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THE MECHANISM OF PHASE TRANSFORMATION TO OBTAIN ZINC-IRON COATINGS

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ABSTRACT

Important changes in the ratio of constitutive phases take place during heating of galvanized parts due to Zn coating layer changed into Zn-Fe alloy. The work deals with a mathematical correlation between diffusion phenomena occurring in layer, depending on temperature and time of heat treatment, and iron content of coating. Both terms define a certain structure.

KEYWORDS: coating layer, interphase surface, heat treatment.

1. Introduction

Various coating procedures, based on zinc, oriented to physico - chemical and mechanical characteristics improvement, have emerged lately.

Zn-Fe alloy protective coatings are considered among favorites due to their high weldability, resistance to corrosion, excellent varnishability, lower specific weight of layer, and thus of the whole product, resulting in zinc saving. Zinc alloying with iron is put into operation using diffusion procedures during heating of galvanized products.

2. Experimental conditions

Galvanized steel samples, with chemical composition: 0.05 % C, 0.26 % Mn; 0.02 % Si; 0.012 % P; 0.015 %S; 0.039 % Al and zinc layer specific weight of 108 g/m^2 were heated for 1÷30 minutes at 500÷650 ^{o}C. Heat treated samples were metallographically examined and X - ray diffraction tested with a view to establish structural and chemical composition change due to heat treatment [1].

3. Results and conclusions

As a result of microscopic examination (fig.1) and X-ray diffraction testing (fig. 2) in coating layer were detected phase ratio changes, according to heat treatment parameters. Considering that the physico-chemical and mechanical properties differ for the two phases and phase ratio, the properties of the product are to be decided; these structural changes are of great importance in practice. The desirable coating would be a Zn-Fe coating with 8÷10 % Fe (according to some authors, up to 12% Fe [2]), with a structure consisting mainly of δ_1 phase and a small quantity of Γ phase. Therefore it is necessary an accurate mathematical correlation between layer phenomena, depending on heat treatment parameters and iron content of coating, both defining a certain structure. It was found that structural changes, due to rise temperature occur in three distinct stages:

a). η phase disappearance and ξ phase growth (500-530 ^{0}C)

b). ξ phase gradual disappearance and δ_1 phase growth (530 - 600 ^{0}C).

c). the rapid growths Γ phase (600 – 650 ^{0}C).

The formula and Fe content (wt %) of these Zn-Fe intermetallic phases are given in Table 1.

***Table 1**. Characteristics of Zn-Fe intermetallic phases*

Phase	Formula	Fe content (wt %)
η	Zn	0.003 (c_6)
ζ	FeZn13	6.2-6.0 (c_4-c_5)
δ	FeZn10; $Fe_3 Zn_7$	11.5-7.0 (c_2-c_3)
Γ	Fe5Zn21;Fe3Zn10	20.5-28.0 (c_0-c_1)

These changes include transformations characteristic to a reactive diffusion process. In this type of diffusion, the rate depends on reaction constant ratio, resulting three possible processes [3].

In the case specified (at stage a), under 550 ^{0}C, when the diffusion of iron atoms is negligible, the process is considered as diffusion process.

Stage b) at 550÷600 ^{0}C, when the mobility of iron atoms is rising is considered as intermediate process. Stage c) at 600÷650°C is considered a kinetic process, emphasized by the rapid growth of Γ phase.

The transformations occurring in the stage a) may be considered as reactions at interphase surface level.

Let: x_1, x_2, x_3 – instantaneous points of Γ/δ, δ/ξ, ξ/η interfaces able to change their position with v_1, v_2, v_3 rates and J_I – the iron quantity related to the moving interface and representing the iron given by i phase to i+1 phase (where i =1; 2; 3). Phase growing ratio is calculated using the relations:

$$\frac{d\Gamma}{dt} = v_1; \tag{1}$$

$$\frac{d\delta}{dt} = v_2 - v_1; \tag{2}$$

$$\frac{d\xi}{dt} = v_3 - v_2; \tag{3}$$

The content of iron at interface boundaries (c_0 to c_6 in table 1) was considered according to the Fe-Zn equilibrium diagram [4], showing its constant maintaining up to 550°C.

