Studies have demonstrated that in the process of hot dip galvanizing the decisive influence on the mechanism of zinc coating formation and properties has the quality of the mechanically untreated (raw) surface layer of the galvanized product. The terms “casting surface layer” denote various parameters of the microstructure, including the type of metal matrix, the number of grains and the size of graphite nodules, possible presence of hard spots (the precipitates of eutectic cementite) and parameters of the surface condition. The completed research has allowed linking the manufacturing technology of ductile iron castings with the process of hot dip galvanizing.

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.

During galvanizing treatment of these alloys, the growth of Fe-Zn phases is consistent with the Fe-Zn phase equilibrium diagram. The composition of an alloy layer of the zinc coating comprises the regular bcc $\Gamma_1$ – Fe$_3$Zn$_1$ phase, the regular fcc $\Gamma_2$ – Fe$_2$Zn$_2$ phase, the hexagonal $\delta$ – FeZn$_7$, or FeZn$_{10}$ phases with different morphologies, and the monoclinic $\xi$ – FeZn$_{13}$ phase [1-11]. In the final stage of growth of the zinc coating, during product ascent from the bath, the $\eta$(Zn) layer, which is a solid solution of Fe in zinc, crystallizes.

In the case of the hot dip galvanizing of castings made from ductile iron (currently the most popular high-quality casting alloy subjected to the galvanizing treatment), it is indispensable to take into account a number of factors related to the cast iron microstructure (the number of eutectic grains equivalent to the graphite nodule count, the metal matrix which in the ductile iron before heat treatment or in the case of a substantially high addition of alloying elements consists of pearlite and ferrite) and surface quality of the galvanized product. The surface condition of iron casting is influenced by the moulding technology, and can be defined with roughness parameter $R_a$. During the hot dip galvanizing treatment of castings, its surface is cleaned by degreasing, pickling and fluxing with zinc and ammonium salts. All these operations have one common goal – to prepare the casting surface for the subsequent reaction with liquid zinc. Thus, the galvanizing treatment does not affect the microstructure and surface roughness of product; it only removes the impurities present on casting surface to let the process run without any obstacles. Foundries producing cast components assigned for the subsequent galvanizing treatment can control the microstructure and surface roughness of the manufactured products. The test results included in this study show that both the microstructure and surface roughness of casting have a significant impact on the zinc consumption rate during hot dip galvanizing.

2. Experimental

The study was carried out in a highly methodical way. Given the fact that iron castings, including high-quality ductile iron, are characterized in the cross-section of walls by a gradient structure (Fig. 1), it was considered necessary to gain first some knowledge about possible means to control the content of alloying elements in the microstructure of samples tested.

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

a) the impact of the number of eutectic grains (equivalent to the graphite nodule count),

b) the type and content of phases in the metal matrix (fully ferritic or fully pearlitic and various quantitative combinations of these two phases),

c) varying roughness of the casting surface due to the use of different moulding technologies.

During the implementation of research, a series of cast iron melts were made, which allowed obtaining samples meeting the...
requirements of having a variable number of eutectic grains (the graphite nodule count), a diversified metal matrix and varying roughness of the casting surface. The test samples had the shape of 100 mm × 100 mm plates and varying wall thickness of 5 mm, 10 mm, 20 mm and 30 mm (to better grasp the impact of the casting cooling rate). Different grades of ductile iron were melted. The cast iron chemical composition and various grades used in the tests are compared in Table 1. Castings were made in the form of plates and from those plates the test samples were cut out [12].

### Table 1

| Melt         | Cast iron grade | C   | Si  | Mn  | P  | S   | Mg | Ni |
|--------------|-----------------|-----|-----|-----|----|-----|----|----|
| 1            | EN-GJS-500-7    | 3.58| 2.40| 0.42| 0.021| 0.009 | 0.048 | 0.03 |
| 2            | EN-GJS-600-3    | 3.62| 2.47| 0.53| 0.034| 0.015 | 0.047 | 0.03 |

Chemical treatment of the casting surface as well as cleaning and hot-dip galvanizing were carried out in a conventional manner [13].

