The kinetics of zinc coating growth on hyper-sandelin steels and ductile cast iron

D. Kopyciński[*], E. Guzik

AGH - University of Science and Technology, Reymonta 23, 30-059 Cracow, Poland
*Corresponding author. E-mail address: djk@agh.edu.pl

Abstract

The studies aimed at an analysis of the formation and growth kinetics of zinc coating on reactive silicon-killed steels in a zinc bath. The growth kinetics of the produced zinc coatings was evaluated basing on the power-law growth equation. As regards galvanizing of the surface of products, investigation was done for various steel grades and ductile iron taking into account the quality and thickness of coating. It has been proved that the chemical constitution of basis significantly influences the kinetics of growth of the individual phases in a zinc coating. This relationship was evaluated basing on the, so called, silicon and phosphorus equivalent $E = (Si + 2.5P) \cdot 10^3$, and coating thickness dependences were obtained.

Keywords: Hot-dip galvanizing; Ductile cast iron, Silicon-killed steel, Zinc coating, Intermetallic phases.

1. Introduction

Hot dip galvanizing of reactive steels with high silicon content is a very interesting problem still lacking a complete and practically acceptable solution, although the currently used practice of steel making forces in a way the use of high silicon levels. An important issue in hot dip galvanizing is the phenomenon of the formation of a thick, brittle and dull-grey coating when the content of silicon (and phosphorus) in steel exceeds the critical but quite commonly used level, expressed by equation (1):

$$(Si + 2.5\ P) \cdot 10^3 = E_{Si,P} \qquad (1)$$

Below this value, the obtained coating is characterized by a correct glossy finish and „normal" thickness, while above the critical level of silicon and phosphorus equivalent the coating loses its adhesive force and as such can have poor adhesion,

which means that the zinc volume necessary to produce the finally required coating thickness may be too large and therefore too expensive.

As follows from the studies described in [1,2], the chief solution to the problem of a wide range of the silicon and phosphorus equivalent values in steels (so more in cast iron) available at present in the domestic market seems to be a conformity certificate specifying precisely the composition of the steel used for elements which are to be subjected to the galvanizing treatment or proper selection of steel already at the stage of designing or making these elements (as far as it is possible). Procedure of this type should be effectively implemented in the galvanizing plants which use a wide spectrum of different steel grades, while the plants which make on request galvanizing of single elements should try to optimize the composition of the zinc bath they commonly use.

Recently, some novel solutions have been offered in the field of hot dip galvanizing. One of them, widely used by industry, is the process of zinc-nickel galvanizing [3-5]. The process of

hot - dip galvanizing in Zn-Ni bath is at present considered to be the most practical and effective technology. The mechanism of zinc coating formation in a Technigalva (Zn-Ni) bath has been based on reducing the diffusion rate of iron through intermetallic layers. The nickel contained in the zinc bath concentrates in Zn-Fe alloy phases present in the coating, finally producing the layers characterized by a more compact structure with increased density and hardness of the δ and ζ phases. As a result of these changes, the rate of iron (or Fe-Si) diffusion in the direction of the alloy-liquid bath interface decreases.

Yet, even in this technology of zinc coating, some problems are encountered as regards the high value of silicon and phosphorus equivalent in steels for galvanizing which may give thick coatings with defects and of poor surface quality. In Technigalva process, the nickel present in the bath affects in a significant way the solidification of coating and hence its thickness on the steel surface to a level of 170% E as shown in Figure 1 [6].

So, it is quite important to develop a model of the zinc coating growth on reactive steels. To achieve this goal, an attempt should be made to describe the growth of a front layer of the Fe-Zn zinc coating, knowing that this is an unstable growth, and answer the question if the growth of phases in zinc coating deviates from that described by a binary Fe-Zn equilibrium system. Therefore, any studies in this respect require, first, that the problem of a mechanism of the zinc coating formation is solved, assuming an approach which allows for the following factors: first – isothermal solidification of intermetallic phases connected with the ternary systems of Fe-Zn-X, where: X-Al, Ni, Ti, V, second – the solidification of liquid zinc, and next the rate of Fe-Zn reaction (the variable rate of reaction) and a diffusion transformation of intermetallic phases in the solid state. The problem is of a complex nature because several reactions are proceeding at the same time, providing the phenomenon of steel wetting by liquid zinc and steel decomposition under the effect of zinc are taken into consideration.