Considering J_0 as the total quantity of iron related to the interfaces in the underlayers of coating (fig.3), the law of iron conservation [5] results in the following:

$$J_0 - J_1 = \frac{d\Gamma}{dt} \cdot \frac{c_0 + c_1}{2} = 0.242\frac{d\Gamma}{dt}; \tag{4}$$

$$J_1 - J_2 = \frac{d\delta}{dt} \cdot \frac{c_2 + c_3}{2} = 0.092\frac{d\delta}{dt}; \tag{5}$$

$$J_2 - J_3 = \frac{d\xi}{dt} \cdot \frac{c_4 + c_5}{2} = 0.061\frac{d\xi}{dt}; \tag{6}$$

Total input quantity of iron is in balance with the size of phase growth (local diffusion of iron atoms is moving at the same rate as interface 3), therefore:

$$J_0 = 0.242\frac{d\Gamma}{dt} + 0.092\frac{d\delta}{dt} + 0.061\frac{d\xi}{dt}; \tag{7}$$

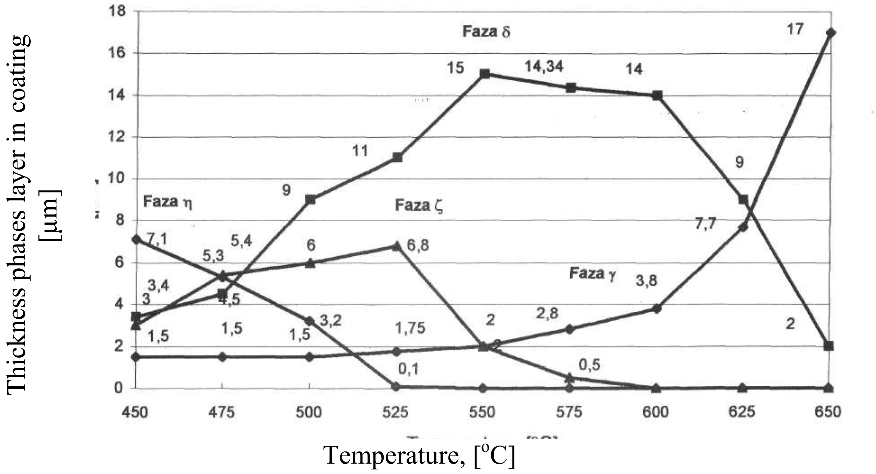
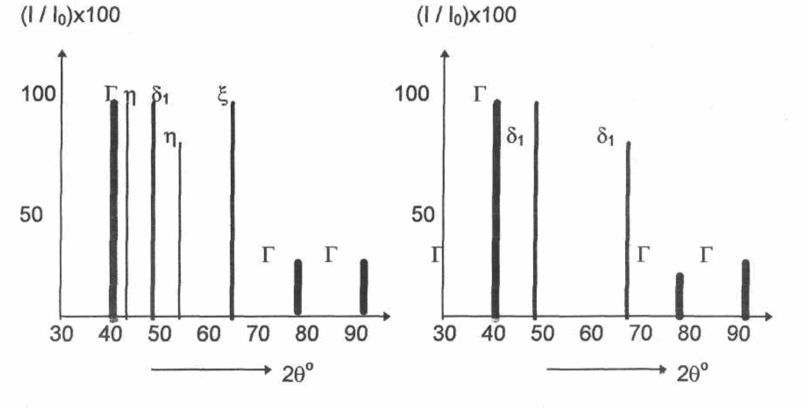
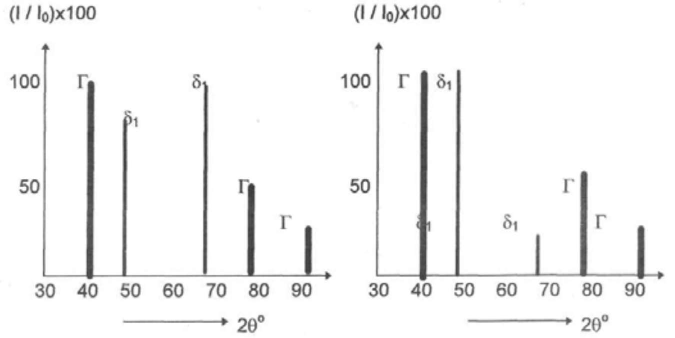


