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D. KOPYCIŃSKI*[#], E. GUZIK*, A. SZCZĘŚNY***SHAPING OPTIMAL ZINC COATING ON THE SURFACE OF HIGH-QUALITY DUCTILE IRON CASTING.
PART II – TECHNOLOGICAL FORMULA AND VALUE OF DIFFUSION COEFFICIENT**

The completed research presented in the first part of the article has allowed linking the manufacturing technology of ductile iron castings with the process of hot dip galvanizing. On the basis of these data simulations were carried out to examine the behaviour of zinc diffusion coefficient D in the galvanized coating. The adopted model of zinc coating growth helped to explain the cases of excessive growth of the intermetallic phases in this type of coating. The paper analyzes covered the relationship between the roughness and phase composition of the top layer of product and the thickness and kinetics of zinc coating growth referred to individual sub-layers of the intermetallic phases. Roughness and phase composition in the surface layer of product were next related to the diffusion coefficient D examined in respective sublayers of the intermetallic phases.

Keywords: hot dip galvanizing, ductile iron, surface roughness, diffusion coefficient

1. Introduction

Hot dip galvanizing is one of the most common methods to protect products made from the Fe-C alloys from the effect of atmospheric corrosion.

It should be noted that in this study, the analysis of zinc coating structure was based on the Fe-Zn phase equilibrium diagram, although in reality the zinc coating growth on the surface of the galvanized product follows the rules of a non-equilibrium phase diagram, unknown so far. Additionally, because of the high value of the undercooling ΔT , it has been assumed that the isothermal crystallization of individual intermetallic phases is proceeding in a dynamic mode [1-12]. An important factor that affects the growth of the protective layer is flux [4]. Also value of diffusion coefficient which can be estimated from the following (Equation 1) [13]:

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

where:

- D – diffusion coefficient,
- t – time, s,
- λ – zinc coating thickness, μm ,
- α – back diffusion [14,15] (estimated on 0.87).

2. Experimental

The aim of this study was to identify the factors (parameters) which affect the thickness of the resulting protective layer, namely:

- a) calculation of technological formula of the zinc coating thickness,
- b) calculation value of diffusion coefficient D ,
- c) identification of intermetallic phases formed during galvanizing process.

3. Results and discussion**3.1. The technological formula of coating growth**

Based on the conducted studies (Part I), several equations were developed to express the dependence between zinc coating growth, the type of moulding technology and casting surface roughness. Kinetic growth Equations (2)-(5) for the zinc coating layer deposited on ductile iron samples with different surface roughness obtained by different moulding technologies are shown below Eqs. (2)-(5).

For tests were selected castings poured into moulds made from the following sands: common bentonite sand (B), loose self-hardening sand with oil (O), loose self-hardening sand

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with furan resin (S) and sand with hydrolyzed ethyl silicate and molochite (M).

$$\lambda_M = 0.86 \cdot t^{0.67}; \quad (2)$$

$$\lambda_O = 1.43 \cdot t^{0.65}; \quad (3)$$

$$\lambda_S = 1.41 \cdot t^{0.63}; \quad (4)$$

$$\lambda_B = 1.44 \cdot t^{0.70} \quad (5)$$

where:

λ_M – zinc coating thickness (casting – mould M), μm ,

λ_O – zinc coating thickness (casting – mould O), μm ,

λ_S – zinc coating thickness (casting – mould S), μm ,

λ_B – zinc coating thickness (casting – mould B), μm .

