

MECHANISM AND KINETICS OF THE FORMATION OF ZINC PACK COATINGS

G. Vourlias, N. Pistofidis, K. Chrissafis*, E. Pavlidou and G. Stergioudis

Physics Department, Aristotle University of Thessaloniki, Thessaloniki, 54 124 Greece

A zinc deposition method that could be used instead hot-dip galvanizing is pack cementation, where the substrate is heated immersed in a powder mixture containing Zn and a halide activator (NH_4Cl). In the present work the mechanism of this process is examined, along with the effect of temperature and heating time on the coating thickness and structure. For this purpose the coating was deposited and characterized with SEM, while the deposition mechanism was investigated with DSC. From the above examination it was deduced that the deposition of Zn takes place with a multiple-step mechanism, which involves several reactions in the gaseous phase including the formation of volatile zinc halides and finally the diffusion of zinc in the crystal lattice of the ferrous substrate. This procedure is accomplished at about 300°C and leads to the growth of a coating composed by two layers referring to Γ and δ phase of the Fe–Zn system. The coating deposition rate seems to be controlled by the zinc diffusion as its determination at 300 and 350°C showed, where it was deduced that the coating thickness is a linear function of the square root of heating time. However the coating structure is not affected by the heating time and temperature.

Keywords: chemical vapor deposition, coating materials, DSC characterization, pack cementation, scanning electron microscopy, thermal analysis

Introduction

One of the most effective methods for the protection of ferrous substrates against aqueous corrosion is the application of zinc coatings [1, 2]. A number of different methods are commercially available for this purpose (Table 1 [1]). The most widespread is hot-dip galvanizing [1–5]. In this case the ferrous substrate is immersed in a bath of molten Zn and as a result it is covered by a layer of Zn with an average thickness of a few tens of micrometers. The effectiveness of this method is undisputable. However its high environmental impact imposes the investigation of alternative coating techniques friendlier to the environment [4].

A promising alternative technique is Chemical Vapour Deposition (CVD) by pack cementation [5–11]. In this case a Zn diffusion coating is formed by heating the substrate in a sealed crucible up to 450°C

covered with a mixture of powders containing Zn and an activator (NH_4Cl). The method prevents the fume formation during the deposition of the zinc coating because the system is isolated. Furthermore the energy consumption during pack cementation is much lower than during hot-dip galvanizing. Furthermore the pack coatings are harder and hence less susceptible to wear. A possible application could be the growth of coatings on objects with irregular shapes in a much easier way than with the conventional techniques.

Although CVD is widely used for the deposition of several elements on different substrates in industrial scale facilities, its application for Zn deposition is relatively rare. The formation of a two-step Al and Zn diffusion coating has been reported a few years ago [12], while more detailed studies including the structure and the corrosion performance of zinc pack coatings have been published elsewhere [5–11].

However the deposition mechanism is not yet clarified. Furthermore there is not enough data for the effect of the temperature at which the coating has been processed and especially about the minimum temperature at which the deposition is feasible. Nevertheless the effect of the heating time on the coating thickness and structure has to be examined. Consequently a systematic investigation on these topics is necessary. An attempt to this direction is accomplished in the present work.

Table 1 Major deposition techniques of metallic zinc coatings [1]

Method	Principle
Hot dip galvanizing	Immersion in a molten zinc bath
Electroplating	Immersion in a chemical bath
Thermal spraying (Metallizing)	Spraying of molten zinc
Pack cementation/ Fluidized bed reactor	Chemical Vapor Deposition

* Author for correspondence: hrisafis@physics.auth.gr

Experimental

Commercial, hot-rolled low carbon steel sheets SAE 1010 (C: 0.11%, Mn: 0.55%, S: 0.012%, P: 0.016%) were used as substrates for the sample preparation. The specimens used were sized to 2·3·3 mm and they were prepared following the conditions which are described in Fig. 1.

The as-prepared substrates were placed inside a powder mixture composed by 2% NH₄Cl and 98% Zn and the system was sealed in crucibles of stainless steel. A Setaram DSC 141 differential scanning calorimeter was used for the on-line observation of the transitional phenomena that take place during the coating formation in order to reveal more details about the formation mechanism. DSC was chosen for this purpose because, apart from the fact that it allows continuous monitoring of the process, it enables the collection of very accurate measurements of temperature inside the crucibles used, at which great importance was assigned. This study was non-isothermally performed by heating the specimens from room temperature up to 500°C with a heating rate of 10 K min⁻¹.