No doubt that better understanding of the phenomena which occur at the liquid zinc-steel (cast iron) interface should be regarded as a tool helpful in control of the conditions under which the microstructure is formed in a zinc coating deposited by hot dip galvanizing on reactive steels, giving some measurable economic advantages.

To achieve this goal it is recommended to proceed with the studies on the kinetics of solidification of the zinc coatings on reactive steel - an issue which will be the subject of the present study.

To examine the kinetics of growth of a zinc coating it is necessary to adopt some values which will illustrate the course of Zn-Fe reaction. It seems that the parameter which will allow a precise determination of the kinetics of growth of a zinc coating is the thickness of the deposited Fe-Zn layer (Γ1 and δ and ζ intermetallic phases of the coating).

The kinetics of growth of a zinc coating can be evaluated using an exponential rule of the growth rate [8]:

$$\lambda = K \cdot t^n \qquad (2)$$

where : λ – layer thickness; K –growth rate constant; t – time of reaction; n – constant of the growth rate.

Table 1 shows various empirically measured values of the time constant n of the growth of the individual alloy phases (for long-time hot-dip galvanizing).

As the studies of the kinetics of growth of the zinc coating show, the values of n are changing with time. For iron containing 0.05% C, 0.046% P, 0.08%S and a zinc bath containing 1.2% Pb and 0.03% Fe the values of n for the entire alloy coating were 0.39 and 0.53 for the short and long dip times, respectively [7]. As follows from Table 2, the values of „n" are, on an average, tending to be „n" = 0.5 for δ phase, while for the phases Γ they are comprised in a range of 0.1 to 0.25 (except for Hortsman studies – see Table 1).
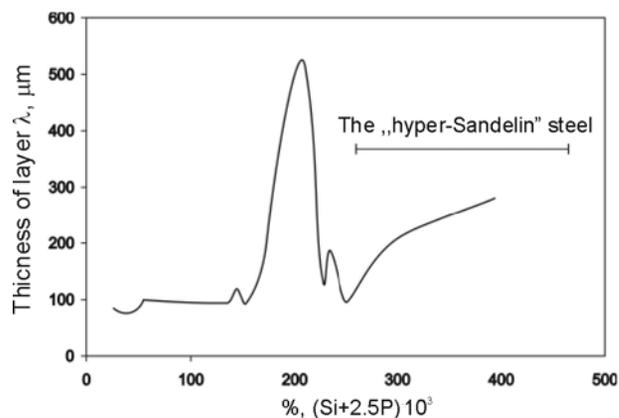

Fig. 1. Effect of Si and P content in the steel on coating thickness when galvanizing with Zn-Ni (450°C, 600 sec.) [6]

Table 1.
Values of time constant n for the growth of the individual alloy phases [7]

Source	Γ	δ	ζ	δ+ζ
Allen	0.25	0.65	0.35	0.55
Rowland	0.13	0.53	0.31	-
Blickwede	0.10	0.60	0.16	-
Horstman	0.50	0.50	-	-
Sjoukes	0.23	0.58	0.26	-
Onishi	0.23	0.49	0.36	0.43

A large difference in the values of n is prevailing in the growth of the entire layer. Yet, for all the intermetallic layers, the value of „n" should reflect the growth of the phase predominant in a zinc coating. According to Figure 2, in short growth time the ζ phase is prevailing, while in long growth time it is the δ phase which is occupying a leading position.
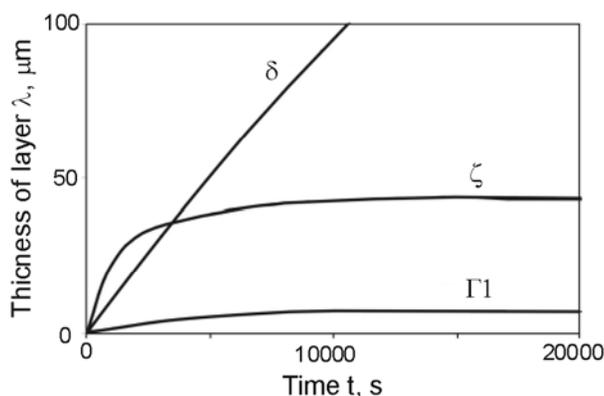
Fig. 2. The growth rate of alloy Γ, δ and ζ phases in zinc bath at a temperature of 457°C [7]

Till now the kinetics of growth of the shaped on the surface of ductile iron casting and silicon-killed steels is not well know.

