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NEW LEAD FREE ZINC ALLOY FOR UNIT MODE HOT-DIP GALVANISING OF STEEL PRODUCTS

NOWY, BEZOŁOWIOWY STOP CYNKU DO JEDNOSTKOWEGO CYNKOWANIA OGNIOWEGO WYROBÓW STALOWYCH

The paper describes research work on development of optimal chemical composition of a new lead free zinc alloy, intended for unit-mode hot-dip galvanising of steel products.

The results of different steel grades (interstitial free steel, steel killed with silicon and reactive steel) galvanising with the use of Zn-Al-Ni-Mn-Sn and Zn-Al-Ni-Mn-Sn-Ti alloys have been presented.

Irrespective of the grade of steel, the obtained zinc coatings are thin, smooth, bright and shinning. They reveal similar advantageous structure, improved corrosion resistance, good diffusion adherence and high plasticity. Titanium addition does not produce the desirable decrease of coating thickness, changing the phase structure of zinc coatings only.

Industrial practice of steel products hot-dip galvanising with new lead free zinc alloy Zn-Al-Ni-Mn-Sn (WEGAL) proved the decrease of zinc alloy consumption to ca. 60 kg per 1 ton of steel products (it means 20% cut off when compared to its previous use) while at the same time quality of the coatings is greatly improved.

Praca przedstawia wyniki badań w zakresie opracowania optymalnego składu chemicznego nowego stopu cynku przeznaczonego do jednostkowego cynkowania ogniowego wyrobów stalowych.

Podjęte badania mają na celu przedstawienie wyników jednostkowego cynkowania różnych gatunków stali (nieuspokojonej, uspokojonej krzemem i reaktywnej) w kąpieli utworzonej ze stopu Zn-Al-Ni-Mn-Sn, uzupełnionej następnie dodatkiem tytanu.

Otrzymane powłoki, niezależnie od gatunku cynkowanej stali, posiadają podobną, korzystną budowę, podwyższoną odporność na korozję, dobrą przyczepność dyfuzyjną do podłoża stalowego i plastyczność. Ich wygląd jest gładki, jasny i błyszczący. Dodatek tytanu nie wywołuje pożądanego zmniejszenia grubości powłok. Wpływa jedynie na ich obraz struktury.

Przemysłowe cynkowanie stopem Zn-Al-Ni-Mn-Sn (WEGAL) przebiega przy średnim zużyciu stopu ok. 60 kg na 1 tonę wyrobów stalowych. Odnotowano oszczędność cynku rzędu 20% w odniesieniu do jego zużycia w okresie przed zastosowaniem przedmiotowego stopu.

1. Introduction

The study is a continuation of the research work conducted previously in Institute of Non-ferrous Metals [1–4] into development of new zinc alloy for unit-mode hot-dip galvanising of steel products.

The subjects of the study were zinc coatings, obtained in the developed zinc bath, which was formed on the basis of electrolytic zinc with four alloy additions: Al, Ni, Mn and Sn – so called WEGAL alloy [5–7], where in the second version titanium was also added. Lead addition was eliminated from the alloys, mainly because of ecological reasons and following the current world tendency in that area [8–9].

The reason behind application of that specific chemical composition was to eliminate quality differences in structure of coatings obtained on various grades of steel, with simultaneous reduction of thickness of coating which are formed on reactive steels. The fulfilment of that requirement is connected with the increase in quality of the produced coatings and with saving of the used alloy. In the result a universal coating is formed.

The task of the three applied alloy additions (Al, Ni, Mn) lies in their simultaneous influence on reduction in excessive growth of coating thickness on reactive steels, including steels with Sandelin effect. Those alloy additions form good conditions to obtain a balanced reactive diffusion stream in each intermediary layer of the coating during its growth. Additionally, each of the additions has a separate, positive influence on the formation of coating on steel products. Aluminium guarantees the shiny

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appearance of the coating, in the result of the protective influence of aluminium oxide. Nickel works in a similar area but through the presence of intermetallic phase, mainly with zinc δ, in the coating [10]. Manganese, on the other hand, improves anti-corrosion qualities of the coating, including resistance to the so-called white rust. The fourth alloy addition – tin – has a positive influence on effective reduction of surface tension of the bath with simultaneous positive influence on exposing of coating grains boundaries (so called coating flower) [11].