For the investigation of the effect of heating time and temperature, the coating deposition was accomplished in the DSC at 300 or 350°C, while the heating time was 0, 1, 5 and 10 h at each temperature.

The as-formed coatings were examined with scanning electron microscopy by using a 20 kVolt JEOL 840A SEM equipped with an OXFORD ISIS 300 EDS analyzer. For this reason cross sections from each specimen were cut, mounted in bakelite and polished down to 5 μm alumina emulsion. SEM was used for the thickness measurements and the determination of the morphology and the chemical composition of the as-formed coatings.

Results and discussion

The initial examination of the deposition mechanism as it is described by the DSC plot (Fig. 2a) shows that

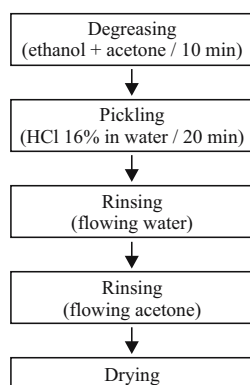


Fig. 1 Preparation of the samples for pack cementation

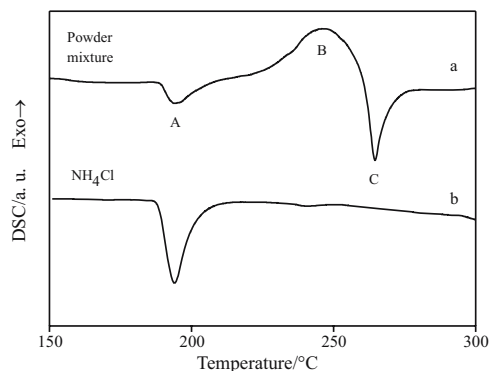


Fig. 2 Curve a – DSC plot of the non-isothermal heating of the pack mixture containing 2% NH₄Cl and 98% Zn. Peak (A) refers to NH₄Cl transformation, peak (B) refers to the composition reactions which lead to the formation of Zn chlorides and peak (C) refers to the decomposition and the formation of zinc. Curve b – DSC plot of pure NH₄Cl at the same temperature area

before the coating formation more than one step take place. The first one is identified by the transformation of α -NH₄Cl to β -NH₄Cl. This transformation is accomplished in solid state, as it could be deduced by the comparison of the respective peak resulting from an endothermic transformation recorded when pure NH₄Cl is heated in a DSC (Fig. 2b [13]).

Two more peaks are also recorded, which could be the resultant of several overlapped thermal phenomena. These phenomena are likely to take place in the same or in contradictory directions with regard to the coating formation.

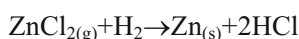
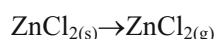
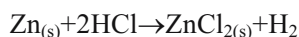
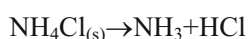
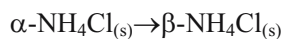
In any case for the first peak (B in Fig. 2), a possible explanation could be a series of composition reactions leading to the formation of volatile zinc chlorides. In this case initial decomposition of NH₄Cl takes place and as a result gaseous NH₃ and HCl are evolved. HCl reacts with Zn forming solid ZnCl₂, while the formation of other compounds such as mixed zinc chloride and ammonium chloride salts (Zn(NH₄)_xCl_{2+x}, $x \geq 1$) is probable [14].

The as-formed salts sublime and take part in the gaseous phase in a number of chemical reactions on the surface of the substrate, such as reductions or decompositions of the chlorides or displacement reactions with Fe atoms from the steel [15]. Through these reactions metallic zinc is deposited on steel, while HCl is regenerated which is recycled and as a result the above described process is repeated. In any case all these reactions are included in the two final peaks of the DSC plot. The zinc which is deposited through these reactions diffuses in the crystal lattice of the substrate resulting to the coating morphology which will be described later.

However, since zinc is a reactive metal the reaction of HCl with the coating is not improbable. Hence the decomposition of the coating is also possible

at the same circumstances through the formation of volatile chlorides. All the same, the fact that the coating is finally deposited indicates that this process is rather limited. Thus its contribution to the DSC plot has to be very small.