2. Research method and the technique of hot-dip galvanizing

Zinc coatings were produced on a specially designed research stand where the temperature was measured and controlled by means of a Ni-CrNi thermocouple, with an accuracy of adjustment ±2°C.

Galvanizing of the individual steel grades was performed in a „Technigalva" zinc bath. Due to this technique it was possible to effectively reduce the silicon effect during galvanizing of individual elements, that is, to avoid the formation of excessively thick zinc coatings.

Four representative grades of reactive steels and two ductile iron types were selected for the studies. The chemical composition of those steels (according to chemical analysis) with the actual values of equivalent $E_{Si,P}$ is given in Table 2. Within own research, the rectangular specimens of dimensions 50 x 10 x 10 mm were prepared from the individual steel grades, and after chemical treatment they were subjected to the process of hot dip galvanizing according to a common practice, which assumes cleaning, etching in HCl (or HF for ductile iron), rinsing with water, fluxing (about 3 minutes), dipping in zinc bath at a temperature of about 450°C, and cooling in water.

Table 2.
Steel grades and ductile iron with the measured content of Si and P as well as $E_{Si,P}$ values wt., wt%.

Material type	Si, %	P, %	$E_{Si,P}$, %
St 3S	0.447[*]	0.0150	484
AH 36	0.334	0.0200	384
R35	0.265	0.0120	295
DH 36	0.200	0.0089	222
EN-GJS-400-15	2.590	0.0210	2640
EN-GJS-500-7	2.370	0.0270	2440

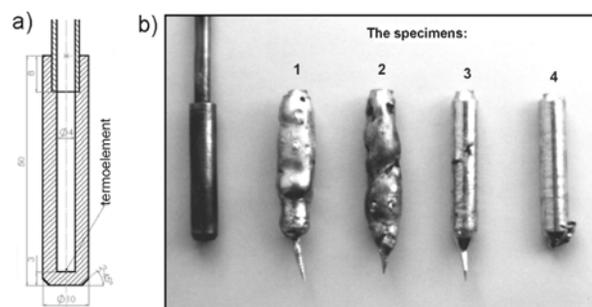[*] - the chemical composition is corresponding rather to St0S steel grade

Fig. 3. The scheme cylindrical specimen - (a) and cylindrical specimens with zinc coatings produced by hot-dip galvanizing in a zinc bath for the time of : specimen No. 1 - 3 seconds, specimen No. 2 - 4 seconds, specimen No.3 - 6 seconds, specimen No. 4 - 10 seconds - (b)

The coating growth rate for very short times (i.e. up to 10 sec.) was examined on cylindrical specimens of dimensions ϕ 10 x 50 mm. The appearance of these specimens after galvanizing is shown in Figure 3.

3. Results and discussion

As stated in introduction, the studies on the kinetics of growth of the zinc coating were focused on an evaluation of the thickness of the growing layer of the products of reaction, that is, of the growing layer of Fe-Zn alloy. For the sake of comparison, total thickness of the Fe-Zn alloy layers and of the solidifying zinc layer (the η layer) was determined as well.

The time constant of growth n indicates the type of the kinetics of growth of a zinc coating and it can also serve as a tool to make comparisons. The value of n=1.0 indicates a linear character of the growth of alloy phase, while n=0.5 indicates a parabolic growth of the coating thickness. The values below or above 0.5 indicate a more or less parabolic nature of the zinc coating growth.

In Table 3 the values of the time constant of growth „n" are compiled for the carried out studies on microstructure of coatings using rectangular steel specimens.

A microstructural analysis of the examined zinc coatings has indicated that each of the formed coatings had a multi-layer structure composed of the intermetallic Fe-Zn phases of δ, ζ and η type. It has also been observed that on the steel surface after machining the crystals of δ phase are definitely prevailing, leaving less space in the coating for the crystallites of the ζ phase and, consequently, producing the coating less thick. The microstructures of the examined steels revealed the presence of layers composed of mixed ζ and η phases.

