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THE STRUCTURE OF INTERMEDIATE LAYERS OF HOT-DIPPED Al-Zn COATINGS ON CARBON STEEL SHEETS

STRUKTURA WARSTWY REAKCYJNEJ POWŁOK Al-Zn OTRZYMANYCH METODĄ ZANURZENIOWĄ NA BLACHACH STALOWYCH

The high efficient method to protect the steel sheets is an Al-Zn coating by hot – dipping. Good properties of the coatings layer were obtained from the baths of Al-Zn alloys with silicon addition. Three baths were used: AlZn44Si1, AlZn43Si2 and AlZn42Si3 at the temperatures 630 and 670°C in different dipping times between 15 to 180 s. The optical, scanning microscopy and XRD analysis were applied. The best layers were obtained from the AlZn43Si2 bath in which the reaction zone was very thin. The main phases formed as a result of the reactions in diffusion zone were identified as: $Al_{20}Fe_5Si_2$, $Al_5Fe_2$and $Al_{13}Fe_4$.

Keywords: Coatings, intermetallic compounds, layers, alloy, substrate.

Zastosowanie pokrywania blach stalowych metodą zanurzeniową w kąpielach aluminiowo-cynkowych jest wydajną metodą stosowaną dla ich ochrony przed korozją. Wysokie własności pokryć uzyskano w kąpielach aluminiowo-cynkowych przy zastosowaniu dodatku krzemu. Badania prowadzono dla kąpieli o składach: AlZn44Si1, AlZn43Si2 i AlZn42Si3 dla temperatur 630 i 670°C i różnych czasów zanurzania od 15 do 180 sek. Badania prowadzono metodami: mikroskopii optycznej i skaningowej oraz rentgenowskiej analizy fazowej. Najlepsze warstwy uzyskano w kąpieli AlZn43Si2 uzyskując bardzo cienkie warstwy reakcyjne. Podstawowymi fazami wygenerowanymi na drodze reakcji w warstwie dyfuzyjnej były: $Al_{20}Fe_5Si_2$, Al_5Fe_2 i $Al_{13}Fe_4$.

1. Introduction

The aluminium-zinc coatings by hot-dipping is an efficient method to protect the sheets or different elements of steel against corrosion. The mechanical properties of the protective layer depends mainly on the composition of the alloy and the temperature of a dipping bath. The formation of layer during dipping of a steel sheet in a liquid bath induces diffusion reactions between the components of the alloy and steel [1]. These reactions lead to the generation of the different Al-Fe-Zn intermetallic compounds [2]. The mechanical properties of the layer and particularly the adhesion to the steel base depends on the type and structure of interlayer, composed of these intermetallic compounds, joining to the steel substrate with the external layer of Al-Zn coatings [3, 4]. In the case of the Al-Zn bath, at the temperature above 878 K, the intermediate layer grow according to Selverian [1], at a very high rate and the iron panel dissolve completely in about 2 min. forming thick hard and brittle layer [5]. The brittleness of the layer increase with its thickness [6, 7].

The reduction of the diffusion layer thickness, can be controlled by alloying additions [8], particularly addition of silicon, retarding formation and growth of intermetallics of Al-Fe type [8, 9]. In the presence of Si the thin layer of a reaction zone is generated. It is composed of Al-Fe-Si compounds, which inhibit the diffusion of aluminium into the steel substrate and formation of further Al-Fe compounds [5]. In that case the layer is much thinner, much more adhesive and not too hard and brittle. Silicon addition stabilize the intermetallic phases, retard their growth, decrease stresses between sublayers and increases the adhesion of the layer to the steel substrate [1, 5, 6, 7, 8].