Consequently a possible mechanism could be roughly described by the following chemical reactions:



If the Gibbs free energy change (ΔG) of these reactions is calculated at 300 or at 350°C and at 1 atm, it is observed that in every case $\Delta G < 0$ (apart of the sublimation where by definition $\Delta G = 0$). The negative value for ΔG indicates that these reactions are thermodynamically feasible at these circumstances. However the mechanism is more complicated because several parallel reactions take place and as a result several different byproducts are formed which are also affected by the partial pressures of the system components [16]. As a result the above reactions could be used only as a general description. For more detailed results further investigation is necessary involving a precise analysis of the reaction products

and an accurate estimation of the pressure changes inside the crucible.

In any case, from the above analysis it is clear that the coating formation takes place after a certain number of steps, which includes different chemical and physical phenomena. These phenomena, following the DSC plot, are accomplished at about 300°C, since above this temperature there are no peaks recorded up to 500°C (apart from the zinc melting that takes place at 419°C and is not involved in the deposition process). This process finally leads to the deposition of pure zinc on the ferrous substrate which is diffused in the iron crystal lattice forming the final coating. As a matter of fact, this procedure (diffusion) is usually the most time-consuming step of the deposition sequence.

However for the application of zinc pack cementation in industrial scale facilities the mechanism is not very important. What is imperative is the determination of the speed of the entire process, along with the minimum temperature at which the deposition is feasible. From this data an efficient time and energy management would be possible. As a result important energy savings would be achieved, since the determination of the optimum temperature and heating time combination (in order to obtain the growth of the necessary coating thickness for efficient corrosion protection) would be specified.

For this purpose the thickness and the structure of the deposited coatings was studied at 300 and 350°C for 0, 1, 5 and 10 h of heating. As it was previously mentioned these temperatures were chosen because following the plot of Fig. 2 the recorded phenomena are accomplished at about 300°C.

The observation with SEM (Figs 3, 4) and the microanalysis with EDS (Table 2) showed that almost every coating is characterized by a two-layered structure. The inner layer which is closer to the ferrous substrate contains about 24–28% Fe and refers to the Γ -phase of the Fe–Zn system, while the outer layer contains 10–11% Fe and corresponds to the δ -phase [5–11]. This structure, which was also verified with X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) [5–11], is similar in every coating regardless the deposition temperature and the heating time, apart from the sample exposed at 300°C for 0 h. In this case, as Fig. 3a shows, only a loose phase is deposited which is mainly composed by Zn. The Fe–Zn phases are not present. This phenomenon implies that there is a combination of minimum temperature and minimum heating time in order to take place the coating growth. From the experiments conducted during this work the two possible combinations are 1 h heating at 300°C or 0 h heating at 350°C. The coating formation at 0 h of heating at 350°C is not peculiar because, although the system

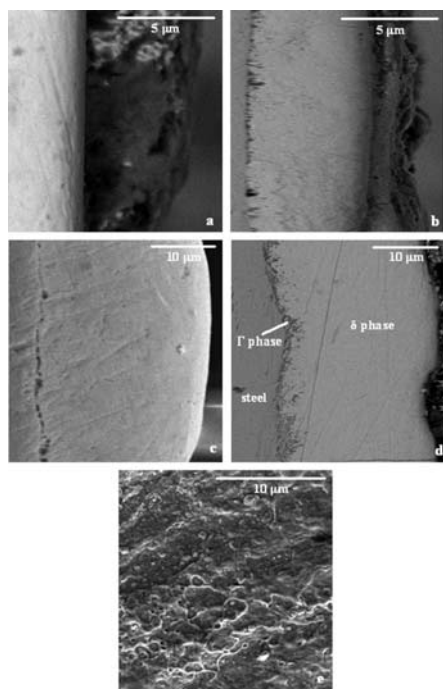


Fig. 3 SEM micrograph of the cross-section of the coating formed at 300°C after a – 0, b – 1, c – 5 and d – 10 h of heating. The plain view of the coating after 10 h of heating is also presented

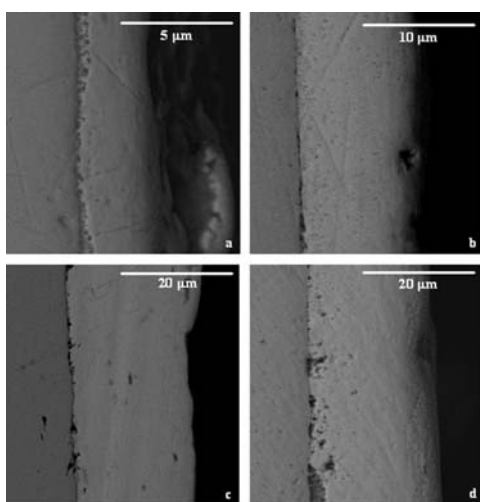


Fig. 4 SEM micrograph of the cross-section of the coating formed at 350°C after a – 0, b – 1, c – 5 and d – 10 h of heating

(powder and substrate) does not remain at 350°C, its temperature reaches this value during the previous non-isothermal heating. As a result there is time from 300 to 350°C during non-isothermal heating which allow the coating deposition.

