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Diffusion Coefficient in the Zinc Coating Shaped on the Surface of Cast Iron and Steel Alloys

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Abstract

The article presents the method to assess the diffusion coefficient D in the sub-layer of intermetallic phases formed during hot-dip galvanizing “Armco” iron and ductile cast iron EN-GJS-500-7. Hot-dip galvanizing is one of the most popular forms of long-term protection of Fe-C alloys against corrosion. The process for producing a protective layer of sufficient quality is closely related to diffusion of atoms of zinc and iron. The simulation consist in performed a hot-dip galvanizing in laboratory condition above Fe-C alloys, in the Department of Engineering of Cast Alloys and Composites. Galvanizing time ranged from 15 to 300 seconds. Then metallographic specimens were prepared, intermetallic layers were measured and diffusion coefficient (D) were calculated. It was found that the diffusion coefficient obtained during hot-dip galvanizing “Armco” iron and zinc is about two orders of magnitude less than the coefficient obtained on ductile cast iron EN-GJS-500-7.

Keywords: Hot dip galvanizing, Intermetallic sublayer, Diffusion coefficient

1. Introduction

Directly after dipping in the liquid zinc, on the surface of the galvanizing element the layer of frozen zinc is formed. It is formed as a result of rapid crystallization, and then melt after some time. This stage of formation the zinc coating can be called “heat”. Then the alloy layer of the coating is formed, which consists the partial layers (sublayers) of intermetallic Fe-Zn phase. In the initial stage of crystallization of the coating on the surface of the product dipping into the liquid zinc subcooled liquid layer is formed with a thickness dx and a nominal concentration of N_0 . The condition of this process is the notion of a peritectic reaction, which is in accordance with phase equilibrium system Fe-Zn [1-11], shown in Figure 1. The system

comprises three peritectic points arranged in cascade and eutectic point E, which are usually disregard in the publications. In such nonequilibrium conditions different phases of Fe-Zn are formed and create sub-layer of phase in the expected sequence (according to the phase equilibrium and the value of supercooling ΔT marked in Fig. 1b) : Γ_1 , δ and ζ .

The released heat of crystallization from forming intermetallic phases is removal for the solid phase in a specified period, in the direction of the product. Crystallization of exogenous (directional) intermetallic Fe-Zn results from the temperature gradient G . The reason for its existence are the periodic alignment galvanized wall temperature of the product to the zinc bath temperature. At the final stage of the zinc coating accretion, during the ascent of the product from the bath, the phase layer $\eta(\text{Zn})$ crystallized. In the

"residual" zinc, remaining on the surface of the alloy layer, nucleate randomly dendrites (spangle).

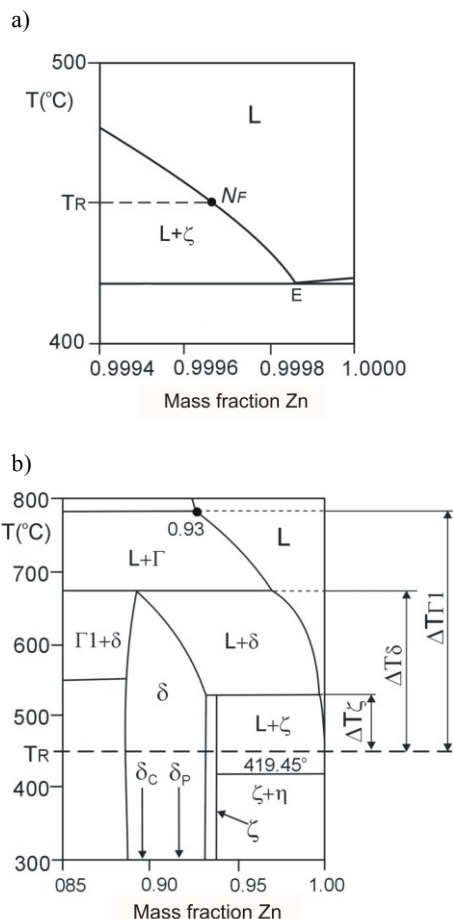


Fig. 1. Part of the phase equilibrium diagram of Fe-Zn alloys of a Zn-rich side, showing the existence of a eutectic point - a) and taking into account the phase stoichiometric chemical composition of ζ phase with two morphologies of δ phase - b)