The dipping bath called Galvalume of the composition: Al43.4Zn1.6Si [10] taking into account above assumptions was developed. It allowed to obtain coatings of a very good properties particularly corrosion resistant and adhesive to substrate. The intermediate layer is built

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from the Al-Fe and Al-Fe-Si phases and is composed from two or more sublayers according to composition diversification. Dillmann et al. [11] investigated the composition changes in different zones of the reaction layer. In external sublayer the major phases are composed of only aluminium and silicon, but three phases were identified: Al_5FeSi, Al_8Fe_2Si and Al_3Fe, in the middle. Deeper, near the steel substrate, only Al_8Fe_2Si was detected. According to Al-Fe phase diagram [12] in dependence on the composition of coating the phases: Al_3Fe (θ), Al_5Fe_2 (η) and after the transformation in solid state Al_2Fe (ζ) two superstructures $Fe_3Al(\beta_1)$ and $FeAl$ (β_2) can be generated [11, 13]. In the Al-Fe-Si alloy with low Si content according to the ternary phase diagram [12] following phases can be considered: Al_8Fe_2Si (α), $Al_{20}Fe_5Si_2$ and Al_5FeSi (β). At the higher Si content Al_4FeSi_2 and Al_3FeSi phases can be formed. According to [1] the Al_5Fe_2 phase grew with <0002> axis perpendicular to steel surface forming strong preferred orientation of the (0002)-type. It makes the phase analysis hard and difficult to interpret.

The coatings layer is formed on the substrate by several complex mechanisms influenced by: solidification, diffusion in the temperatures of the bath, diffusion in a solid state and recrystallization [10]. In this case the identification of the generated phases need to describe the growth mechanism of the coating layer. They are formed in the process of diffusional interactions in the reaction zone (diffusional zone). According to Akdeniz et al. [5] and Liberski [14] the growth of diffusion layers begins with the formation of a thin (about 10 μm thick) Al_3Fe intermetallic followed by a rapid growth of Al_5Fe_2, which penetrates into steel substrate. In that case, only the latter compound will be found in that layer. The formation of a thin Al-Fe-Si interlayer retards the dissolving of steel base at the very beginning of the dipping process.

In the present work the phase composition of the intermediate, diffusion layer and its influence on the formation and the whole coating layer is investigated and discussed.

2. Experimental

2.1. Materials and methods of investigations

Low-carbon-steel sheets were used as panels for coating by hot-dipping process. Different baths containing: Al44Zn1Si; Al43Zn2Si and Al42Zn3Si (in wt.%) were used. The baths were prepared from pure metals: Al – ARO (99.99) and Zn of 99.99 purity. The dip plating of the steel panels was performed in baths at temperatures between 610-690°C, measured by the thermocouple touching the panel. The panels were mechanically cleaned before metallization, then cleaned in trichloroethylene, pickled in HCl water solution at room temperature, hold in liquid flux (on the basis of K_2ZrF_6) at about 60°C and dried in a drying chamber at 140°C.

The composition of the bath changed after dipping in the direction of slightly higher amount of Si and lower of Al. About 0.6 to 1.0 wt. pct. of iron transferred to the solution of iron during the dipping process.

2.2. Structure studies

Neophot 32 and Leica optical microscopes were used to observe cross sections of metallized panels, cut, grinded, polished and etched in a 5% HNO_3 alcoholic solution. Scanning electron microscope (Philips XL – 30 with EDS – Link device and Philips 525 with EDS were used for structure analysis of cross sections and steel substrates quantitative analysis. XRD phase analysis was performed using Philips PW 1710 diffractometer with Co*Kα* and Cu*Kα* radiation monochromatised with the graphite monochromator. The diffraction patterns were analyzed in a direct test – a comparative analysis to the data from the "Inorganic Index to the Powder Diffraction File" of the JCPDS [16] or calculated from the crystallographic data.

3. Results and discussion

3.1. The optical microscope investigations

The structure of cross sections of the steel panels after dipping process at the temperatures between 630 to 670°C for 180 s. was observed. The best uniform layers were obtained after dipping in the bath of the alloy containing 2% Si. The average coating thickness was about 15 μm and it was only slightly dependent on the bath temperature, but mainly on the silicon content and dipping time. The microstructure in the Fig. 1 was taken from the layer formed by dipping in the bath AlZn43Si2. at 670°C in the time 180 s. It can be seen that the reaction zone of this layer is composed of two different sublayers and an overlay. It shows that the phase composition of the diffusion layer changes at different distances from the substrate. The retardation of the growth and its stabilization depends on the Si content in the alloy. Figures 2 and 3 show microstructures of layers with silicon content 1 and 3 Si%, respectively, (at temperature of 670°C and in the dipping time of 180 s.). As early as after 15 s. the complete layer consisting the reaction zone and overlay (Fig. 4) was formed. It is in agreement with the data of Ebrill et al. [15] stating that the layer started to form within 20 ms time, contrary to Selverian et al. [1] suggesting 100 s. incubation time of the Fe_2Al_5 formation