Nevertheless from the above examination it could be deduced that the variation of temperature and heating time does not affect the coating morphology which is similar in every case, as long as the system is above the minimum temperature or the minimum time. This observation indicates that the deposition mechanism is affected neither by the deposition temperature nor by the heating time. These factors only trigger the necessary phenomena and consequently when they are not sufficient the deposition is inhibited. However when the growth is favoured, they do not seem to alter the coating.

As far as it concerns the coating morphology, what is rather characteristic is the lack of dendrites or discernible grains. This means that the coating is formed through diffusion. This opinion is supported by the fact that the same morphology is observed for these phases when zinc coatings are deposited with hot-dipping. In this case it is undoubtedly that these phases are formed with diffusion [2].

It is also interesting to examine the coating surface. In this case small particles are distinguished attached on the surface, along with a large number of circular craters. The EDS analysis of these particles shows that they are mainly composed by Zn. Consequently they are remnants of the zinc powder. The formation of the craters could also be explained in a similar way, because the particles that were detached from the coating could have formed the observed craters.

Table 2 Average composition of the phases composing the zinc pack coatings based on EDS measurements

Phase	Fe/mass%	Formula [2]
Γ	24–28	$\text{Fe}_{11}\text{Zn}_{40}$
δ	10–11	FeZn_{10}

However, the existence of zinc particles is not unexpected. What is rather impressive is the fact that the EDS analysis shows that the surface of the coating is composed by pure zinc and not the δ -phase. This could be attributed to the attachment of a loose phase on the coating. This phase is probably zinc that was transferred with the mechanism previously explained but not yet diffused. Hence this observation is also supporting the fact that diffusion is the slowest step of the process.

Nevertheless, although the morphology is the same regardless the temperature and the heating time, the coating thickness changes significantly. The results of these measurements are summarized in Fig. 5a.

From these plots it is obvious that the coating thickness increases with heating time. This behaviour is similar at both temperatures although the thickness at 350°C is higher. As a matter of fact the two curves seem to be almost parallel. However, the growth is not linear, even though the thickness increase is monotone. By contrast certain saturation is observed at higher deposition times, regardless the deposition temperature, which leads to a decrease of the deposition rate to a value close to zero. This behaviour implies that the coating growth is diffusion controlled. This means that the other steps of the deposition mechanism are very fast compared to the diffusion of metallic zinc in the substrate.

To verify this hypothesis the coating thickness was drawn *vs.* the square root of heating time (\sqrt{t}) and a straight line was achieved for both of the examined temperatures (Fig. 5b). The exact equations that describe the two curves were calculated using the method of the least squares and are incorporated in the plots of Fig. 5. These equations are sufficient for preliminary calculations in industrial scale facilities. Of course larger scale experiments in a suitable pilot-plant are necessary for the formulation of equations with wider range of application. However these equations verify the fact that the rate of the coating growth at the two different temperatures increases in a similar way in both cases, as the lines are almost parallel. The fact also that their gradient is positive shows that the coating thickness constantly increases.

Apart from the above conclusions, the linear behaviour of these curves verifies that thickness is a function of \sqrt{t} . As a result, if the second law of Fick [17] is taken into account, it is obvious that the deposition is diffusion controlled. Hence, the other phenomena that take place during the coating formation are much

