

On the phase sequence formation of zinc protective coatings on low carbon steel in fluidized bed reactor

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The structure of Zn coatings and the sequence of iron-zinc phases formed in fluidized bed reactor at 400 °C for 30 min/1 h/1 h30 min/2 h holding time have been studied in the present work. Several experiments were carried out using NH₄Cl as activator in the form of powder or pill. The coated samples were observed with SEM microscopy and they were characterized with EDS and XRD analysis. From this procedure the formation of two-layered coatings was achieved. The main phases observed were gamma and delta phase of the Fe-Zn phase diagram. Some of the as-received coatings are likely to provide sufficient anticorrosive protection while others are of low quality because of porous areas in their mass.

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1. Introduction

Zinc is known to be an ideal material for steel protection. This is because apart from the fact that it behaves as barrier, it is also more anodic than steel and as a result it acts as a sacrificial anode in aqueous environments [1-8].

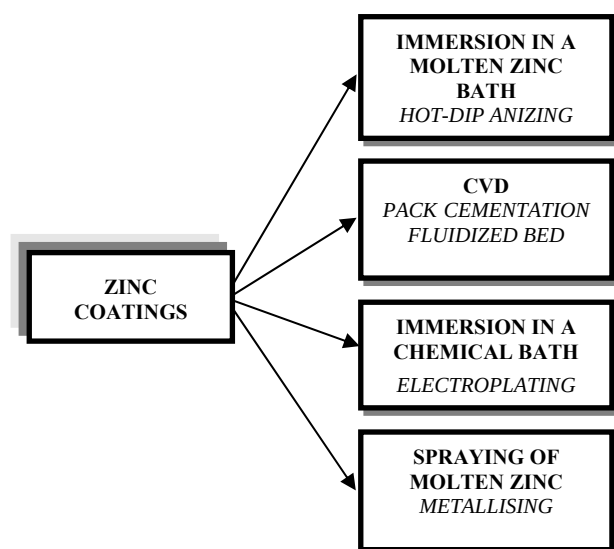


Fig. 1. Overview of the deposition methods of zinc coatings on ferrous substrates.

There are multiple methods for casting Zn coatings, which are commercially available (Fig. 1) [6]. The most widely used is hot-dip galvanizing [3-8]. In this case the ferrous substrate after the necessary surface treatment is immersed in a bath of molten Zn at about 450 °C 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. A different method that could be used instead of hot-dip galvanizing is chemical vapor deposition (CVD) with pack cementation [9-10]. In this case the powder containing Zn (donor) and a halide activator such as NH₄Cl is stacked in a tube, at 400 °C, with perforated bottom (reactor body). A gas is introduced from the holes of the tube bottom resulting in the fluidization (fluid-like behavior) of the powder (Fig. 2). Although the as-cast coatings are comparable with those grown with hot dip galvanizing, pack cementation presents certain disadvantages [7-10]:

(1) The powders used tend to sinter at the process temperature.

(2) The process is slow because the treated parts have to be loaded and unloaded from the furnace at room temperature.

(3) The control of the homogeneity of the pack coatings is rather difficult.