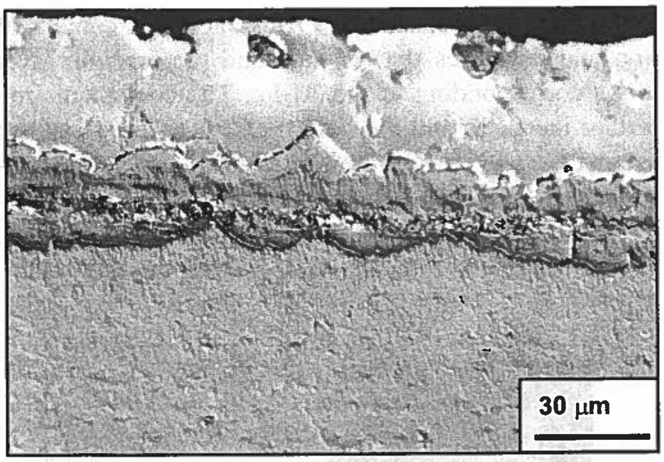

Fig. 1. Optical microstructure of the cross section of diffusion layer formed at 670°C in the dipping time 180 s. in the AlZn43Si2 alloy bath showing two sublayers in the range of the reaction zone

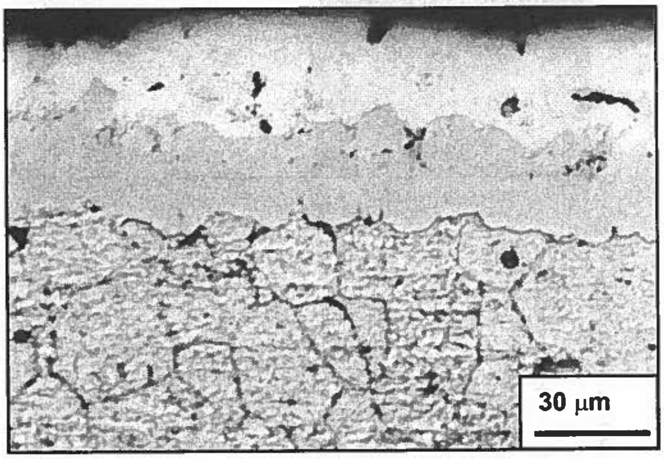

Fig. 2. Optical microstructure of the cross section of the substrate and diffusion layer of the AlZn44Si1 alloy at the temperature of 670°C in the dipping time 180 s

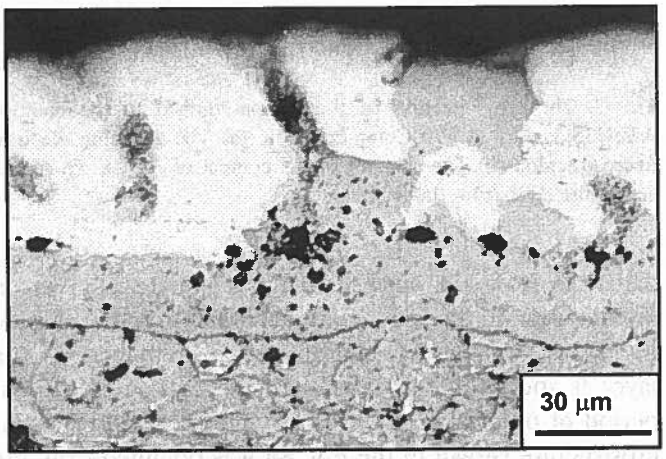

Fig. 3. Optical microstructure of the cross section of the substrate and diffusion layer of the AlZn42Si3 alloy at the temperature of 670°C in the dipping time 180 s

in the presence of Si. The dependence of the variation of the reaction layer thickness vs. silicon amount, (produced in the bath at 670°C temperature and in the dipping time 180 s.) is given in the diagram on the Fig. 5. The variation of the thickness of reaction zone with increasing silicon amount is in good agreement with the data of Akdeniz et al. [5]. The increase of the silicon addition caused the decrease of the reaction layer thickness, what is in agreement with the results of Selverian et al. [1], who obtained the thinnest diffusion layer for 3% Si addition. Akdeniz et al. [5] obtained the similar results but for higher silicon amount of about 4% Si. According to [1] at higher amount of Si the layer is thicker contrary to [5] where it was reported that the layer remains constant at the smallest level.