### 3. Results and discussion

#### 3.1. The impact of the number of eutectic grains (nodule count)

To control the microstructure of test samples, proper heat treatment was applied. The purpose of the heat treatment was to produce in the cast iron microstructure a homogeneous metal matrix – pearlitic or ferritic, or mixed with the previously assumed ferrite/pearlite content ratio. In the case of a homogeneous metal matrix, the ferritic type was adopted for the studies, including the effect of graphite nodules on the kinetics of zinc coating growth. Therefore, for different casting wall thicknesses of 5 mm, 10 mm, 20 mm, 30 mm, different numbers of grains, i.e. different nodule counts, were obtained (the nodule count is equivalent to the number of grains of the globular graphite eutectic). Using specially tailored operation of the ferritizing annealing, samples with a ferritic matrix and the microstructure shown in Figure 2 were obtained. After this treatment, the samples were subjected to the process of hot dip galvanizing.

![Fig. 1. General scheme of gradient structure in the ductile iron casting with marked changes in the casting cross-section (a) and outer layer of casting called casting skin](image-a)

![Fig. 2. Microstructure of the surface layer formed in ductile iron samples subjected to ferritizing annealing; varied thickness of the layer amounting to: 5 mm – a) 10 mm – b) 20 mm – c) 30 mm – d), nital etching](image-b)

The metallographic studies of the zinc coating formed on samples cut out from the cast plates of 5, 10, 20, 30 mm thickness have proved that the number of eutectic grains, including the size and content of graphite, has no influence on the structure and kinetics of zinc coating growth (Fig. 3). This is a very important conclusion as it allows for the evaluation of an impact of the casting surface roughness and pearlite and ferrite content in the surface layers of ductile iron samples.

#### 3.2. The effect of cast iron metal matrix

In the next stage of the study, the constituents of the ductile iron metal matrix were differentiated by means of a normalizing annealing developed specially for this purpose. Samples with different content of pearlite and ferrite were obtained, i.e. ferrite – 100%, ferrite – 65% and pearlite – 35%, ferrite – 45% and pearlite – 55% and pearlite – 100% (Fig. 4).
In the next stage of studies, the hot dip galvanizing process was applied to the obtained samples and equations expressing the zinc coating growth were derived: (2) – for the metal matrix P0% F100%, (3) – for the metal matrix P35% F65%, (4) – for the metal matrix P55% F45%, and (5) – for the metal matrix F0% P100%:

\[ \lambda = 3.34 t^{0.5}; \quad \lambda = 2.58 t^{0.5}; \quad (2), (3) \]

\[ \lambda = 2.29 t^{0.5}; \quad \lambda = 1.85 t^{0.5} \quad (4), (5) \]

The following constants, which later in the study were used in the analysis of test results, were determined:

\[ \lambda_{P0F100}/\lambda_{P100F0} = 1.805 \]
\[ \lambda_{P100F0}/\lambda_{P0F100} = 0.55 \]

From the values of the constants shown above it follows that the higher is the content of ferrite in the metal matrix of the sample, the higher is the value of the zinc coating thickness \( \lambda \). At the same time, the alloy layer formed on the surface of the sample with microstructure composed in 100% of ferrite has almost double thickness of the Zn coating (the alloy layer is thicker by 80%) compared to the alloy layer formed on the surface of the sample with microstructure composed in 100% of pearlite. The thickness of the zinc coating growing on the surface of cast iron with a pearlitic matrix represents 55% of the thickness \( \lambda \) of the coating growing on the surface of a ferritic sample. The kinetics of the zinc coating growth is shown in Figure 5.

3.3. The effect of casting surface roughness

The quality of cast surface, roughness included, depends on several factors, among which the most important from the point of view of technology are the size of matrix grains and the degree of mould compaction. These two factors determine the size of the space between matrix grains and the level of capillary pressure formed therein, which gives castings with different surface roughness. Molten metal was cast into foundry moulds made by various technologies to reproduce Y-shaped ingots according to the PN-EN 1563 standard. 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 with furan resin (S) and sand with hydrolyzed ethyl silicate and molochite (M). Figure 6 shows the cross-sectional view and appearance of the test surfaces.

