MICROSTRUCTURE AND GROWTH KINETICS OF ALLOY LAYER IN THE Fe- Zn SYSTEM

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Abstract

From the moment of immersion, the reaction between molten zinc and solid iron starts forming intermetallic phases. This diffusion controlled process is responsible for the final phase composition of zinc coating. Several samples were created by hot-dipping at various immersion times at T = 723 K (450 °C). Dipping times were divided into two groups. Short term immersion for studying early stages of phase nucleation and growth and long term immersion for observing later phase change and quasi-equilibrium states. For characterization of phases present an EDX was used to determine iron concentration across the alloy layer. After metallographic preparation each phase layer thickness was carefully measured all along with the total thickness of the alloy layer. Results of these measurements were compared with the latest findings. Keeping the same conditions of immersion and only changing the duration allowed us to estimate nucleation and growth kinetics of the layer forming process.

Keywords: Zinc, iron, growth kinetics, intermetallic phases

1. INTRODUCTION

The galvanizing process is widely used for the improvement of corrosion resistance of steel products in many industries including automotive, construction and electrical appliances. It is usually preformed at a temperature of approximately 450 °C. It provides two types of protection - barrier protection, which protects the surface from corrosive environment and galvanic protection. During a cathodic reaction the more active zinc corrodes preferentially than steel preventing it from anodic corrosion [1,2]. After solidification the coating is composed of different layers of Fe-Zn intermetallic phases. They vary in composition, morphology and hardness. No inhibition layer is formed during the process resulting in a uniform nucleation throughout the surface [3]. Already 5 s after immersion the ζ (zeta) phase with Fe content ranging from 5 - 6.2 wt.% and having columnar morphology forms a continuous layer. Simultaneously within first seconds the δ (delta) phase layer is formed. Although this phase has two variations δ_k and δ_p they both have columnar structure. The closest layer to the steel surface is the Γ (gamma) phase with Fe content of 23.5 - 28 wt.%. The incubation time for Γ phase is 30 s. This phase has a planar morphology and two modifications as well differing in crystal structure and iron content. Its modification, the Γ_1 phase has an Fe content of 17 - 19.5 wt.%. The outer most layer which can be observed is a substitutional solid solution of Fe in Zn, this phase is referred to as an η (eta) phase. All layers are formed in the first 2 minutes after immersion of pure Fe into Zn melt. The last process affecting growth of intermediate phases appears after 30 minutes. [4,5] The growth kinetics of layers can be expressed by a power-law equation [6,7,8]:

$$x = Kt^n \qquad (1)$$

where *x* is the layer thickness, *K* is the growth rate constant, *t* is the reaction time and *n* is the time exponent. In case that $n = 1$ the graph is a straight line and at $n = 0.5$ is an ideal parabola [4]. Many studies were done for long immersion which does not precisely match real hot-dipping process. The purpose of this paper is to estimate the growth kinetics of layers in the coating. This will serve as basis for further research in the field of thermodynamic modelling.

2. EXPERIMENTAL PROCEDURES

The chemical composition of substrate has a significant impact on the resulting coating phase thickness and structure. An iron wire manufactured by drawing with high purity of 99.99 % Fe was used for hot-dip galvanizing in molten Zn with the same purity. Surface roughness influences nucleation at the interface. To remove oxides and smoothen the surface a fine sand paper (2500, 4000) was used. Before immersion into a molten zinc a dry flux containing 54 % $ZnCl_2$ and 46 % NH_4Cl was applied to the surface of the wire. Bath temperature was set to 450 °C and the melt was cleansed using Zincogen flux. A series of short immersion times from 5 to 120 s were chosen for studying growth kinetics. Long term immersion was chosen for studying a quasi-equilibrium state after 1200, 3600 and 9000 s. After withdrawal rapid cooling into water was applied to all samples. Only sample after 9000 s was left to spontaneously solidify directly in the crucible and cool to room temperature. The samples were cross-sectioned, grinded (600, 1200, 2500, 4000), polished by an alcohol based Struers diamond slurry (3 µm, 1 µm) and etched in Nital 0.5 % for 5 - 10 s. Observations of layer thickness were performed using Zeiss optical microscope. Chemical composition was measured using JEOL JSM 7600F scanning electron microscope equipped with Oxford Instruments EDX. The thickness of individual layers was measured with ImageJ software.

