



Impact of zinc halide addition on the growth of zinc-rich layers generated by sherardizing



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ABSTRACT

The growth kinetics of Fe–Zn phases formed by vapor–solid diffusion reactions between evaporated zinc and a low carbon steel substrate are examined. Experiments with various zinc powder mixtures were performed in sealed quartz glass ampoules at 663 K and for annealing times up to 16 h. The formed intermetallic phases are investigated by optical microscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy. Emphasis is put on the addition of various zinc halides (ZnCl_2 , ZnBr_2 , ZnI_2) to the process that causes an increase in total layer thickness. The results presented show that this increase is due to a modification of the zinc powder properties that improves the sherardizing process. Finite difference methods are used to simulate the Fe–Zn phase growth during sherardizing. The understanding gained from experiments and simulations of Fe–Zn multiphase growth will help to improve the sherardizing of steel in industrial facilities.

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1. Introduction

Galvanizing is the most important method to protect steel products against corrosion. Steel substrates benefit from the galvanic and barrier protection of a zinc or zinc alloy coating. The predominant method for the creation of protective zinc layers in steel processing industries is hot dip galvanizing [1,2]. Fe–Zn phases with a pure zinc layer on top are formed by immersing steel in a bath of molten zinc [3–5]. If the process is followed by diffusion heat treatments to form a fully alloyed coating, it is called galvannealing [3].

Another established method for the formation of corrosion resistant Fe–Zn layers on steel is sherardizing. In this process steel substrates are covered in zinc powder and annealed below the melting point of zinc resulting in the formation of intermetallic Fe–Zn phases on the steel surface [6,7]. Despite the effectiveness of hot dip galvanizing [3,8] sherardizing has several advantages. Sherardizing leads to highly uniform layer thicknesses that allows coating of irregular shapes and threaded parts [2,6]. Due to its lower process temperature compared to hot dip galvanizing sherardizing conserves functional properties

like hardness [6,7]. In addition the protective layer formed by sherardizing consists solely of intermetallic Fe–Zn phases [7,9,10]. Thus, no further heat treatment is needed to create fully alloyed coatings as applied in galvannealing.

The comparatively little research on sherardizing focuses on pack cementation [1,2,8,11–13]. In most of these studies the zinc powder contains a halide activator (NH_4Cl , ZnCl_2). This activator is reported to facilitate the zinc deposition on the steel substrate by chemical vapor deposition [1]. This mechanism is similar to the deposition of aluminum on iron- or nickel-based materials during pack aluminizing [14–17]. In other works [18,19] it is stated that the Fe–Zn layer formation during sherardizing is mediated by the vapor pressure of zinc itself without addition of any halide activators. However, Schmitz et al. [18] reported an increase in layer thickness when a certain amount of ZnCl_2 is added to the sherardizing process.

The aim of the present work is to investigate the impact of various zinc halides (ZnX_2 with $\text{X} \in \{\text{Cl}, \text{Br}, \text{I}\}$) on the formation of Fe–Zn phases on steel substrate. For this purpose we anneal steel samples in zinc powder in sealed quartz glass ampoules. On one hand experiments are carried out in pack cementation without any additives. On the other hand we performed sherardizing under rotation with ZnX_2 added to the zinc powder. We report the impact of the zinc halides on the composition of the interdiffusion layer and on the growth kinetics of the individual Fe–Zn phases. The growth kinetics are compared to those obtained by sherardizing in pack cementation. Finite difference methods (FDM)

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were applied to simulate the growth of the Fe–Zn phases and to explain their growth kinetics.

2. Experimental

Samples were cut from DC04 sheets, a low carbon steel, whose composition is given in Table 1. The lateral dimensions of the samples are $6 \times 10 \text{ mm}^2$ with a thickness of 1.5 mm. The samples were grinded and polished on both sides. Grinding was performed on SiC paper up to 1200 grit followed by two further polishing steps with 9 and $3 \mu\text{m}$ diamond suspensions on polishing cloths. The steel samples prepared this way were sealed under argon atmosphere in quartz glass ampoules with zinc powder 4P64 provided by Umicore and annealed. The argon pressure was set to establish a pressure of 1 atm at the annealing temperature according to the second law of Gay-Lussac. In the following two different experimental conditions established during annealing are described, i.e., sherardizing in pack cementation and under rotation.

In pack cementation the samples were fully embedded in zinc powder as illustrated in Fig. 1a. Annealing was performed at 663 K for different periods of time (1–16 h) in a preheated multi-zone resistance furnace to ensure a homogeneous temperature profile across the ampoule.

For annealing under rotation (see Fig. 1b) the zinc powder was mixed with small amounts of ZnX_2 with $X \in \{\text{Cl}, \text{Br}, \text{I}\}$. The zinc halides and the zinc powder were dried for several hours in a compartment dryer at 130°C before mixing. After mixing the powders were dried again over night and subsequently processed as quickly as possible. The powder mixture filled the ampoule to one third to ensure sufficient flow properties of the powder and zinc covering of the sample. The total mass of the powder mixture was about 11 g for an ampoule with an inner diameter of 1.2 cm and length of 9 cm. Rotation was performed by fixing the ampoule to a long quartz glass rod that was mounted to a rotation motor with a rotation speed of 10 rpm. Annealing was carried out at 663 K for different periods of time (1–16 h) in the furnace mentioned above.