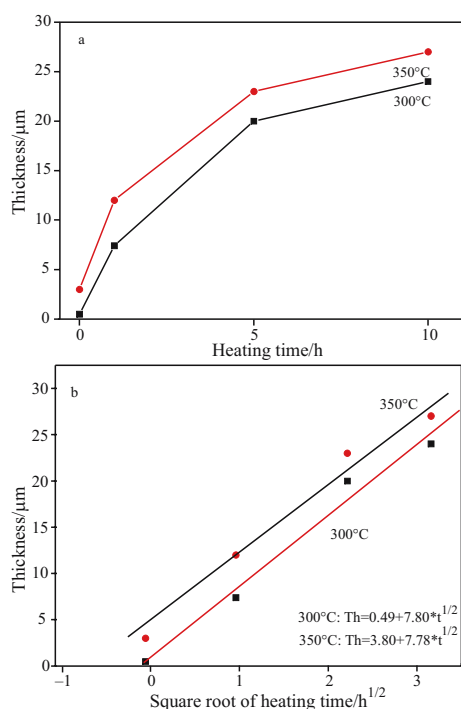


Fig. 5 Plots of the coating thickness with regard to a – heating time and the b – square root of heating time at 300 and 350°C

faster. If they had been controlled the phenomenon, a different equation would have described the relation of thickness with the heating time. This aspect could be justified if we take into account that they every other transformation in the system takes place at the gaseous phase, while diffusion takes place in solid state.

Conclusions

From the above examination a multiple-step mechanism for the formation of Zn pack coatings was established. The final step of this mechanism is the diffusion of zinc in the crystal lattice of the ferrous substrate. This step is likely to control the rate of the entire process because the coating thickness is proportional to the square root of time at both of the examined temperatures. As a matter of fact the coating growth at both temperatures is described by almost parallel lines. However, the same parameters (temperature and heating time) do not affect the coating structure, which is always composed by two layers referring to Γ and δ -phase of the Fe–Zn system, when the temperature or the heating time are above certain minimum values.

References

- 1 American Galvanizers Association, Zinc Coatings-Microstructures of Various Zinc Coatings, AGA, Colorado, 2000.
- 2 A. R. Marder, *Prog. Mater. Sci.*, 45 (2000) 191.
- 3 D. Wetzel, Batch hot-dip galvanizing, ASM Handbook, Vol. 5: Surface Engineering, ASM, New York, 1994.
- 4 P. Maass and P. Peissker, *Handbuch Feuerverzinken*, Wiley-VCH, 1993.
- 5 N. Pistofidis, G. Vourlias, E. Pavlidou, K. Chrissafis, G. Stergioudis, E. K. Polychroniadis and D. Tsipas, *J. Therm. Anal. Cal.*, 84 (2006) 417.
- 6 N. Pistofidis, G. Vourlias, D. Chaliampalias, E. Pavlidou, K. Chrissafis, G. Stergioudis, E. K. Polychroniadis and D. Tsipas, *J. Therm. Anal. Cal.*, 84 (2006) 191.
- 7 N. Pistofidis, G. Vourlias, D. Chaliampalias, E. Pavlidou, G. Stergioudis and E. K. Polychroniadis, *Surf. Interface Anal.*, 38 (2006) 252.
- 8 G. Vourlias, N. Pistofidis, D. Chaliampalias, P. Patsalas, G. Stergioudis and D. Tsipas, *Surf. Coat. Technol.*, 200 (2006) 6594.
- 9 G. Vourlias, N. Pistofidis, D. Chaliampalias, E. Pavlidou, G. Stergioudis and E. K. Polychroniadis, *J. Alloys Compd.*, 416 (2006) 125.
- 10 N. Pistofidis, G. Vourlias, D. Chaliampalias, K. Chrysafis, G. Stergioudis and E. K. Polychroniadis, *J. Alloys Compd.*, 407 (2006) 221.
- 11 G. Vourlias, N. Pistofidis, D. Chaliampalias, K. Chrissafis, E. Pavlidou and G. Stergioudis, *J. Therm. Anal. Cal.*, 87 (2007) 401.
- 12 O. T. de Rincon, J. Ludovic, E. Huerta, N. Romwero, M. F. de Romero, O. Perez, W. Campos and A. Navarro, *Mater. Performance*, 36 (1997) 28.
- 13 M. Olszak-Humienik, *Thermochim. Acta*, 378 (2001) 107.
- 14 Clara Fillaux, Thèse de Doctorat de l' Université Paris 6, Paris, 2004.
- 15 B. Nciri and L. Vandenbulcke, *J. Less-Com. Met.*, 95 (1983) 55.
- 16 S. H. Son and F. Tsukihashi, *ISIJ Int.*, 43 (2003) 1356.
- 17 M. Ashby, H. Shercliff and D. Cebon, *Materials: Engineering, Science, Processing and Design*, BH, London, 2004.

Received: November 2, 2006

Accepted: June 12, 2007

DOI: 10.1007/s10973-006-8237-3