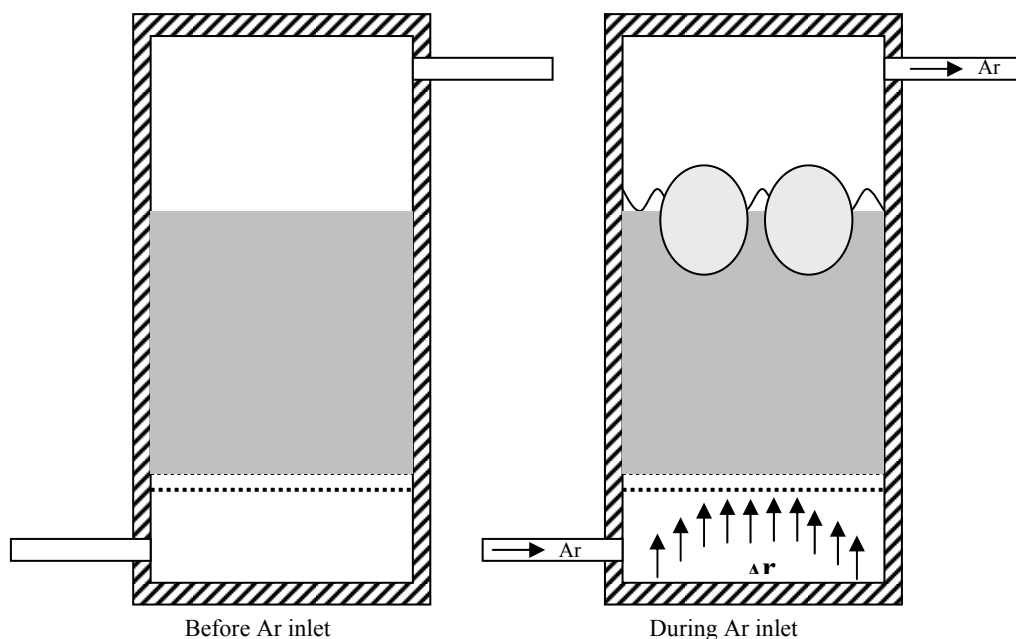


Fig. 2. Schematic overview of the fluidization before and during argon inlet in the reactor.

An alternative CVD process is fluidized bed coating procedure (FBR) which offers some advantages. In this case the powder is stacked in a tube with perforated bottom (reactor body). A gas is introduced from the holes of the tube bottom resulting in the fluidization (fluid-like behavior) of the powder. The ferrous substrate is hanged in the tube so as to be in contact with the fluidized powder [12-20]. This method combines the inherent advantages of a fluidised bed reactor (uniform temperature and effective mixing of the reacting elements) with the principles of CVD. As a result the system rapidly attains thermal equilibrium because of the high mass and heat transfer rates imposed by the gas flow in the reactor body. The deposition reaction at the treatment temperature between the chemical components of the donor and the activator, forms the precursor vapors of the coating element. The coating is formed by the reaction of the substrate with the as produced precursor vapors. Moreover FBR allows the insertion or removal of the specimens from the reactor body at any time or temperature required. Nevertheless the coating powder could be reused after the deposition process since the gas flow prevents sintering.

Up to now several coating procedures have been achieved with fluidized bed reactor such as aluminizing, aluminochromizing, aluminosiliconizing, carburizing, carbonitriding [15-20]. The main aim of this work is the examination of zinc deposition feasibility with fluidized bed technique in laboratory scale. Furthermore a comparison with zinc pack coatings is attempted. Moreover preliminary conclusions could be drawn for their corrosion resistance taking into account Reference [11].

2. Experimental procedure

Commercial, hot-rolled low carbon steel sheets SAE 1010 were used as substrates for the sample preparation. The coupons were sized to 15mm × 10mm × 2.2mm. Sandblast was used for preliminary surface cleaning while surface finishing was accomplished with polishing up to 600 grid SiC paper.

The zinc deposition was realized in the fluidized bed reactor of Fig. 3. This system consists of five main parts:

- 1) fluidized bed reactor unit;
- 2) gas providing system;
- 3) furnace for heating the reactor;
- 4) control panels and measuring instruments;
- 5) filter for trapping of hazardous substances unit.

The fluidization took place in a stainless steel tube (reactor body) where the pack powder is contained. The powder used was composed by 40%wt. zinc and 60%wt. high purity alumina powder (Al_2O_3) as filler. The process was carried out in a furnace at 400 °C under Ar (99.999%) atmosphere, which was inserted from the bottom of the furnace (fluidization gas), for 30min, 1h, 1 h 30 min and 2 h. The argon flow rate at the entrance orifice was the appropriate in order to prevent the precipitation of the particles at the orifice and their drifting outside of the reactor body.

Two sets of experiments were carried out as they are outlined in Table 1. When the halide salt activator was in pill form it was inserted from the upper part of the FBR setup. Contrary when it was in powder state, it was sublimated from a additional furnace and the vapours were inserted from the bottom of FBR setup.