Fig. 1. *Dimensions of the phase layers depending on the heat treatment temperature*



a) 500°C – 4.23% Fe

b) 550°C – 8.10% Fe



a) 600^{0}C – 13.98% Fe b) 650^{0}C – 18.21% Fe

Fig. 2. *Results of the diffractometric analysis on samples treated at various temperatures*

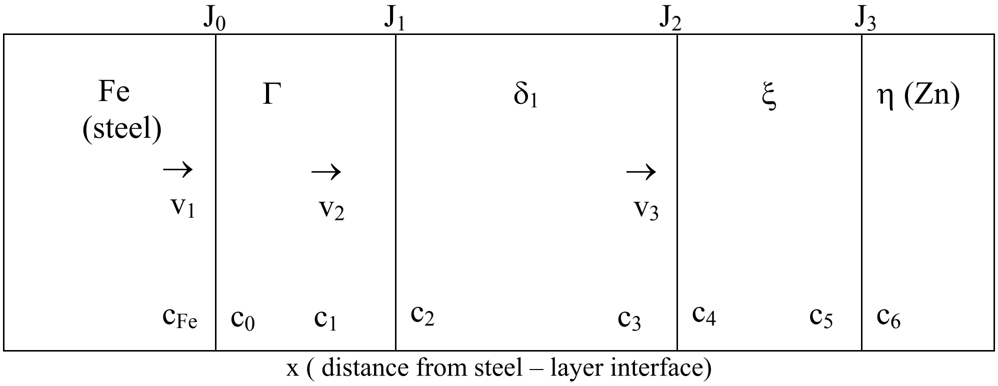


Fig. 3. *Coating layer diagram in kinetic process modeling.*

The quantity of iron on various interfaces is related to the difference of chemical potential of iron through the chemical constant K_i (i=0; 1; 2; 3)

$$J_i = K_i(\mu_{Fe}^a - \mu_{Fe}^b); \quad (8)$$

where: $K_{i(T)} = K_i e^{\frac{-Q_{ai}}{RT}}$;

where $\mu_{Fe}^a =$ chemical potential of iron at interface left side; $\mu_{Fe}^b =$ chemical potential of iron at interface right side; Q_{ai} = interface activating energy.

The chemical potential of iron can be approximated with its concentration, resulting J_0, J_1, J_2, J_3 using relation (8)

$$J_0 = K_0(c_{Fe}-c_0) = 0.72K_0 \quad (9)$$
$$J_1 = K_1(c_1-c_2) = 0.09K_1 \quad (10)$$
$$J_2 = K_2(c_3-c_4) = 0.01K_2 \quad (11)$$
$$J_3 = K_3(c_5-c_6) = 0.06K_3 \quad (12)$$

Replacing these values in relations (4),(5),(6) are obtained:

$$\left(\frac{d\Gamma}{dt}\right)_a = 2{,}975K_0 - 0{,}372K_1; \quad (13)$$

$$\left(\frac{d\delta}{dt}\right)_a = 0.978K_1 - 0.109K_2; \quad (14)$$

$$\left(\frac{d\xi}{dt}\right)_a = 0.164K_2 - 0{,}984K_3; \quad (15)$$

Considering the relations (1), (2), (3) are obtained:

$$v_1 = 2.975K_0-0.372K_1 \quad (16)$$
$$v_2 = 2.975K_0-0.606K_1-0.109K_2 \quad (17)$$
$$v_3 = 2.975K_0+0.606K_1=0.055K_2-0.98K_3 \quad (18)$$