2. Methodology

Crystallization kinetics study of the zinc coating was carried out using appropriately selected samples which have been hot-dip galvanized in laboratory of the Department of Engineering of Cast Alloys and Composites. The chemical preparation (using preparations used in industry) of the sample surface before entry into the liquid zinc, included treatments used in galvanizing plants, considered in the following order: purifying with degreasing, rinsing in water, pickling in 15% hydrochloric acid solution the samples made from "Armco" iron and ductile iron EN-GJS-500-7, rinsing in water, fluxing (in the technology used in the industry - 180 s) in a solution containing: zinc chloride to 300 g/l ammonium chloride to 150 g/l. Appointed iron content in the flux was 0.41 g/l. The last step before the inserting the sample into a zinc bath was drying the surface with coating the flux. Zinc

bath prepared from the electrolytic zinc Z2 with content according to the certificate issued by the Quality Control Department Casting Zinc "Silesian town" (in wt.%): 99.995 Zn, 0.0005 Pb, 0.0013 Cd, 0.0002 Fe, 0.0001 Sn, 0.0001 Cu, 0.0001 Al. For study of zinc coating formation used an Armco iron. The chemical composition of the material (according to the purchase certificate) contained (in wt.%): 0.036 C, under 0.01 Si, 0.01 P, 0.1 Mn, 0.09 Al, and remainder Fe. Samples were subjected to hot-dip galvanizing in a time from 15 to 300 sec. Then made the microsections and measured the thickness of the protective layer. Hot-dip galvanizing process was carried out on samples of "Armco" iron and ductile iron EN-GJS-500-7. Examples of the microstructures of zinc coating formed in a 300 second of galvanizing process are shown in Fig. 2 and 3.

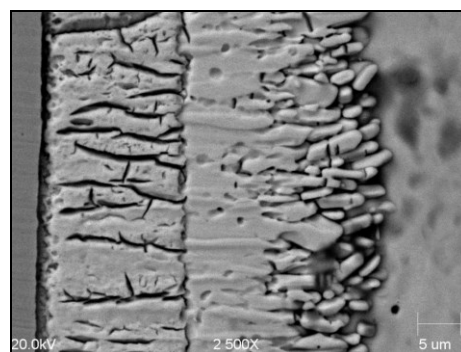


Fig. 2. The zinc coating obtained on the sample surface of Armco iron

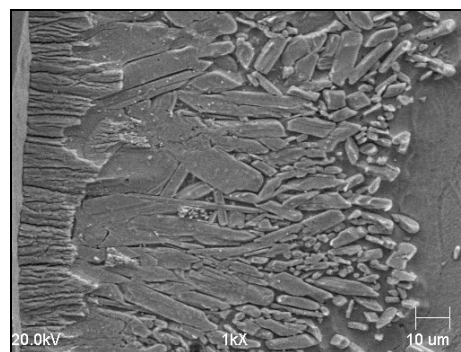


Fig. 3. The zinc coating obtained on the sample surface of ductile iron EN-GJS-500-7

3. Simulation of the diffusion coefficient

The analysis of the paper [12], suggest that the description of the segregation allows to theoretical consideration of crystallization process for various conditions of formation a solid phase, using the equation describing back-diffusion parameter α :

$$\alpha = \frac{D \cdot t_L}{\lambda^2} \quad (1)$$

where: D – diffusion coefficient in the solid phase component,
 t_L – crystallization time, λ – coating thickness

In the model presented in [13], defines a theoretical diffusionless crystallization (for boundary conditions $\alpha=0$, $\beta \rightarrow 0$, $D \rightarrow 0$), according to equations of homogeneous component concentration in the liquid phase N_L (2), segregation in the solid phase N_S (3) and the theoretical description of the equilibrium crystallization (for boundary conditions : $\alpha = 1$, $\beta \rightarrow 1$, $D \neq 0$).

$$N_L = N_0(1-x)^{k-1} \quad (2)$$

$$N_S = k \cdot N_0 \cdot (1-x)^{k-1} \quad (3)$$

In addition, it was decided to consider the influence of the flux during the crystallization of intermetallic Fe-Zn (Fig. 4). The analysis can be assumed that the development of a model for galvanizing technology using chemical preparation surface of the product, including the flux, requires the assumptions of a hypothesis concerning its disappearance in the process.