In view of some technical problems with determination of the kinetics of growth of the delta phase on St3S steels with rolled surfaces, the thickness values of the delta phase from the steel surface after machining have been adopted. The δ phase shows dense network of crazes which can account for the formation of the, so called, paths of iron-to-zinc and zinc-to-iron diffusion.

Figures 6 show the characteristic growth pattern of zinc coating on AH36 steel grades in Technigalva bath.

From the data compiled in Table 3 and from Figures 4 it follows that the relative values of constant „n" for the growth of individual alloy layers are different. For example, the mean value of n (regarding the examined four steel grades) is 0.20 for the δ phase, while for the ζ phase it increases up to 0.84. The difference is a result of various rates of iron diffusion within the individual phases, those being, in turn, the result of various diffusion rates at the phase boundary.

Table 3.
Measured values of the time constant of growth n for various phases present in coatings

Steel grade	δ	ζ	
St3S	0.15 [(*)]	1	
AH36	0.20	0.83	
R35	0.22	0.82	
DH36	0.21	0.83	
Mean for steels	0.20	0.87	
Ductile iron	0.98	$\zeta_2 = 0.66$	$\zeta_1 = 0.48$

(*) - value of the time constant n for delta phase on the steel surface after machining;

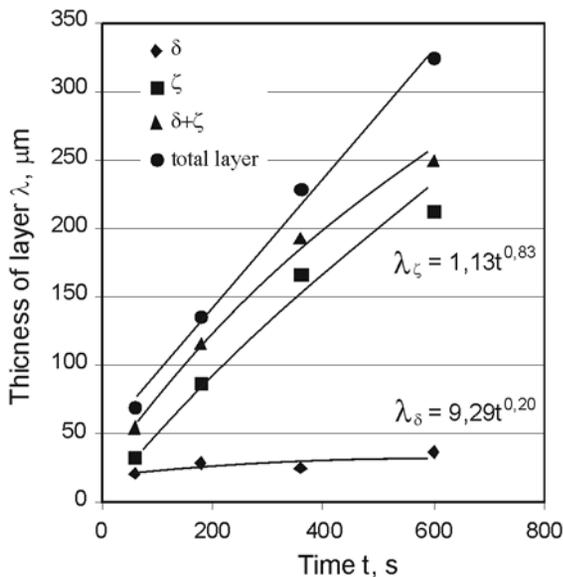ζ_1, ζ_2 – phase increasing on casting surface after machining and now one.

Fig. 4. Time of holding AH 36 steel in Technigalva bath at 450°C vs thickness of individual phases in zinc coating: δ, ζ layers, (δ + ζ) layer, and total for (δ + ζ + η) layers

From the above results it follows that in the first period of the coating formation, the diffusion is proceeding at a high rate. So, a thesis can be proposed that within the time of up to 600sec. (the maximum time used in the process of steel galvanizing), the ζ phase is growing very rapidly (the values of n tend towards 1.0), while the δ phase is growing very slowly (the values of „n" below 0.5).

When this time is exceeded, the growth of ζ phase will be impeded while the growth of δ phase will be proceeding at a very high rate. The growth of zinc coating on the surface of DH36 steel in 6th second and in the 60th is shown in Figures 5 and 6. It results from these microstructures that in the 6th second of zinc galvanizing the Γ and δ phases are well shaped but in the 60th second Γ phase disappears (hence the growth of Γ phase is difficult to evaluate) and ζ phase to growth (Fig. 6).
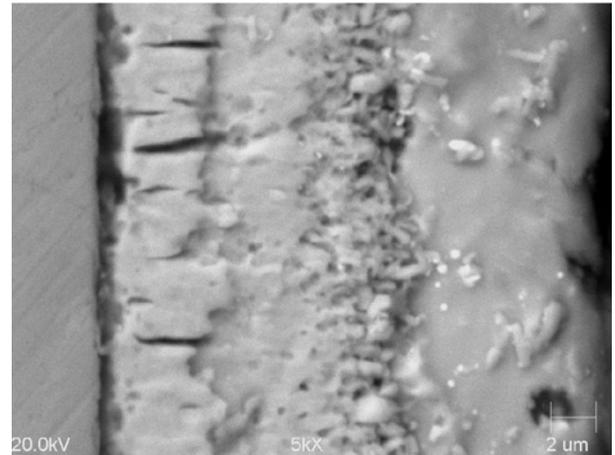