Using the above equations and knowing the surface roughness values, the $\lambda = f(t)$ equation was transformed into a $\lambda = f(R_a)$ dependence. This operation allowed expressing the growth of zinc coating as a function of the surface roughness R_a in the range of the R_a parameter values from 16,7 μm to 43 μm . Then equations for the zinc coating growth of the $\lambda = f(R_a)$ type were developed for different times of the hot dip galvanizing treatment. The obtained relationships are summarized below Eq. (6)-(19):

$$\lambda = 1.94 R_a^{0.56} \quad \text{for } t = 30 \text{ sec.} \quad (6)$$

$$\lambda = 2.79 R_a^{0.59} \quad \text{for } t = 60 \text{ sec.} \quad (7)$$

$$\lambda = 4.01 R_a^{0.62} \quad \text{for } t = 120 \text{ sec.} \quad (8)$$

$$\lambda = 4.96 R_a^{0.64} \quad \text{for } t = 180 \text{ sec.} \quad (9)$$

$$\lambda = 5.77 R_a^{0.65} \quad \text{for } t = 240 \text{ sec.} \quad (10)$$

$$\lambda = 6.48 R_a^{0.66} \quad \text{for } t = 300 \text{ sec.} \quad (11)$$

$$\lambda = 7.13 R_a^{0.67} \quad \text{for } t = 360 \text{ sec.} \quad (12)$$

$$\lambda = 7.73 R_a^{0.68} \quad \text{for } t = 420 \text{ sec.} \quad (13)$$

$$\lambda = 8.28 R_a^{0.68} \quad \text{for } t = 480 \text{ sec.} \quad (14)$$

$$\lambda = 8.81 R_a^{0.69} \quad \text{for } t = 540 \text{ sec.} \quad (15)$$

$$\lambda = 9.31 R_a^{0.69} \quad \text{for } t = 600 \text{ sec.} \quad (16)$$

$$\lambda = 10.09 R_a^{0.70} \quad \text{for } t = 700 \text{ sec.} \quad (17)$$

$$\lambda = 10.81 R_a^{0.71} \quad \text{for } t = 800 \text{ sec.} \quad (18)$$

$$\lambda = 11.50 R_a^{0.71} \quad \text{for } t = 900 \text{ sec.} \quad (19)$$

From the derived relationships of coating growth referred to the surface roughness parameter R_a of ductile iron samples and to the time t of the hot dip galvanizing treatment, the value of the constant A and the exponent n were determined, to develop next a general “technological formula” of the zinc coating growth, which took the form of (20):

$$\lambda_{R_a} = 0,33t^{0,52} \cdot R_a^{0,45t^{0,07}} \quad (20)$$

As a result of these studies it was found that a relationship exists between the surface roughness of castings, varying due to different moulding technologies used, and the zinc coating thickness. Moreover, this relationship becomes apparent even after a short time of the hot dip galvanizing, i.e. after 30 sec-

onds of the process duration. Studies have shown that with the increasing value of the casting surface roughness R_a , the zinc coating thickness is also increasing. This relationship is more noticeable after 180 seconds of the hot dip galvanizing process and deepens with process duration. Remembering that the equation is based on the parameters of coating microstructure formed on the surface of ductile iron samples with a pearlitic matrix, it has been considered necessary to introduce a coefficient m allowing for corrections in the zinc coating thickness. It is the fact well known that ferrite present in the substrate can significantly alter the zinc coating thickness λ . The value of the coefficient m was determined from equations (2)-(5) from Part I of the article, and it is nothing else but a ratio of the λ values calculated for individual fractions of the ferrite content in metal matrix. The calculated coefficient m has been introduced to the “technological formula” and as a result of this operation, the equation in its final form was obtained (21):

$$\lambda_{R_a} = m \cdot 0,33t^{0,52} \cdot R_a^{0,45t^{0,07}} \quad (21)$$

where the values of the coefficient m are given in Table 1.

TABLE 1

The values of the coefficient m

Percent ferrite content in the sample metal matrix	F0	F20	F40	F60	F80	F100
m	1.00	1.11	1.21	1.36	1.57	1.81

3.2. Model of coating growth and the diffusion coefficient D

Equation (21) can replace several equations for the kinetics of zinc coating growth related to the manufacturing conditions (Table 2), and as such can be used in zinc galvanizing plants to predict the zinc coating thickness in a range of products, allowing for the time of galvanizing treatment t in the range of 30 sec.÷900 sec. and surface roughness parameter R_a comprised in the range of 16.71÷43.05 μm .