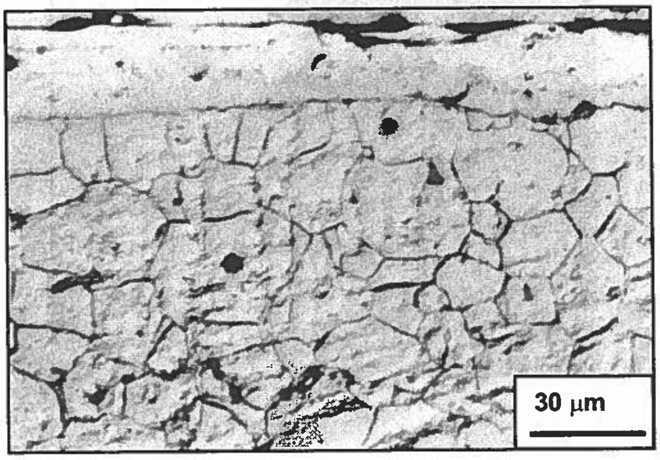

Fig. 4. Optical microstructure of the cross section of the substrate and diffusion layer formed in the AlZn43Si2 bath after the short dipping time of 15 s. at 670°C

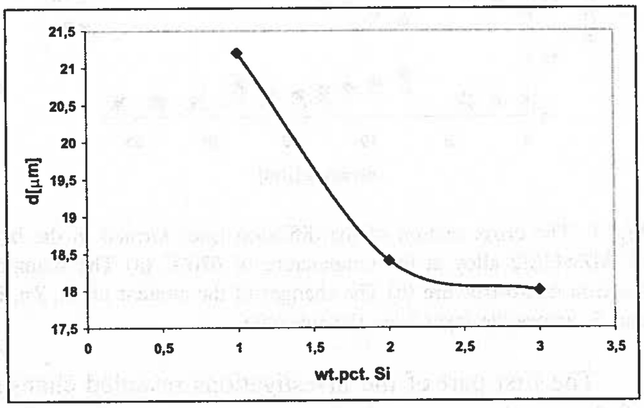

Fig. 5. The dependence of diffusion layer thickness vs. silicon amount dipped in the AlZn(44-42)Si(1-3) alloy baths at the temperature 670°C in the 180 s time

3.2. The scanning microscope investigations

The structure of cross sections of the steel panels after dipping process was observed in different samples, where the substrate, interlayer (reaction zone) and superficial layer (overlay: Al-Zn) were observed. The composition across the thickness (from the steel base to the surface) was studied using EDS detector. The results are given in the diagrams of the dependence of the amount (in. wt. %) of investigated substances Al, Zn, Si and Fe vs. distance from the overlay surface (in the steps of about 3 μm) for different dipping times and two temperatures. These measurements enabled the determination of the thickness of the reaction layer between the steel base and the Al-Zn layer. The thickness of this layer changed with the varying parameters of the dipping process, such as time, temperature and composition of the baths, particularly silicon content.