Annealing under rotation and pack cementation was terminated by quenching the ampoules in water. The annealing times are adjusted by a heating correction [20] that leads to shorter effective annealing times. The thickness of the total layer Δx and of individual Fe–Zn phases formed by sherardizing was determined by means of optical and scanning electron microscopy (SEM) on polished cross sections. The employed Nova NanoSEM system is equipped with an energy dispersive X-ray (EDX) spectrometer. The cross sections were etched with a Nital etchant (1 ml concentrated nitric acid dissolved in 99 ml ethanol) for about 30 s to uncover the individual Fe–Zn phases and to determine their layer thicknesses.

In addition the total layer thickness Δx was deduced from the weight increase Δm of the sample measured after sherardizing

$$\Delta x = \frac{\Delta m / \bar{c}(Zn)}{\bar{\rho} \cdot A} \quad (1)$$

where $\bar{\rho} = 7.2 \text{ g} \cdot \text{cm}^{-3}$ is the average coating density, $\bar{c}(Zn)$ the average mole fraction of zinc in the coating, and A the sample surface. $\bar{c}(Zn)$ was determined by integrating the concentration profiles that were obtained by EDX linescans across the Fe–Zn layer. The value of $\bar{c}(Zn)$ slightly differs for the two experimental conditions ($\bar{c}(Zn)_{\text{rotation}} = 0.86$, $\bar{c}(Zn)_{\text{pack cementation}} = 0.85$).

Table 1

Composition of the DC04 steel sample in wt.% used in present experiments.

Steel alloy	C	Al	Si	P	S	Mn
DC04	0.036	0.040	0.015	0.014	0.015	0.267

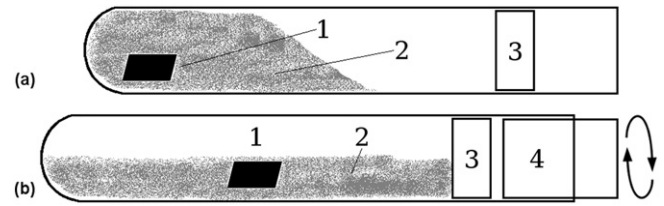


Fig. 1. Quartz glass ampoules for annealing (a) in pack cementation and (b) under rotation. 1: steel sample, 2: zinc powder, 3: glass plug, 4: glass rod.

3. Results

3.1. Sherardizing in pack cementation

Fig. 2 shows the total layer thickness Δx as function of annealing time t for pack cementation at 663 K. The gray and black squares represent the data obtained by the weight increase of the steel (FeC) samples and optical microscopy measurements on samples prepared in cross section, respectively. Both methods provide consistent results. The data obtained by optical microscopy are considered to be more trustworthy because the layer thickness was determined directly from cross-sectioned samples. Accordingly, the total layer thickness is determined by means of optical microscopy unless stated otherwise.

The total layer thickness as function of annealing time can be described with an empiric growth law [3,4]

$$\Delta x = K \cdot t^n \quad (2)$$

where K and n represent the growth-rate constant and the growth-rate time constant, respectively. The value of n is indicative of the process that mediates layer growth. A linear growth rate ($n = 1$) points to an interface controlled growth, $n = 0.5$ is expected for a diffusion-controlled layer growth [3]. The layer growth under pack cementation is best described with $n \approx 0.59$. This indicates a predominantly diffusion controlled growth mode consistent with results of Vourlias et al. [10], who observed a diffusion-controlled growth of the total Fe–Zn layer under pack cementation at 673 and 723 K.

The growth kinetic of the total layer is determined by the kinetics of the individual intermetallic phases grown during the sherardizing process. The intermetallic phases formed at 663 K by pack cementation for

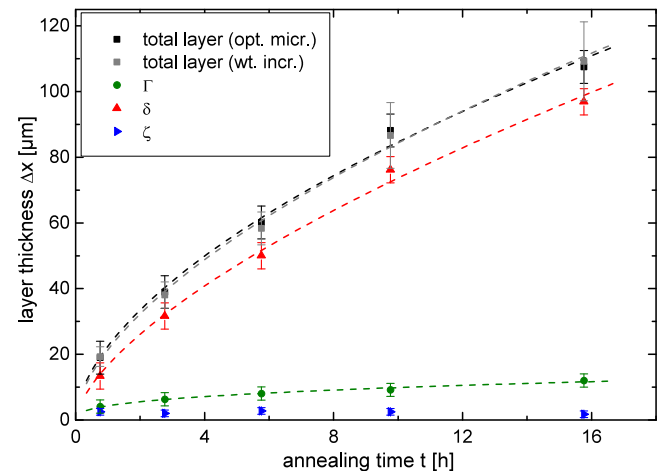


Fig. 2. Total layer and phase thickness as function of annealing time under pack cementation at 663 K. The data of the total layer thickness obtained by optical microscopy and weight increase are indicated by black and gray squares, respectively. The thicknesses of the Γ -, δ - and ζ -phases are indicated by green circles, red triangles and blue triangles, respectively. The dashed lines are least square fits to Eq. (2) displayed in the respective color of the data.

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