As a result of multi-faceted metallographic analysis of samples, the morphology of zinc coating formed on products characterized by high silicon content was evaluated (Figs. 1-2). The test results indicate that the formation of intermetallic Fe-Zn phases on the surface of ductile iron castings under isothermal conditions is proceeding according to the crystallization sequence where Γ_1 phase is not the first one to nucleate and grow, but priority has the δ phase followed by the ζ phase. Furthermore, during the hot dip galvanizing of such products, the thermodynamic conditions can promote in zinc coating the formation of ζ phase alone.

In the following studies it has been assumed that under isothermal conditions the peritectic phase formation in zinc coating on the surface of products cast from iron or steel is consistent with the crystallization sequence. Therefore, in the studies, the phase equilibrium diagram of Zn-Fe alloys has been used, as-

TABLE 2

Examples of equations expressing the kinetics of zinc coating growth in the case of varying content of phases in the metal matrix, varying surface roughness and diffusion coefficient D [cm^2/s] calculated for the alloy layer formed in zinc coating after 300 seconds of the galvanizing treatment

R_a [μm] D [cm^2/s]	F0% P100%	F30% P70%	F50% P50%	F70% P30%	F100% P0%
10	$\lambda = 0.86t^{0.62}$	$\lambda = 0.99t^{0.62}$	$\lambda = 1.09t^{0.62}$	$\lambda = 1.25t^{0.62}$	$\lambda = 1.55t^{0.62}$
$D =$	$2.54 \cdot 10^{-8}$	$3.41 \cdot 10^{-8}$	$4.14 \cdot 10^{-8}$	$5.37 \cdot 10^{-8}$	$8.27 \cdot 10^{-8}$
20	$\lambda = 1.144t^{0.651}$	$\lambda = 1.326t^{0.651}$	$\lambda = 1.462t^{0.651}$	$\lambda = 1.663t^{0.651}$	$\lambda = 2.065t^{0.651}$
$D =$	$6.37 \cdot 10^{-8}$	$8.56 \cdot 10^{-8}$	$1.04 \cdot 10^{-7}$	$1.35 \cdot 10^{-7}$	$2.08 \cdot 10^{-7}$
30	$\lambda = 1.35t^{0.67}$	$\lambda = 1.57t^{0.67}$	$\lambda = 1.70t^{0.67}$	$\lambda = 1.97t^{0.67}$	$\lambda = 2.44t^{0.67}$
$D =$	$10.96 \cdot 10^{-8}$	$14.74 \cdot 10^{-8}$	$17.28 \cdot 10^{-8}$	$23.16 \cdot 10^{-8}$	$35.72 \cdot 10^{-8}$
40	$\lambda = 1.526t^{0.681}$	$\lambda = 1.769t^{0.681}$	$\lambda = 1.950t^{0.681}$	$\lambda = 2.219t^{0.681}$	$\lambda = 2.755t^{0.681}$
$D =$	$1.60 \cdot 10^{-7}$	$2.15 \cdot 10^{-7}$	$2.61 \cdot 10^{-7}$	$3.38 \cdot 10^{-7}$	$5.21 \cdot 10^{-7}$
50	$\lambda = 1.67t^{0.69}$	$\lambda = 1.94t^{0.69}$	$\lambda = 2.14t^{0.69}$	$\lambda = 2.43t^{0.69}$	$\lambda = 3.02t^{0.69}$
$D =$	$21.54 \cdot 10^{-8}$	$28.96 \cdot 10^{-8}$	$35.20 \cdot 10^{-8}$	$45.58 \cdot 10^{-8}$	$70.25 \cdot 10^{-8}$
60	$\lambda = 1.806t^{0.699}$	$\lambda = 2.094t^{0.699}$	$\lambda = 2.309t^{0.699}$	$\lambda = 2.627t^{0.699}$	$\lambda = 3.261t^{0.699}$
$D =$	$2.75 \cdot 10^{-7}$	$3.69 \cdot 10^{-7}$	$4.49 \cdot 10^{-7}$	$5.81 \cdot 10^{-7}$	$8.96 \cdot 10^{-7}$
70	$\lambda = 1.93t^{0.71}$	$\lambda = 2.23t^{0.71}$	$\lambda = 2.43t^{0.71}$	$\lambda = 2.80t^{0.71}$	$\lambda = 3.48t^{0.71}$
$D =$	$33.83 \cdot 10^{-8}$	$45.48 \cdot 10^{-8}$	$53.68 \cdot 10^{-8}$	$71.56 \cdot 10^{-8}$	$110.28 \cdot 10^{-8}$
80	$\lambda = 2.036t^{0.711}$	$\lambda = 2.361t^{0.711}$	$\lambda = 2.603t^{0.711}$	$\lambda = 2.961t^{0.711}$	$\lambda = 3.676t^{0.711}$
$D =$	$4.00 \cdot 10^{-7}$	$6.35 \cdot 10^{-7}$	$7.72 \cdot 10^{-7}$	$8.47 \cdot 10^{-7}$	$1.10 \cdot 10^{-6}$
90	$\lambda = 2.14t^{0.72}$	$\lambda = 2.48t^{0.72}$	$\lambda = 2.73t^{0.72}$	$\lambda = 3.11t^{0.72}$	$\lambda = 3.86t^{0.72}$
$D =$	$47.27 \cdot 10^{-8}$	$63.55 \cdot 10^{-8}$	$77.24 \cdot 10^{-8}$	$99.96 \cdot 10^{-8}$	$154.16 \cdot 10^{-8}$
100	$\lambda = 2.234t^{0.721}$	$\lambda = 2.593t^{0.721}$	$\lambda = 2.856t^{0.721}$	$\lambda = 3.249t^{0.721}$	$\lambda = 4.034t^{0.721}$
$D =$	$5.40 \cdot 10^{-7}$	$7.28 \cdot 10^{-7}$	$8.83 \cdot 10^{-7}$	$1.14 \cdot 10^{-6}$	$1.76 \cdot 10^{-6}$