In the described context the role of titanium is not sufficiently understood [12], especially in the case of a bath, which is already enriched with specific components.

In the result of steel products galvanising with a use of ordinary zinc, usually with lead and aluminium, we obtain zinc coatings, which can vary in structure and thickness. Among the grades of steel, which are subjected to galvanising, are also grades which contain silicon in the volume larger than or equal to 0.04%, and at the same time their sum Si + 2.5P is in the range from 0.09 to 0.2%. In the case of such steels some negative qualities can be observed in the coatings, significant for the Sandelin effect [13]. They are rough, brittle and several times thicker than the coatings obtained on the steels, e.g. interstitial free steels, which are still considered as preferred for galvanising.

Recently a study by Schubert and Schulz was published [14], where classification of steel for galvanising was presented, based on silicon content in the steel composition, as well as new information on mechanism of growth of coatings on various grades of steel. The authors also presented a method for solving the currently existing problem of diversified structure of coatings, which is based on application of zinc alloy only, which will contain, among others, such additions as: aluminium, tin and nickel.

Up till now it was established that zinc coating of ordinary thickness and advantageous structure contains the following phases: Γ, δ_{1k}, δ_{1p}, ζ, η. It forms only on the low-silicon steel, interstitial free steels and, additionally, when its volume does not exceed 0.035%. On the other hand, the thickest coatings – even 8 times thicker when compared to the previously described ordinary coating – form on steels, where silicon volume is contained in the range 0.035–0.12% Si (reactive steels from the range of Sandelin effect). In the coatings of that type there is usually thin δ_1 phase on which grown phases ζ and ζ+η are mainly observed. There are also coatings of higher thickness, which reach only up to 1.6 of the ordinary coating thickness. The latest can be found on the steels, which contain silicon in the volume of 0.12–0.28% (steels in the range of Sebisty effect). In the phase composition of those coatings the same intermetallic Fe-Zn compounds, as before, can be found, but in different, more advantageous volume. The last, indicated by the authors of the study [14] range of coatings, also of increased thickness (over 3 times when compared to the ordinary coating with presence of the similar, as before, phases), is related to the high-silicon steels, and that means they contain more than 0.28% Si.

The objective of the studies is to present results of hot galvanising of interstitial free steel, steel killed with silicon and reactive steel in the investigated baths. The composition of the new zinc alloy, which was applied in galvanising, can be treated as a proposal for a method to oppose the disadvantageous, excessive increase in zinc coating thickness and its improper structure, and the objective of the method is to determine the optimal conditions for galvanising products made from reactive types of steel.

2. Experimental

For the galvanising electrolytic zinc of the grade Z1 (99.995% Zn) was used, where aluminium, nickel, manganese and tin were added. For penetration of nickel and manganese, the previously prepared two-component master alloys with zinc were used. Flat steel samples (interstitial free steel 08X: 0.02% Si, 0.012% P, Si + 2.5 P = 0.05%; steel killed with silicon of grade 20: 0.27% Si, 0.015% P, Si + 2.5 P = 0.31% and steel in the grade 55: 0.24% Si, 0.008% P, Si + 2.5 P = 0.26% as well as reactive steel St3SX: 0.07% Si, 0.02% P, Si + 2.5 P = 0.12% and also St3S: 0.15% Si, 0.032% P, Si + 2.5 P = 0.23%), of dimensions: l x w x t = 80×30×1 mm, were chemically prepared, dried and immersed in the prepared baths Zn-Al-Ni-Mn-Sn (WEGAL) and Zn-Al-Ni-Mn-Sn-Ti, of the temperature of 440+2°C and maintained there for 1, 3, 5 and 10 minutes. Titanium addition was used in the volume of 0.05% and 0.1%. Cooling down of the galvanised samples was conducted in stable conditions, in the air only.

Metallographical microsections were prepared from the galvanised samples and used for determination of coatings thickness and for documenting of their structure, with a use of metallographical microscope OLYMPUS GX71. Thickness of the coatings was measured by FISCHER instrument DELTASCOPE MP30.

The examined samples were also subjected to pure bending at the angle of 180° on steel shaft of radius 5 mm. Observation of the bent samples was conducted by an unarmed eye.

3. Discussion

The results of investigations include analysis of microstructure and measurements of coatings thickness on the examined steels (08X, 20, 55, St3SX, St3S), galvanised in new baths (Fig. 1–5). During the binding test adherence and plasticity of the examined coatings were evaluated.