Table 1. Summary of experimental conditions.

Specimen	State of the activator (NH ₄ Cl)	Holding Time
K1	Pill/Powder	30min
K2	Pill/Powder	1h
K3	Pill/Powder	1h30min
K4	Pill/Powder	2h

For the examination of the morphology of the as-cast coatings, cross sections from each specimen have been segmented, mounted in polyester resin, polished up to 1 μm diamond paste and etched in a 2% Nital solution (2% HNO₃ in CH₃CH₂OH). The observation was performed by using a 20 kV JEOL 840 A Scanning Electron Microscope (SEM) equipped with an OXFORD ISIS 300 Energy Dispersive X-Ray Spectroscopy (EDS) analyzer and the necessary software in order to perform point microanalysis, linear microanalysis or chemical mapping of the surface under examination.

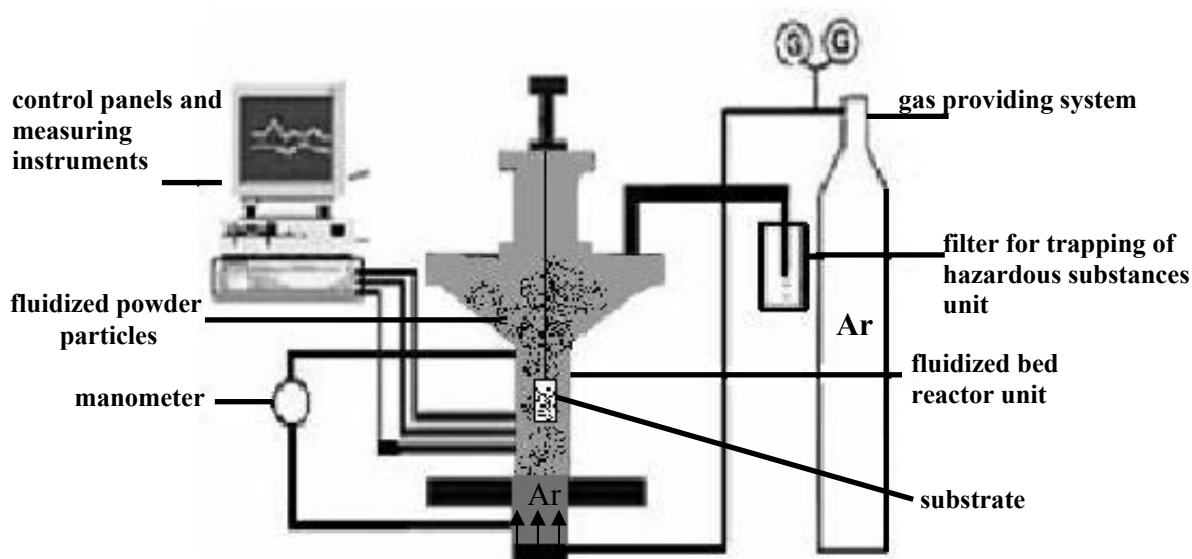


Fig. 3. Schematic drawing of the fluidized bed setup.

The nature of the phases was determined using X-ray diffraction (XRD). The XRD experiments were accomplished in a conventional powder diffractometer (SEIFERT 3003 TT - CuK α radiation) in Bragg-Brentano geometry. No contribution from the stainless steel substrate has been recorded in the XRD patterns, as determined by the penetration depth of the X-ray beam following the analysis described in ref. [21].

3. Results and discussion

Some typical micrographs of FBR zinc coatings cross sections of samples K1, K2 are presented in Fig. 4. From these micrographs it is obvious that the coating quality, formed at 400 °C and 30 min/1h holding time, is very poor (Fig. 4). The coating thickness is inhomogeneous and large areas of the ferrous substrate are exposed. These phenomena are not affected by the activator form. In any case, coatings of that quality are useless for any kind of applications.