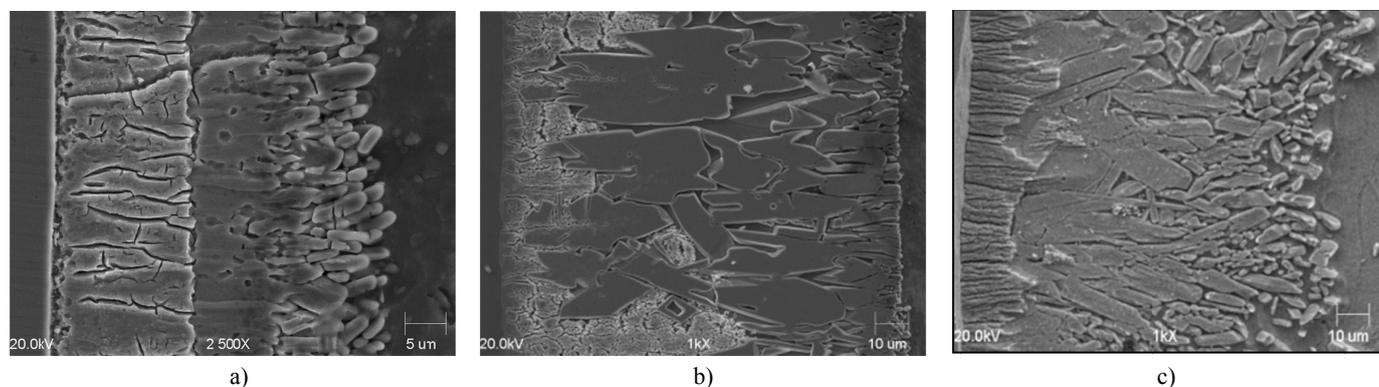


Fig. 1. The example of zinc coating morphology obtained after 300 seconds of the hot dip galvanizing process: Armco iron (a), high-silicon steel (b), and ductile iron (c); SEM microstructure