3. RESULTS

Figure 1 shows the cross-section of the coating layer dipped for 5, 20 and 60 s, respectively. In the first stages two layers formed at the Fe surface. Chemical composition of the cross-section (see **Figure 2**) was used to determine the phases present in the coating. The first phases to nucleate are the δ and ζ phase. After 30 s a new discontinuous layer is formed at the surface interface. It is clearly visible after 60 s as seen at the micrograph in **Figure 1**. Because of its small thickness it was difficult to measure its chemical composition by using EDX analysis. The outermost η (eta) phase layer was not subjected to measurement because it does not contribute to the final properties.

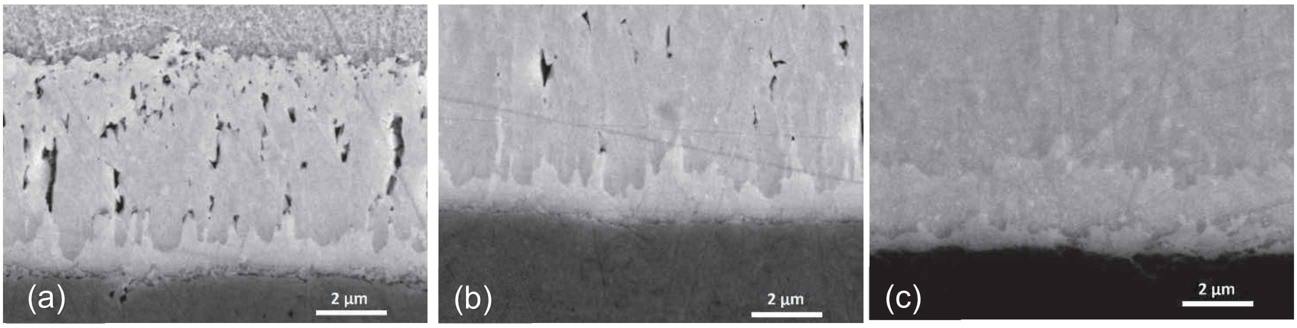

Figure 1 Interface microstructure after (a) 5 s (b) 20 s (c) 60 s. Composition contrast SEM images

The EDX analysis confirmed the expected phases present in the coating which is exemplyfied in **Figure 2**. The average composition of the ζ and δ layer after 5 s was 92.5 and 85.1 wt.% respecitively. After 60 s these layers contained 93.6 and 87.9 wt.% Zn for ζ and δ phase respectively. A new phase appeared with an averge composition of 73.91 wt.% Zn which matches the Γ phase.

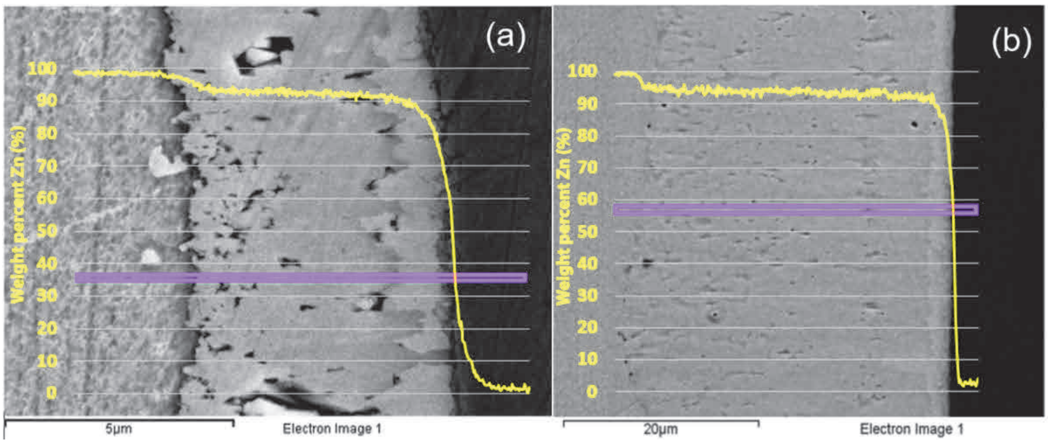

Figure 2 Local chemical analysis of the layer cross-section using SEM EDX (a) 5 s (b) 60 s. The y-axis represents the wt.% Zn

Kainuma [7] claims that the δ phase has two modifications that become appear in $60 < t < 300$ s time range. Pokorny [5] published that this separation occurs at dwell time 8 - 10 min. Our current experiments show the first separated δ_p phase appeared in the microstructure after 1200 s and continued to grow at the expense of the ζ phase. At 9000 s the ζ phase was completely transformed into δ_p phase. The thickness of the δ_k continued to grow independently in a linear manner as can be seen in **Figure 3**.