Metallographic sections of the examined castings were characterized by a pearlitic matrix observed in the surface layer of casting known as a casting skin. This area was free from the presence of large graphite precipitates. The resultant microstructure is shown in Figure 7.
Next, surface roughness of the samples was examined with Vecco profilometer, specifying, among others, the $R_a$ surface parameter, which in further studies was used as an indicator of the surface condition in castings obtained by various moulding technologies. An example of visualization of the examined surface is shown in Figure 8. The process of hot dip galvanizing was carried out in a zinc bath at a temperature of 450°C during the time of 30, 60, 120, 180, 300, 600 and 900 sec. As a next step, multi-faceted metallographic analysis of the microstructure of zinc coating formed on the surface of the examined samples was carried out.

The sample surfaces were chemically treated and hot dip galvanized for the time from 30 sec. to 900 sec. Examples of microstructures obtained in the resulting zinc coatings are shown in Figure 9, while Figure 10 shows plotted curves of the coating growth kinetics.
Fig. 8. Example of visualization of the 3D geometry of the surface of sample cut out from the casting made in B type sand mould and the determined surface roughness parameters

Fig. 9. The growth of alloy layer in Zn coating on the surface of ductile iron samples characterized by different surface roughness parameters subjected to hot dip galvanizing carried out for 60 s (a–d) and 600 s (e–h). Moulds M – (a,e); S – (b,f); O – (c,g); B – (d,h)

Fig. 10. The kinetics of growth of the Fe-Zn alloy layer in zinc coating formed on the surface of ductile iron samples with different roughness parameters $R_a$
4. Conclusions

Based on the conducted studies it was possible to formulate the following conclusions:
1. The condition of surface layer in the high-quality ductile iron casting has a significant impact on the mechanism of the formation of protective zinc coating and hence also on the properties of this coating.
2. It has been proved that individual parameters of the surface layer of ductile iron casting have a prominent effect on the thickness of the resulting protective coating and its growth kinetics.
3. The manufacturing technology of ductile iron castings was interrelated with the process of hot dip galvanizing and indispensable knowledge was obtained to produce protective coatings of the required thickness and morphology, economically justified and providing the required corrosion resistance to the manufactured product.

Acknowledgements

The work was funded by the NCN based on the decision number DEC-2012/05/B/ST8/00100.

REFERENCES

[1] A.R. Marder, Prog. Mater. Sci. 45, 191-271 (2000).
[2] A. Tatarek, P. Liberski, H. Kania, P. Podolski, Mater. Eng. 6, 788-791 (2008).
[3] H. Kania, P. Liberski, Inżynieria Materialowa 3, 375-380 (2008).
[4] P. Liberski, H. Kania, P. Podolski, A. Tatarek, L. Kwiatkowski, Physico Chemical Mechanics of Materials 7, 301-307 (2008).
[5] P. Liberski, A. Tatarek, P. Podolski, H. Kania. Ochrona przed korozją 4, 173-178 (2007).
[6] W. Wolczyński, Z. Pogoda, G. Garzel, B. Kucharska, A. Sypień, T. Okane, Arch. Metall. Mater. 59, 1223-1233 (2014)
[7] D. Kopyciński, A. Szczeńsny, The Model of Peritectic Phases Crystallization in Zinc Coating, Frontiers in Solidification, TMS 2016 145th Annual Meeting, 101-105 (2016).
[8] D. Kopyciński, E. Guzik, Sol. St. Phen. 197, 77-82 (2013).
[9] V. Kuklik, J. Kudlacek, Hot-Dip Galvanizing of Steel Structures 1st Edition, 2016 Butterworth-Heinemann
[10] W.J. Smith, F.E. Goodwin, Materials Science and Materials Engineering 4, 2556-2576 (2010).
[11] F. Ozturk, Z. Evis, S. Kilic, Materials Science and Materials Engineering 3, 178-190 (2017).
[12] D. Kopyciński, A. Szczeńsny, Archives of Foundry Engineering 12, 101-104 (2012).
[13] D. Kopyciński, E. Guzik, A. Szczeńsny, D. Siekaniec, Archives of Foundry Engineering 15, 47-50 (2015).