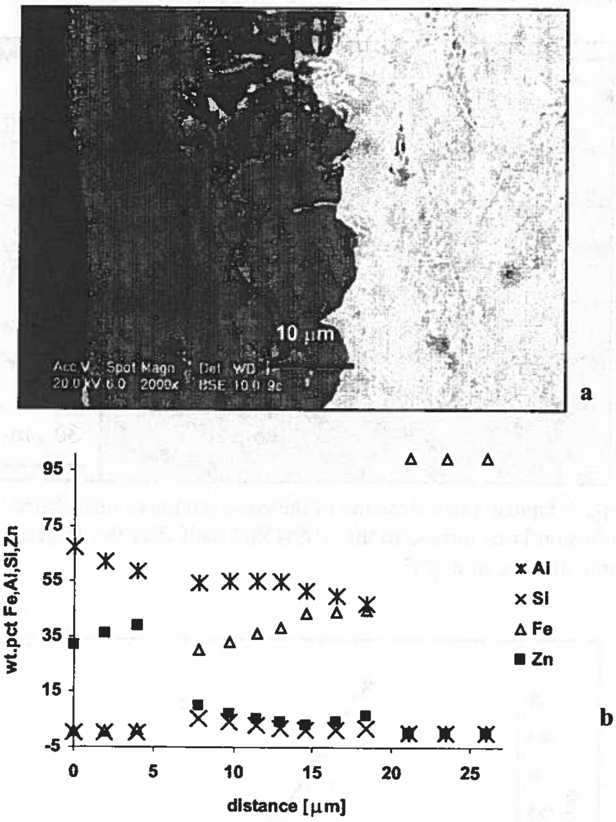

Fig. 6. The cross section of the diffusion layer formed in the bath of AlZn43Si2 alloy at the temperature of 670°C (a) The scanning electron microstructure (b) The changes of the content of Al, Zn, Fe and Si across the layer from the substrate

The first part of the investigations revealed changes of the reaction zone thickness vs. composition of the bath. It was measured on the cross section of the samples of the steel panels dipped in alloys with increasing Si amount (1-3 wt.%) at the temperatures between 630-690°C during 180 s. In the Figure 6a the SEM microstructure of the sample dipped in the bath AlZn43Si2 at the temperature 670°C and in the dipping time 180 s. is shown. The mean thickness of the reaction layer reached 18.3 µm. The changes of the composition, in relation to the distance from the surface of the layer to the substrate, is given in the diagram on the Fig. 6b. One can see that external layer contain the composition close to the bath. At a distance of 7 µm increases content of iron and decreases that of zinc and the reaction layer forms corresponding to the Al_3Fe. The content of iron further increases and the composition can be described as Al_5Fe_2. The composition of silicon only slightly increases up to 6%. In Fig. 7a one can see the microstructure of the sample dipped in the bath at 670°C for 15 s. The composition of the reaction layer at the different distances from the surface to the substrate is given in the diagram on the Fig. 7b. In comparison to the sample in Fig. 6 the zinc content in the external part of the layer is much higher, what indicate that in the initial period of dipping zinc diffusion is more rapid. The microstructure shown in the Fig. 8a was obtained from the sample dipped during 120 s. at 630°C. The variation of the composition of this layer is given in the diagram on the Fig. 8b. In comparison to previous micrographs iron increases faster in spite of lower dipping temperature. Due to irregular character of its composition changes it might be due to formation of columnar Al_3Fe crystals as reported in [14].

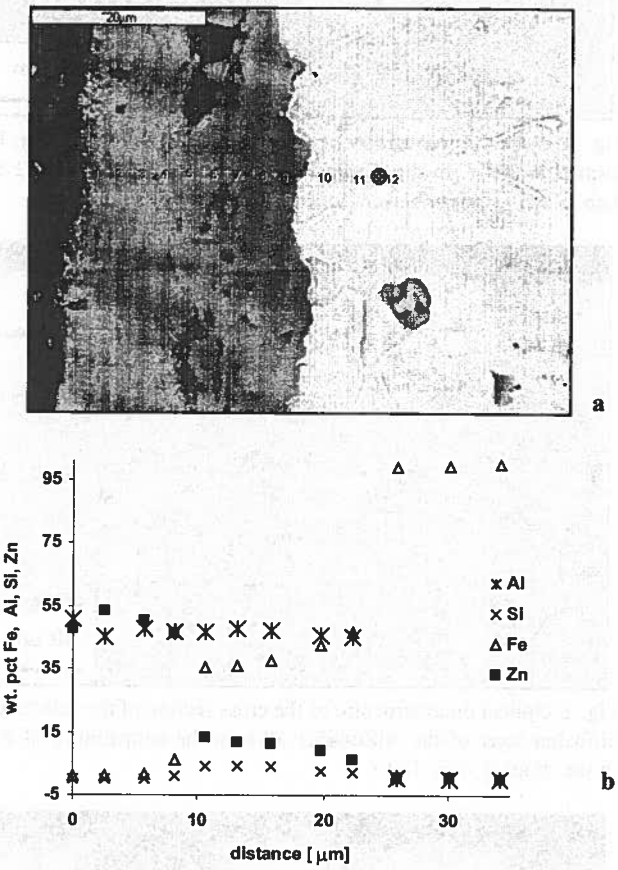

Fig. 7. The cross section of the sample dipped in the bath of AlZn43Si2 alloy at 670°C for the 15 s. (a) The scanning electron microstructure. (b) The changes of the content of Al, Zn, Fe and Si across the layer from the substrate