suming that it is the nominal zinc concentration N_o in a periodically formed layer dx that controls the zinc coating morphology. When the concentration N_o exceeds the level of 93% Zn, the δ phase nucleates and grows (Fig. 3, left column), followed by the ζ phase. When the concentration N_o in the layer dx exceeds the level of 94% Zn, the nucleating δ phase is no longer capable of creating its own continuous sublayer and nucleates parallel with the ζ phase (Fig. 3, middle column). The δ phase is totally eliminated from the zinc coating, when zinc concentration in the layer dx reaches 95% (Fig. 3, right column). Thus defined mechanism of zinc coating growth enables simulation of the diffusion coefficient D according to equation (1), the sample values are summarized in Fig. 3.

4. Conclusions

Based on the conducted studies it was possible to formulate the following conclusions:

1. It has been proved that under isothermal conditions the formation of intermetallic Fe-Zn phases in zinc coating on the surface of ductile iron casting proceeds according to the crystallization sequence where the Γ_1 phase is not formed and the first phase to form is the δ phase and then the ζ phase. Furthermore, when such products are subjected to the hot dip galvanizing, the thermodynamic conditions created in the growing zinc coating are often sufficient for the formation of the ζ phase alone.

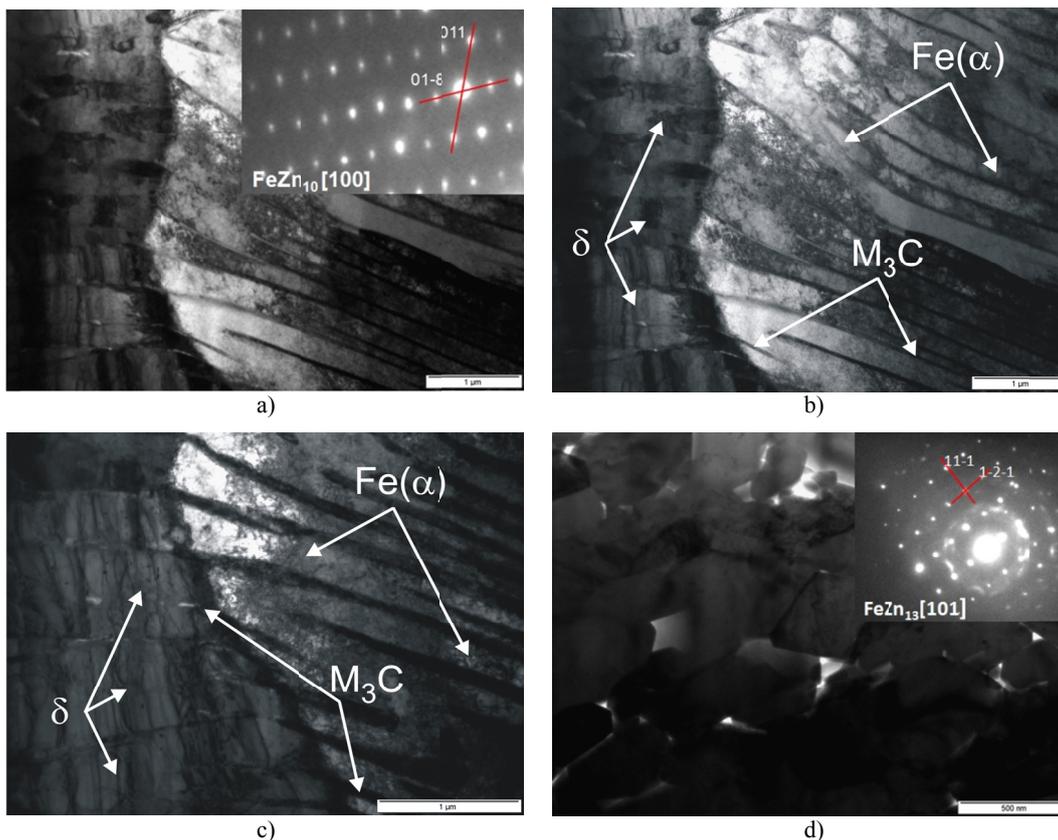


Fig. 2. The phase composition of an area lying between the surface layer of ductile iron casting and the first intermetallic phase formed in zinc coating – the δ phase, FeZn_{10} (a) and (b, c), combined with the second intermetallic phase formed in zinc coating – the ζ phase, FeZn_{13} (d); SEM microstructure