In stage b) $\left(\frac{d\Gamma}{dt}\right)_a = \left(\frac{d\Gamma}{dt}\right)_b$, ξ phase is rapidly eliminated in favor of δ_1 phase, as a consequence of its showing at the surface, and with no effect concerning Γ phase growth. Thus, ξ phase plays the role previously by η phase. It cannot dissolve more iron than the equilibrium amount and it changes into δ_1 phase ($J_2 = 0$). In stage c), temperature rising over 600^{o}C leads to an increasement of iron diffusion coefficient and Γ phase is rapidly growing until complete disappearance of δ phase ($J_1 = 0$) and:

$$\left(\frac{d\Gamma}{dt}\right)_c = -\left(\frac{d\delta}{dt}\right)_b; \quad (19)$$

Computation of the experimental data concerning heat treatment influence on iron content of layer results in various relations reflecting diffusion process operation. At 550°C (fig.4), the diffusion process is carried out as intermediate process – stage b, respectively.

The function is:

$$y = a\left(1 - e^{-bx}\right); \tag{20}$$

where: r = 0.989185
y = % Fe
x = heat treatment period (s)

a = 8.3322985
b = 0.42589374

At 600 °C (fig.5), the process is carried out as kinetic process – stage c, respectively. The function is:

$$y = \frac{ax}{b + x}; \tag{21}$$

where: r = 0.9568720
y = %Fe
x = heat treatment period (s)
a = 15·110744
b = 0.23708356

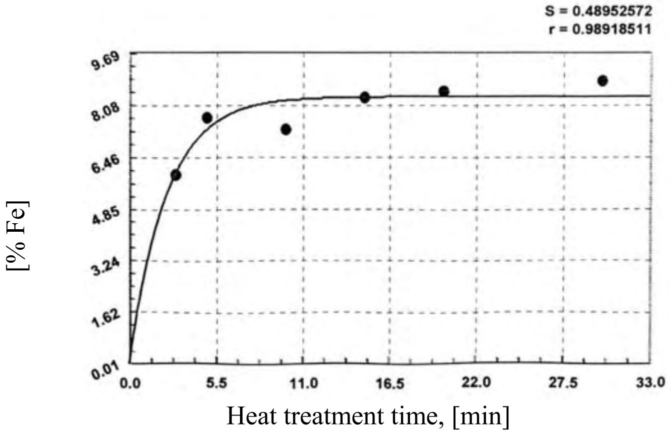


Fig. 4. *Diagram of iron content variation as function of heat treatment time at 550 °C.*

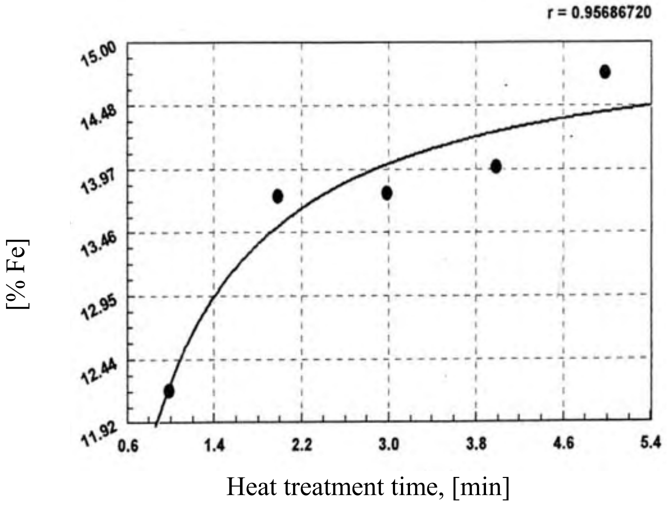


Fig.5*. Diagram of iron content as function of heat treatment time at 600 °C.*

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