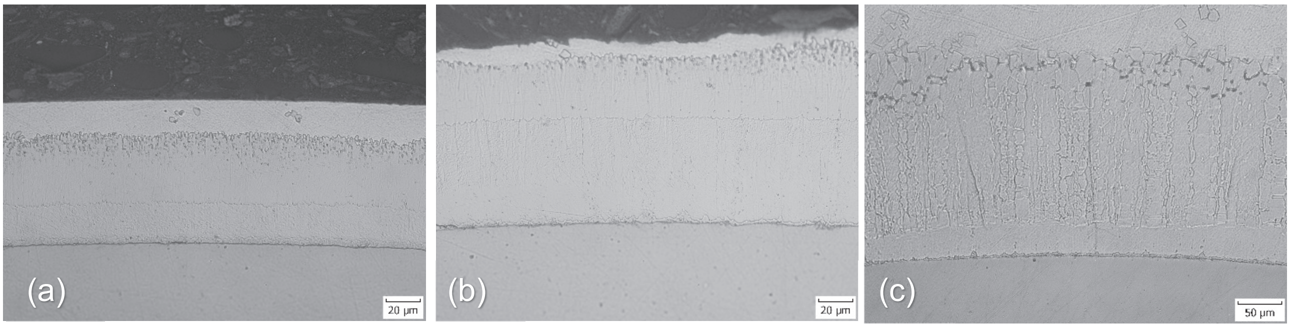

Figure 3 Interface microstructure after (a) 1200 s (b) 3600 s (c) 9000 s

4. DISCUSSION

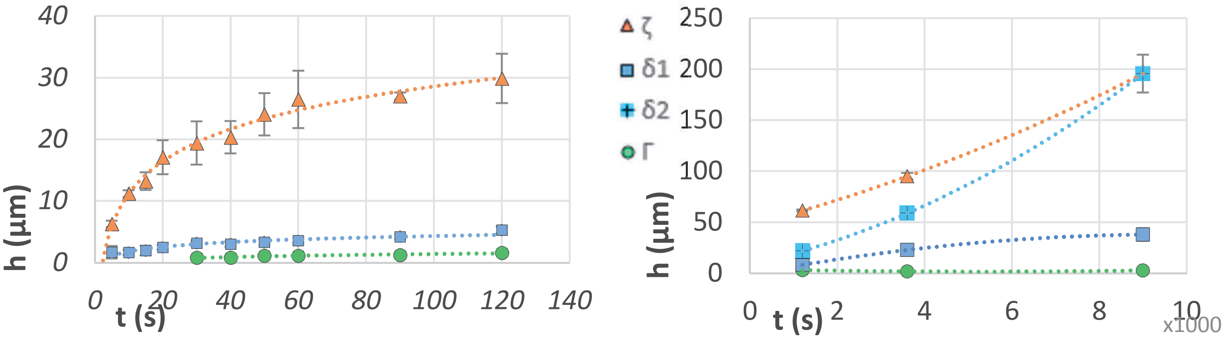

Figure 4 Individual layer thickness versus immersion time. Short term immersion (left) and term immersion (right)

Lines in **Figure 4** represent a mathematical approximation of the growth rate. They represent the total layer thickness of the individual phase. Error bars approximately show the local change of layer thickness. Each point was the average value from a minimum of 10 measurements. From this dependency it is possible to estimate the growh rate constant in the equation (1). It is evident that the ζ phase dominates during short immersion time which is in full agreement with published results [9].