Fig.5. Microstructure SEM of zinc coating produced at 450°C on steels AH 36 in galvanizing time – 6 sec. (specimen No. 3 with Fig. 3)
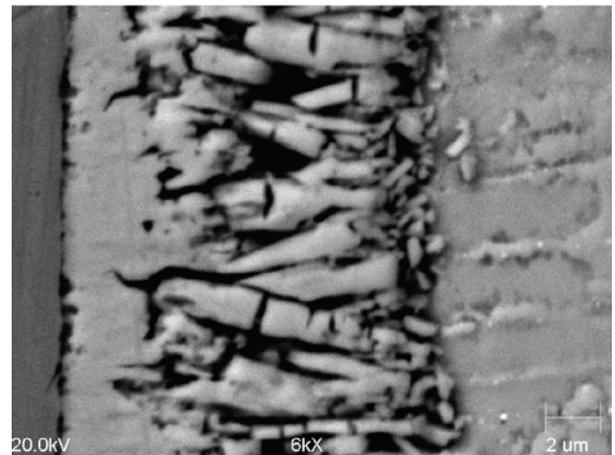

Fig.6. Microstructure SEM of zinc coating produced at 450°C on steels AH 36 in galvanizing time – 60 sec. (specimen No. 4 with Fig. 3) - the growth of η phase dendrite

Further growth of the alloy phase is at the cost of another phase which has been formed at the initial stage of the coating growth. The surface of the δ/ζ and ζ/η phases is shifting towards the zinc coating, while the surface of the α(Fe)/Γ phase is heading towards the steel.

Considering big values of factor, obtaining of zinc layer on the surface of iron castings can be difficult. The analysis of microstructure of zinc layers shaped on iron shows irregular

multilayer structure formed mostly by ζ phase and δ phase. The EDS analysis didn't proof existing of Γ1 phase.

In figure 7 it microstructure of layer shaped in 300th second of galvanizing. The characteristic feature is low compactness of phase δ sublayer that isn't observed in some places. On the surface (after machining) where liquid zinc contacts with graphite, δ phase isn't shaped (Fig 8).
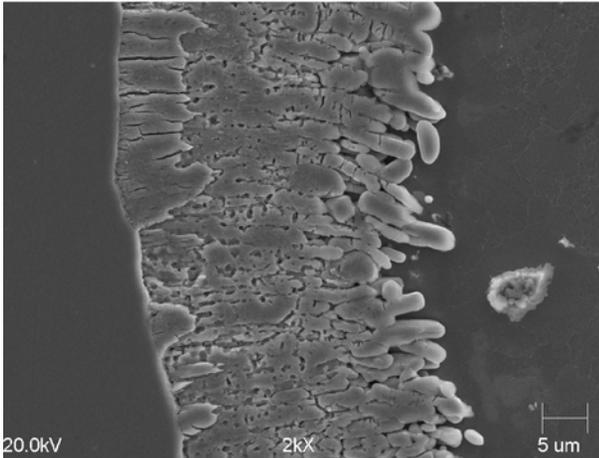

Fig. 7. The growth of Fe-Zn layer at the crude surface of ductile cast iron during galvanizing process at time 300 sec.
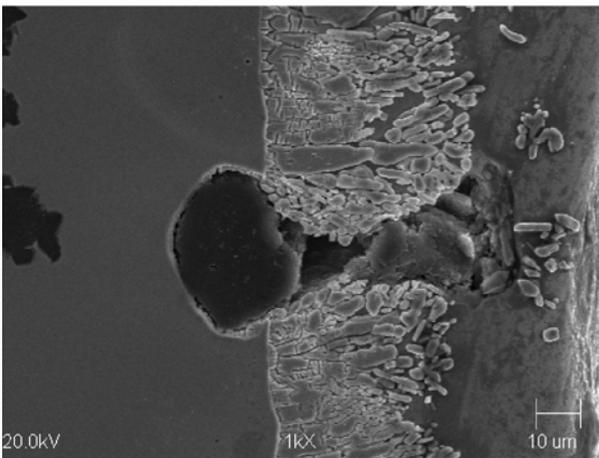

Fig. 8. The growth of Fe-Zn layer at the surface after mechanical working of ductile cast iron during galvanizing process at time 30 sec.