The coating quality is improved when holding time is increased. Fig. 5 is a typical SE micrograph of the K3 coating cross section formed at 1h 30 min holding time. This sample, as it was mentioned earlier (Table 1) was inserted in preheated reactor body at 400 °C. From the

micrograph of the Fig. 5 it is obvious that this coating is continuous without gaps reaching the ferrous substrate. Its thickness is extended to 90 μm . However numerous pores are formed on the upper part of the coating which does not communicate with each other, as Fig. 5 shows, while the layer under the porous area is compact and homogeneous. In any case it seems that the coating prohibits the substrate of being exposed to the environment. Nevertheless, the presence of the pores may reduce its anticorrosive performance as they could facilitate pitting corrosion [22].

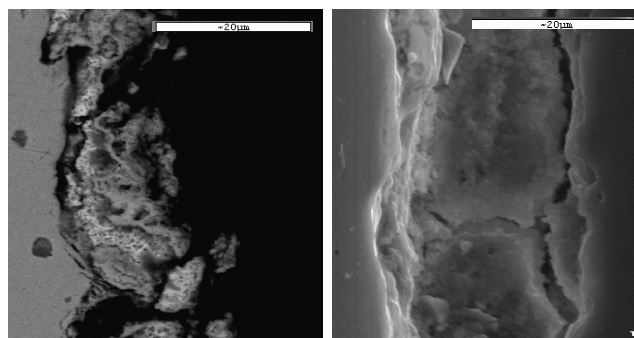


Fig. 4. SE micrographs of samples K1 (a) and K2 (b).

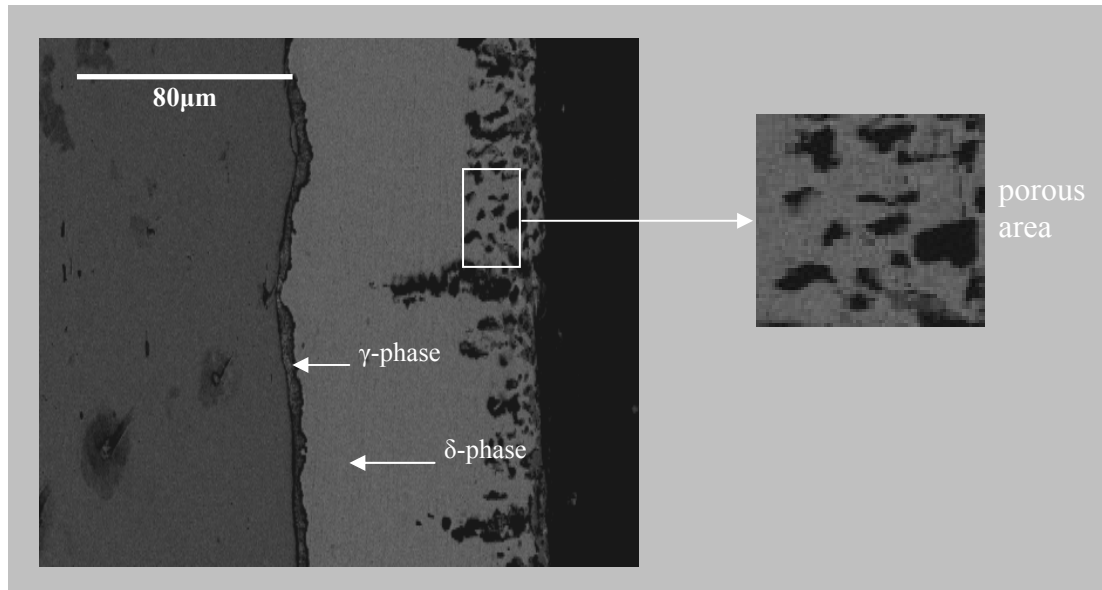


Fig. 5. SE micrograph of K3 samples and magnification of porous area of the coating.