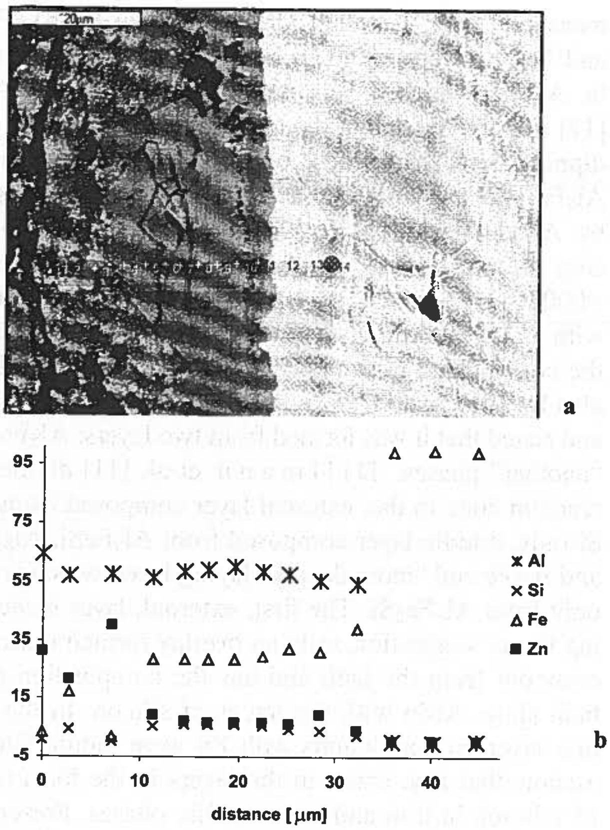

Fig. 8. The cross section of the sample dipped in the bath of AlZn43Si2 alloy at 630°C for the 120 s. (a) The scanning electron microstructure (b) the changes of the content of Al, Zn, Fe and Si across the layer from the substrate

The investigations of the kinetic of the growth of the reaction layer were performed using panels dipped in the bath of the AlZn43Si2 alloy, at temperatures of 630 and 670°C within the time interval of 5, 15, 30, 45, 60 and 120 s. As early as after 5 s. of the dipping time (at 670°C) the layer 10.25 µm thick has grown. The increase of the time up to 120 s. caused growth of the layer up to 17.50 µm. The thickness of the reaction layer formed in the bath at 630°C increased from 7.82 µm to 15.31 µm in the time interval between 5 sec. to 120 sec. The analysis of the results obtained for different dipping times allowed us to receive the dependence of the thickness of layer vs. dipping time given in the Fig. 9. It can be seen that with increasing dipping time the thickness of the intermediate layer (reaction zone) grows according to the linear relationship. Summarizing structure studies one can state that two basic layers were found:

- first consisting of aluminum-zinc solid solution with solved small amounts of Si and Fe, generally up to 0.6% Fe.
- second layer between the first one and the steel substrate composed of intermetallic compounds $Al_xFe_ySi_z$ and Al_xFe_y. This layer is important regarding the mechanical properties of the layer.