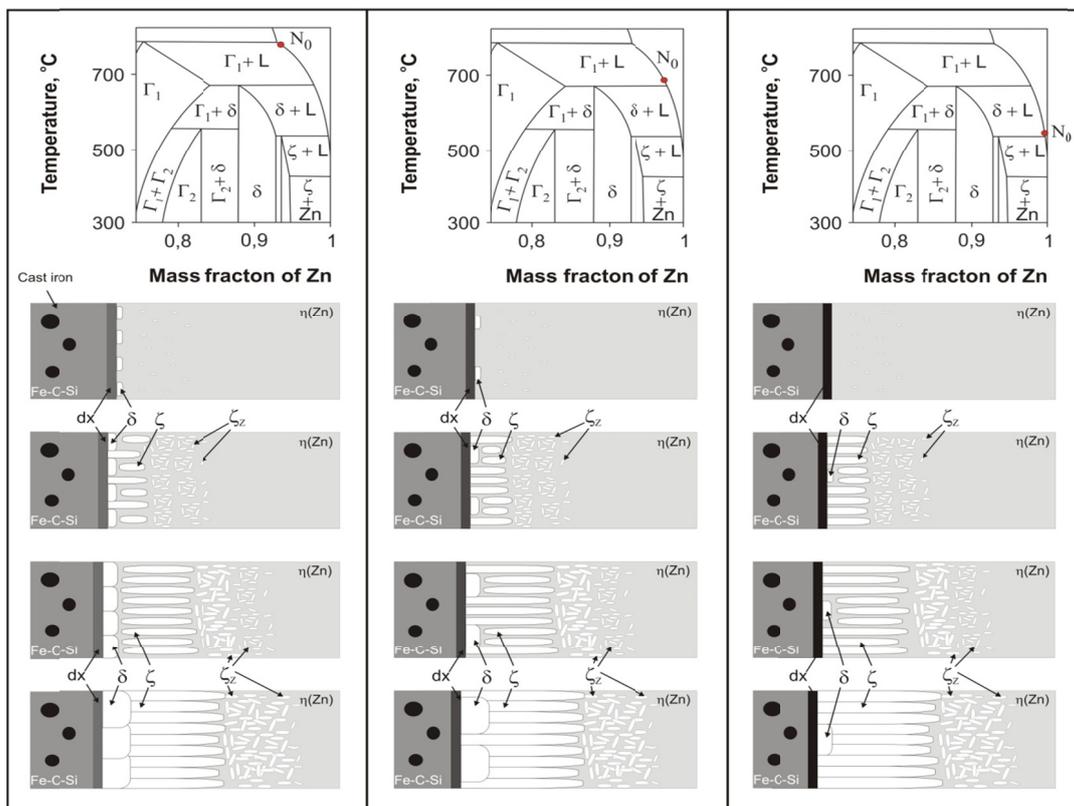


Fig. 3. The mechanism of zinc coating growth on the surface of ductile iron casting with varying concentration N_0 in the layer dx ; the continuous sublayer of δ phase – (left column), the discontinuous sublayer of δ phase – (middle column), absence of δ phase precipitates in the initial stage of isothermal crystallization – (right column)

2. A "technological formula", important from the point of view of technology, was developed to show the kinetics of zinc coating growth on the surface of ductile iron casting, where the zinc coating thickness λ was referred to parameters such as the galvanizing time t , the surface roughness R_a and the phase composition of metal matrix. The diffusion coefficient D was also estimated.

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