EDS analysis (Fig. 6) performed on the same samples revealed the distribution of Fe and Zn in the coating cross section. From these data it was concluded that the coating has a two-layered structure. The Fe concentration implies that the layer in contact with the substrate (inner part) refers to the gamma-phase, while the outer layer corresponds to the delta-phase of the Fe-Zn phase diagram [3]. The formation of these phases was probably accomplished through Zn inward diffusion in the ferrous substrate [13]. These remarks agree also with the XRD results for the as-cast samples. In XRD patterns of K3 sample (Fig. 7) characteristic peaks referring to gamma phase and characteristic peaks referring to delta phase [23].

Hence K3 samples are composed by the first two layers of the hot-dip galvanized coatings [3]. The zeta and the eta phase are absent. The absence of the zeta phase could be explained by the fact that the coating procedure in FBR is not so aggressive as in hot-dip galvanizing, where the substrate is immersed in molten zinc at 450 °C [3]. Since zeta phase is formed with Fe diffusion through gamma and delta phase [3], its growth in the FBR at lower temperature is rather impossible. On the other hand, the eta phase is formed during hot-dip galvanizing because of the surface tension of molten zinc. As the substrate is emerging from the melt, liquid zinc is drifted and solidified, forming the eta phase. As a result the absence of liquid phase in FBR prohibits its formation.

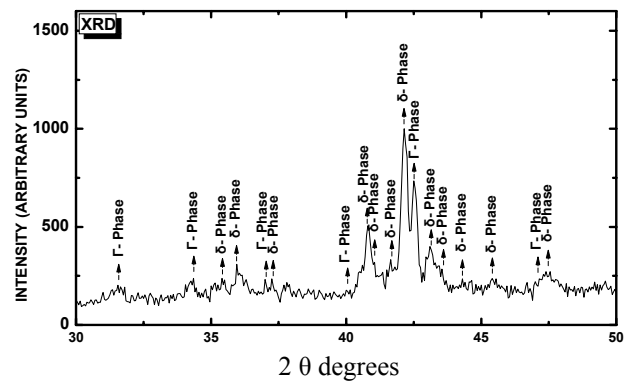


Fig. 6. EDS analysis of the K3 samples.

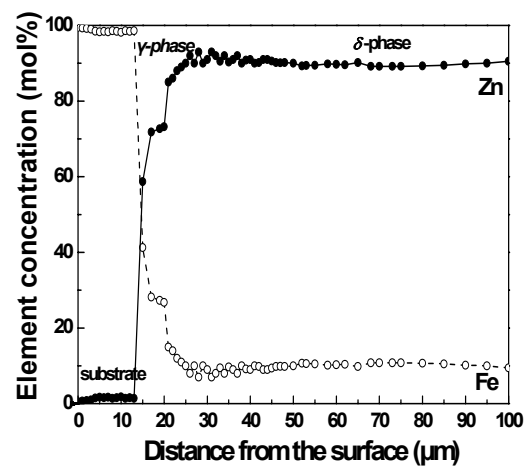


Fig. 7. XRD pattern of FBR coatings of K3 samples.

What is rather difficult to be explained is the pore formation at the upper part of the K3 coating. The formation of loose phases on top of the coatings formed with fluidized bed reactor is not an unusual phenomenon [9]. These phases are due to sintering of the powder which comes in contact with the already coated surface. A similar phenomenon could be responsible in K3 coating because the micrograph of this coating at higher magnification (Fig. 2) reveals spherical bodies that form pores. Afterwards, diffusion of zinc leads to a homogenization of the coating. However the remaining pores could also be explained due to Kirkendall effect [24]. A fast diffusion process of zinc into steel could lead to the formation of pores at this part of the coating.

In Fig. 8 a typical SE micrograph of K4 sample is presented, which was inserted in a preheated FBR at 400 °C while the holding time was 2h. Two layers could be observed, while the morphology is very similar to that of the K3 samples, although the pore density in the outer zone of the coating is lower and their length shorter.

In any case the coating is compact and covers the whole surface of the substrate providing the necessary corrosion barrier. Its thickness was found to be about 110 μm and seems to be able to provide adequate protection to the substrate. However the pores could facilitate pitting corrosion [22]. With the help of EDS and XRD it is concluded that also in this case the inner layer refers to the gamma-phase while the outer layer refers to the delta-phase of the Fe-Zn phase diagram.