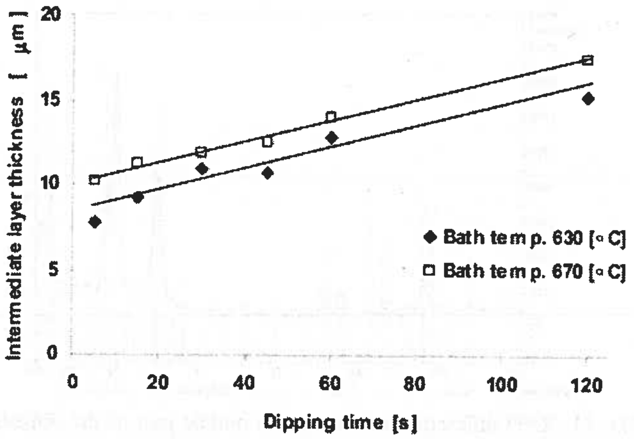

Fig. 9. The diagram of the dependence of the diffusion zone thickness vs dipping time of the layer produced in the AlZn43Si2 bath alloy at the temperatures 630 and 670°C

Mechanism of the formation of the second layer also called reaction layer was discussed in several papers [1, 5, 11, 14, 15] where existence of similar intermetallic compounds was identified.

3.3. XRD – phase analysis

X-ray diffraction studies were carried out using samples cut out from panels after hot dipping (at temperatures 630°C and 670°C) in AlZn43Si2 alloy dipped in the bath during: 5 s., 15 s., and 120 s. The patterns were obtained from the surface and after grinding to the middle layer, parallel to the surface. It can be seen in the Figs. 10 and 11 where the diffraction patterns of the middle layer obtained from the AlZn43Si2 bath at 630 and 670°C are presented.

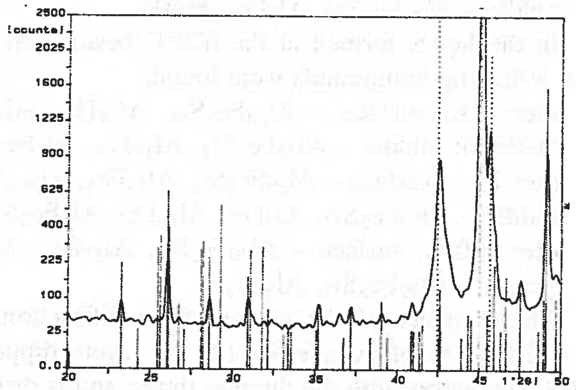

Fig. 10. XRD diffraction pattern of the middle part of the diffusion zone of the layer formed in the AlZn43Si2 alloy bath at 630°C after 120 s. dipping time

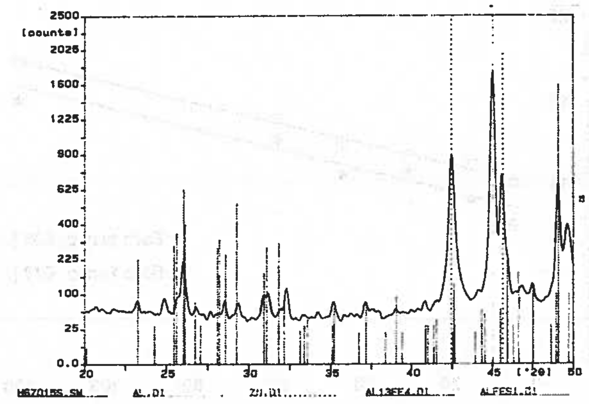

Fig. 11. XRD diffraction pattern of the middle part of the diffusion zone formed in the AlZn43Si2 alloy bath at 670°C after 120 s. of dipping time

The analysis was performed on the basis of Inorganic Index [16] or calculated according to the crystallographic data for the compounds: $Al_{20}Fe_5Si_2$; Al_7Fe_2Si; Al_5Fe_2; Al_2Fe; AlFe; $Al_{13}Fe_4$ and $AlFe_3$, Al, Fe and Zn. Analysis was carried out using computer calculation of the relative score and dispersion (of indications) which determine the probability of the occurrence of the given intermetallics, as verified by the usual comparative analysis.

In both types of samples (surface and reaction layer) and for both dipping temperatures following phases were found: Al, Zn, Fe and $Al_{20}Fe_5Si_2$. At the temperature 630°C the higher amount of the latter phase (according to the intensity of the diffraction line d = 2.154 Å) was found in the deeper layer but at the 670°C it was not detected.