It follows from data in Table 3 and in Fig. 9 that during hot – dip galvanizing of cast iron the volumen of constant n for d phase is dose to 1.0 and for ζ phase n ≈ 0.5. Results of this researchers differ from that ones concerning reactive steel. Therefore it can be found that the mechanism of zinc layer growth on the surface of high-silicon steel differs from the mechanism of the protecting layer growth on iron casting surface. If the value of exponent „n" is clear to 0.5 we can state that its is standard bulk diffusion, and this phase should be more compact than the phase should be more

compact than the phase characterized by exponent n close to 1.0, because it is the case of boundary diffusion. The exponent „n" ≤ 0.5 shows that during zinc coat growth the transformations in solid started.
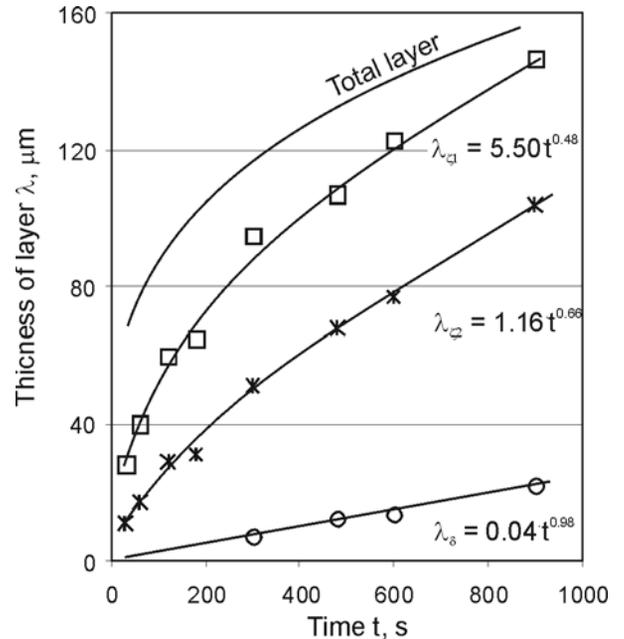

Fig. 9. Time of holding ductile cast iron in bath at 450°C vs thickness of individual phases in zinc coating: δ, ζ layers, and total layers for (δ + ζ + η)
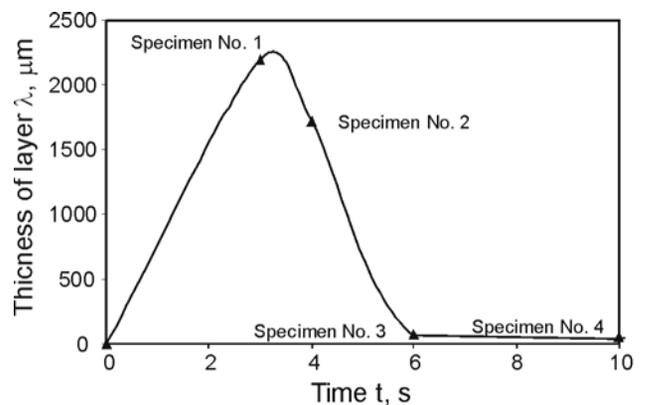

Fig. 10. Zinc coating thickness on cylindrical specimens vs dipping time in zinc bath

The results of the tests are shown in Figure 10 and they indicate that at the initial stage of the zinc coating growth, the layers of zinc are "freezing" on steel immersed in the zinc bath. Therefore it is suggested to adopt a model of the Fe-Zn phases growth. The growth of a zinc coating is divided into the four successive stages: the first stage is freezing of zinc, the second stage is melting of the frozen zinc layer and nucleation of the Γ phase, first, and δ and ζ phases next, the third stage is growth of the Zn-Fe alloy phases (the growth of δ phase with the dominate

growth of ζ phase) and the four stage the growth of η phase dendrites (after getting out of zinc bath).

The η layer structure that is formed during solidification affects not only the corrosion behavior but also the lacquer adhesiveness during hot dip galvanizing in Duplex system.