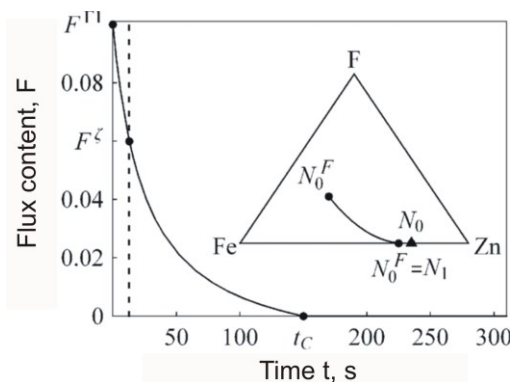


Fig. 4. Hypothetical function describing the influence of the flux in the iron galvanizing and theoretical interpretation increasing of zinc coating in terms to a hypothetical path of crystallization in the ternary system Fe-Zn-F (chemical preparation surfaces, including flux)

It was assumed for the compilation of test results, that 90% of the flux disappears during solidification and melting in first step of the hot-dip galvanizing (frozen zinc stage)

The other 10% (or 0.1 in a mass fraction) is involved in the process of crystallization - as a pad for heterogeneous nucleation for the various phases - Fig. 4

Figure 5 shows influence of the back diffusion coefficient α on diffusion coefficient D in sublayer of ζ phase shaped on Armco iron. Figure 6 shows the same influence, shaped on nodular cast iron EN-GJS-500-7.

These graphs were created by the transformation of equation (1) and attach the value of zinc coating thickness depending on the time of galvanizing.

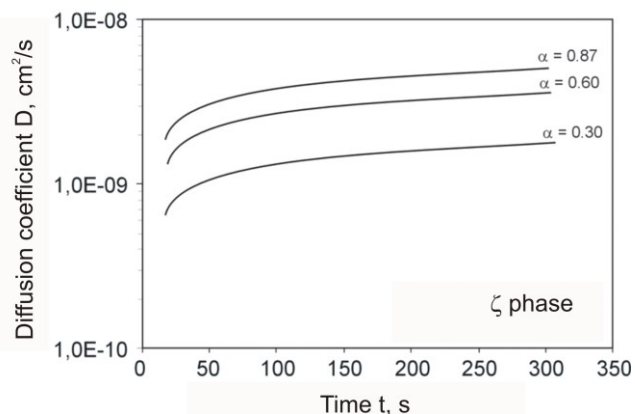


Fig. 5. Effect of back-diffusion coefficient α on the diffusion coefficient D in sublayer of ζ phase (for Armco iron)

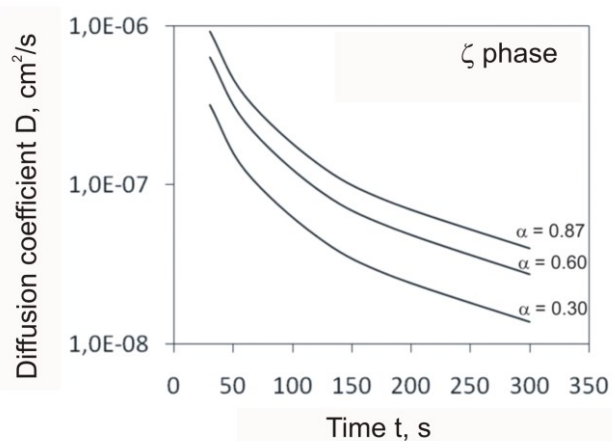


Fig. 6. Effect of back-diffusion coefficient α on the diffusion coefficient D in sublayer of ζ phase (for ductile iron EN-GJS-500-7)

4. Summary

During the hot dip galvanizing Fe-C alloy, depending on its type, the coating is formed in a different way. This also determines the value of the diffusion coefficient D . The presented results (Fig. 15 and 16) shows that the value of the diffusion coefficient in the hot-dip galvanizing of Armco iron sample is about two orders of magnitude smaller than in the case of hot-dip galvanizing of ductile iron EN-GJS-500-7. Assumes that in the sublayer the homogeneous concentration was form as a result of redistribution. Based on this, the concentration parameter α should be close to unity, thus in this paper the accepted value is $\alpha = 0.87$. In case of “Armco” iron the longer time of galvanizing process the diffusion coefficient D increase whereas it should be constant, because it does not depend on time (t) of the process or the thickness of the sublayers (λ), it only depends on the temperature. The constant values do not reveal a diffusion coefficient D in the nodular cast iron too, but in this case the

diffusion coefficient decreases in time. This difference may be due to the existence of the diffusion channel, which disappears during the galvanizing process, especially in case of hot-dip galvanizing of Armco iron. In the case of ductile iron can be assumed that the intermetallic layer is less compact, which results in a longer duration of action of the diffusion channel filled with liquid zinc.

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