The growth kinetics follow the Arrhenius type equation, written as:

$$x = Kt^n = At^n exp\left(\frac{-Q}{RT}\right) \tag{2}$$

Generally, the equation fits for$x(0,T) = 0$. There always exists an initial time t_0, incubation time when the nucleation begins. Due to a critical nucleation size there also exists an initial thickness x_0. The incubation time was calculated from the point of intersection on the *x*-axis in **Figure 4**. Thus equation (2) can be rewritten as:

$$x - x_0 = K(t - t_0)^n = A(t - t_0)^n exp\left(\frac{-Q}{RT}\right) \tag{3}$$

$x - x_0$ and $t - t_0$ represent the thickness and time increment, respectively. For simplification the initial thickness at t_0 was neglected as it is unobservable by common techniques. To get a straight line equation, Eq. 3 can be rewritten to:

$$\log(x - x_0) = \log K + n\ \log(\mathrm{t} - t_0) \tag{4}$$

By applying measured values to equation (4) the *n* time exponent is obtained from the slope of linear fit of $\log(t - t_0)$ vs. $\log(x - x_0)$. Onishi reported, that if the growth of phase is governed by diffusion the exponent should have the value of 0.5. Specifically an exponent of *n* = 1, *n* = 0.5 and *n* = 0.33 determines the growth kinetics is controlled by chemical reaction, volume diffusion or grian boundary diffusion, respectively [6,10].

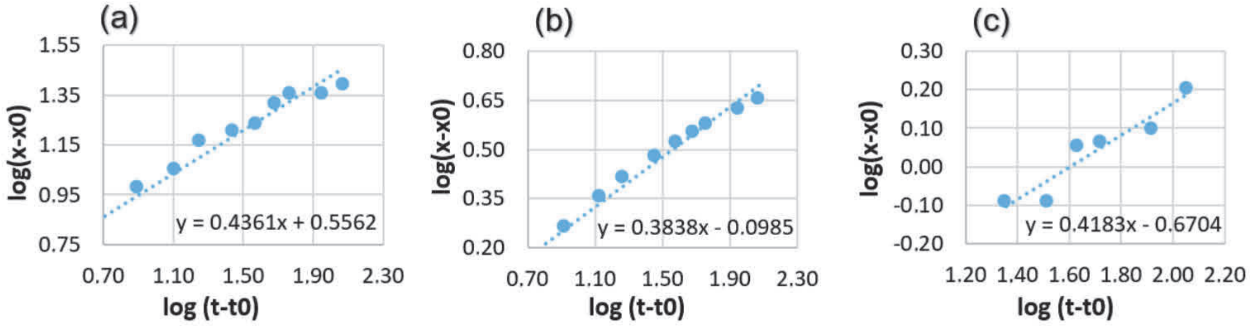

Figure 5 The logarithm of thickness increment vs logarithm of time increment for (a) ζ phase (b) δ phase (c) Γ phase

The growth kinetics were the case study of many authors. Mackowiak [10] presented a summary from various papers. Current results for short immersion times t < 120 s show the preservation of kinetics comparable with previously mentioned works. **Table 1** shows the calculated values of the time exponent determining the type of kinetics.

Table 1 Time exponent for individual layers

Layer	Γ (gamma)	δ (delta)	ζ (zeta)
n_c (-)	0.42	0.38	0.44

For the ζ (zeta) and the Γ (gamma) phases the exponent is close to 0.5 which identifies the diffusion process as volume diffusion. This satisfies the diffusion of Fe atoms through δ (delta) phase in the first stage and though δ (delta) and ζ (zeta) layers in later stage of growth for the ζ (zeta) phase. Likewise the diffusion of Zn atoms for the ζ (zeta) phase. The growth kinetics of these layers is approximately parabolic. For the short time immersion the δ (delta) phase shows slow growth rate which is reflected on the time exponent. As the diffusion and thus layer thickness is dependent on many factors it is difficult to provide unified results.

5. CONCLUSION

The interfacial reactions between solid Fe and molten Zn at 450 °C by hot-dipping were the subject of investigation in this study. Main results are as follows:

1) In the early stages the ζ phase showed the most significant growth rate as it was the one in contact with the melt. The growth rate gradually slowed down with immersion time.
2) Long term immersion showed the separation of δ phase to two modifications - palisade and columnar. δ_p growth increased in time and grew at the expense of the ζ phase until it was completely transformed. δ_k growth remained to continue linearly.
3) Using Arrhenius equation, the time exponent for individual layers was calculated providing information about diffusion during coating formation. Compared with the findings of previous authors the time exponent for long term immersion is comparable with our short term experiments.

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