn equilibrium diagram.
- The addition of silver into molten zinc during galvanization of steel may help in producing brighter, smoother surface and with more visible spangles.
- The total layer thickness of the galvanized coatings seems to be less influenced by the addition of silver. Nevertheless, silver may affect the nature and the characteristics of the individual phases. For example, the thickness of zeta phase increases and becomes much more compact as a result of silver addition.
- Silver addition of 0.09 wt. % Ag seems to produce better corrosion resistant coatings.

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