The above observations are not related to the activator form. Furthermore, the comparison of the above conclusions with the conclusions drawn about zinc packs coatings show that the structure is similar. The same layers are observed with SEM and the chemical composition as it was determined with EDS is the same [11-13]. However slight differences were observed at the XRD patterns (Fig. 9) due mainly to the orientation and the stoichiometry of the as-formed grains. The differences of the intensities concerning the pack coatings could be explained by the smaller size of the grains in pack coatings.

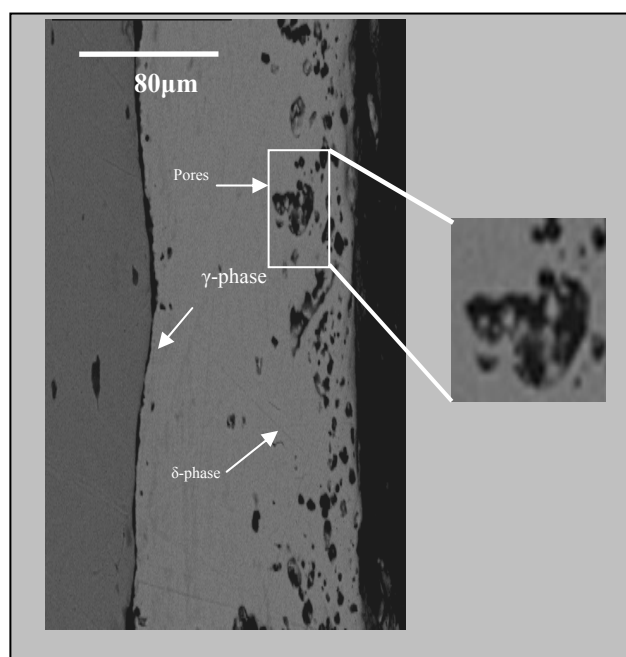


Fig. 8. SE micrograph of K4 samples and magnification of the porous area of the coating.

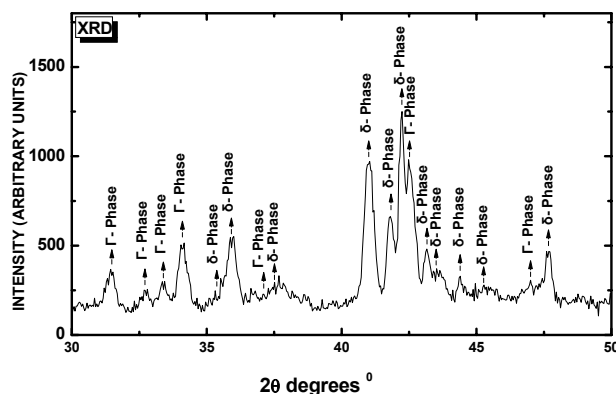


Fig. 9. XRD pattern of zinc pack coatings.

4. Conclusions

Table 2 summarises the previous remarks on K3 and K4 samples concerning the phase formation, the coating features and the coating thickness.

Table 2. Summary of the FBR coatings remarks of K3 and K4 samples.

Specimen	Coating Features	Phase Formation	Average Thickness (μm)
K3	Long porous area on top of the coating	gamma-phase (inner layer) delta-phase (outer layer)	90
K4	Porous area on top of the coating	gamma-phase (inner layer) delta-phase (outer layer)	110

From the above results the following conclusions have been drawn:

1) In every case a two-layered structure is observed composed by the gamma and the delta phase of the Fe-Zn system.

2) A porous layer is observed on top of every coating. The pore density and length decreases as holding time increases.

In any case from the above observations it is obvious that Zn deposition with FBR is feasible. It also seems that the as-cast coatings are suitable for corrosion protection of low alloy steels. However the porous zone could jeopardize their efficiency, as it was mentioned earlier. Hence for their application further research is necessary involving the suitable corrosion tests.

Acknowledgments

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