After the steel product has been taken out from the zinc bath and excess zinc has been removed, the product is handled to a tank with water where the solidification of η phase in zinc coating takes place (already during transport the outer layer of the zinc coating undergoes some solidification).

After undercooling of a liquid zinc layer in respect of the equilibrium temperature of solidification, on the ζ/liquid phase boundary the process of heterogeneous zinc nucleation starts. The forming zinc nuclei have random space orientation and are characterized by dendritic growth. This effect occurs in spite of the fact that on the surface of liquid coating the temperature is lower. In the areas where the steel is not coated by flat dendritic crystals, the unrestrained heat flow towards the surface is still possible, and undercooling in these areas is higher, thus promoting a side growth of the zinc crystals. The effect of the side growth of crystals persists until the moment when the whole surface area of the ζ/liquid phase boundary becomes coated with zinc grains, forming typical precipitates of zinc spangles, or until the moment when the steel product is placed in water and frozen. The dendritic arms are growing in direction of the preferred crystallographic orientations which ensure quick growth, for zinc this orientation being (1100) [8,9]. Then the base plane of a zinc nucleus will be parallel to the substrate surface and all the six orientations <1100> will be parallel to the substrate surface, too. As a consequence, a flat six-arm dendrite will be formed [8,9] with an angle between the dendritic arms amounting to 60°, which is corresponding to the growth orientation (1100). If the base plane is inclined in a more or less non-linear way in respect of the product plane, the appearance of the surface and the shape of zinc dendrites will change.

4. Conclusions

The studies carried out and the analysis of reference literature indicate that on "hyper-Sandelin" steels (in Zn-Ni bath at a temperature of 450^oC and with the time of holding up to 10 minutes maximum) and ductile iron on the surface of iron saturated with zinc, the Γ and δ phases are the firsts one to nucleate, grow and form a layer, followed by the ζ phase which nucleates and grows occupying a boundary area between the δ/liquid zinc zeta phases. The process of the Γ and δ as well as ζ phases nucleation is preceded by a characteristic effect of zinc "freezing" on the steel surface which is shown in Figures 3

and 10. The values of the time constant „n" of the growth rate for delta and zeta phases indicate a leading role of the zeta phase in the process of the zinc coating formation and a slow rate of growth of the delta phase. The Γ phase growth is showed down hence this phase shows tendency to disappear.

References

[1] E. Guzik, D. Kopyciński, Z. Miodowski, M. Winiarski, T. Granatowska, The analysis at sorts of steels used in shipbuilding industry assigned for hot-dip galvanizing process. Ship Design and Research Center. Jubilee Scientific Conference. Gdańsk – Jurata 2001, No. 2 (2001) 189-200 (in Polish).

[2] G. Reumont, J. Foct, P. Perrot, New possibilities for the galvanizing process: The addition of manganese and titanium to the zinc bath. Nineteenth International Galvanizing Conference „Intergalva 2000". Understanding Steel Composition and Zinc Alloys (Part 1), Berlin 2000.

[3] P.S. Kolisnyk, C.J. Allen, Galvanizing Reactive Steel. AGA TECH FORUM. Dallas, Texas, USA. October 12-15 (1994) 199-205.

[4] Z.W. Chen, J.B. See, Dross Phases Formed in Galvanizing Baths Containing (0-0.1) wt% nickel at 450 ^oC. ISIJ International, vol. 33 (1993) 307-312.

[5] P. Maass, P. Peissker, Hot-dip galvanizing. Publishing Agency - Placet. Warsaw, 1998 (in Polish).

[6] P. Beguin, M. Bosschaerts, D. Dhaussy, R. Pankert, M. Gilles, Galveco, a solution for galvanizing reactive steel. Nineteenth International Galvanizing Conference „Intergalva 2000". Understanding Steel Composition and Zinc Alloys (Part 1), Berlin 2000.

[7] J. Mackowiak, N.R. Short, Metallurgy of galvanized coating. International Metals Revievs, vol. 1 (1979) 1-19

[8] E. Fraś, Crystallization of Metals, WNT, Warsaw, 2003 (in Polish).

[9] J. Strutzenberger, J. Faderl: Solidification and spangle formation of hot-dip galvanized zinc coatings. Met. and Mater. Trans. A, 28A (1998) 631-642