In the layers formed at the 630°C besides Al, Zn, Fe a following compounds were found:

- after 5 s.; surface – $Al_{20}Fe_5Si_2$, AlFe, $Al_{86}Fe_{14}$; middle – $Al_{20}Fe_5Si_2$, $Al_{13}Fe_4$; Fe_3Al
- after 15 s.; surface – $Al_{20}Fe_5Si_2$, $AlFe_2$, AlFe; middle – $Al_{20}Fe_5Si_2$, AlFe, Fe_3Al, Al_7Fe_2Si
- after 120 s.: surface – $Al_{20}Fe_5Si_2$, Al_5Fe_2, $Al_{76.8}Fe_{24}$; middle – $Al_{20}Fe_5Si_2$, Al_5Fe_2, $FeAl_2$.

In the layers formed at the 670°C besides Al, Zn, Fe a following compounds were found:

- after 5 s.; surface – $Al_{20}Fe_5Si_2$, $Al_{13}Fe_4$, Al_5Fe_2, Al_7Fe_2Si; middle – $Al_{20}Fe_5Si_2$, $Al_{13}Fe_4$, Al_7Fe_2Si
- after 15 s.; surface – $Al_{20}Fe_5Si_2$, $Al_{13}Fe_4$, $Al_{76.8}Fe_{24}$; middle – $Al_{20}Fe_5Si_2$, Al_5Fe_2, $Al_{13}Fe_4$, Al_7Fe_2Si
- after 120 s.; surface – $Al_{20}Fe_5Si_2$, $Al_{13}Fe_4$, Al_2Fe; middle – $Al_{20}Fe_5Si_2$, Al_5Fe_2.

The intensity of the characteristic diffraction line (d = 2.154 Å) of $Al_{20}Fe_5Si_2$ (in the layers dipped at 630°C) increases with the dipping times, and is distinctly higher in the reaction layers. In the layers formed at 670°C the intensity of this diffraction line is almost the same for all dipping times and the position of the measured layer. Another compounds like Fe_3Al, $FeAl_2$ and Fe_2Al_5 were found in both layers. The intermetallic $Al_{13}Fe_4$ which is very near in composition to Al_3Fe [17] was found in both the temperatures only after short dipping time. In that case occurred the another, namely Al_5Fe_2 – phase what is in accordance with the data given by Akdeniz et al. [5]. The Al_5Fe_2 compound is not easy to find because of the strong texture of the type <0002> [1] and this strongest diffraction line coincide with strongest diffraction line of zinc. The differences in the composition of the layer in reaction zone was found also by Selverian [1] who investigated the reaction zone and stated that it was formed from two layers: Al_5Fe_2 and "another" phases. Dillmann et al. [11] divided the reaction zone in the: external layer composed from Al + Si only, middle layer composed from Al_5FeSi, Al_8Fe_2Si and Al_3Fe and "more deeply" laying layer, which is build only from Al_8Fe_2Si. The first, external, layer is, according to our suggestion, only an overlay formed during the draw out from the bath and has the composition of the bath alloy: AlZn with the traces of silicon. In the reaction layer no compounds with Zn were found. One can assume that zinc exists in the layers in the form of solid solution in iron and intermetallic phases. Presence of iron in the external part of the layer indicate a significant diffusion of this element through the reaction layer. At the same time presence of Al_5Fe_2 near the substrate and its growth during the process (Fig. 8) indicate diffusion of aluminum within the layer. Increase of iron content in the layer was explained by the formation of columnar crystals of Al_3Fe [14]. It can explain also a high iron content at the depth of 3 μm as shown in Fig. 7.

4. Conclusions

1. The reaction zone composed of Al-Fe and Al-Fe-Si intermetallic phases forms already after very short time of dipping of about 15 s. at 630°C.
2. The best adhesion of the layer was obtained in the bath of composition AlZn43Si2 alloy at the temperature of 670°C.
3. The silicon addition to Al-Zn alloy reduces the formation rate of the Al-Fe phases due to generation of the solid reaction layer of the Al-Fe-Si phases which strongly inhibit the diffusion of aluminium into the steel substrate.
4. X-ray phase analysis allowed to identify following intermetallics in the reaction layer at both temperatures investigated: $Al_{20}Fe_5Si_2$ Al_5Fe_2, Al_3Fe. The $Al_{13}Fe_4$ (Al_3Fe [16]) phase is present only in the layer after short dipping time and disappear after longer one.

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