In the described conditions, in which the study of hot galvanising of steel samples was performed, an identical, universal coating type was obtained, irrespective of the grade of galvanised steel (Fig. 1). On the 08X steel, which is preferred for galvanising, a coating formed of thickness 60 μm. On the other steels, which belong to the reactive group, the coating had thickness from 67 to 110 μm.

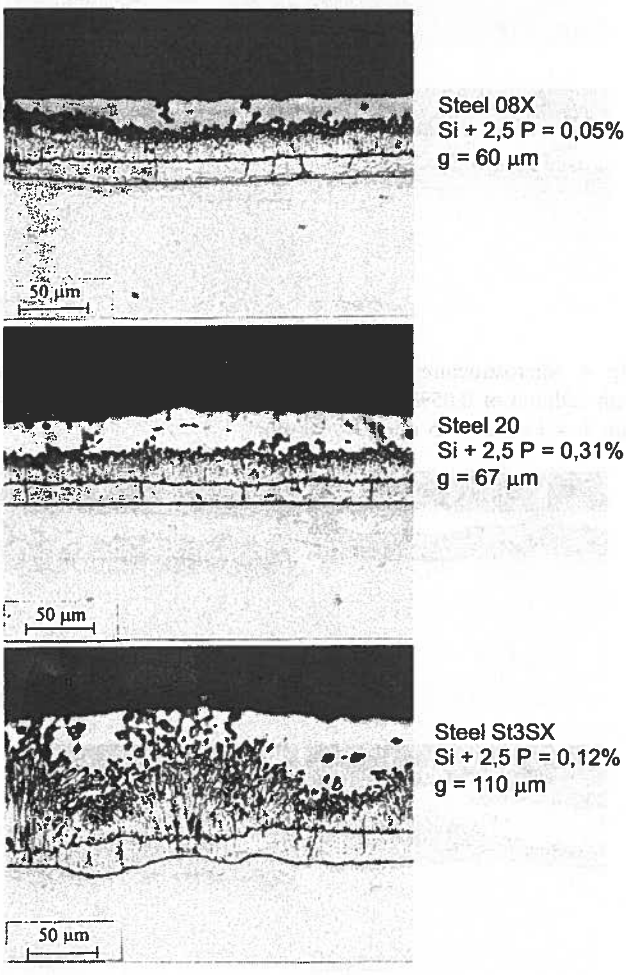

Fig. 1. Microstructure of zinc coatings obtained in industrial conditions on 08X, 20 and St3SX steels in WEGAL bath of temperature 442°C in the period of about 6 min

In every considered case the same intermediary layers of the coating are present, when viewed from the steel basis, composed of intermetallic phases Fe-Zn: δ_1, ζ, η, respectively. The presented structure of the coatings results in uniform and smooth look of the galvanised products, irrespectively of the steel grade.

The presented pictures of the coatings confirm a positive, as expected, limitation of their thickness growth on the steels which contain silicon in their chemical composition, especially in the case of reactive steel St3SX, characterised by the Sandelin effect. In the examined samples of reactive steels we found only about 2-times thicker coating than in the case of the coating on the steel preferred for galvanising, of the grade 08X [15].

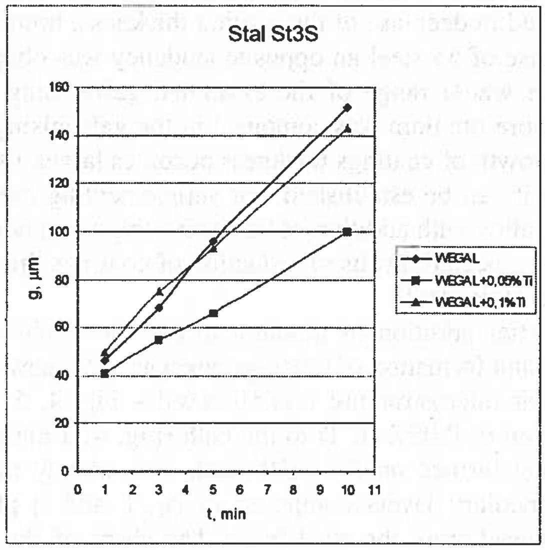

Fig. 2. Relation between the obtained in the examined galvanising baths thickness of coatings and galvanisation time (440°C, steel St3S)

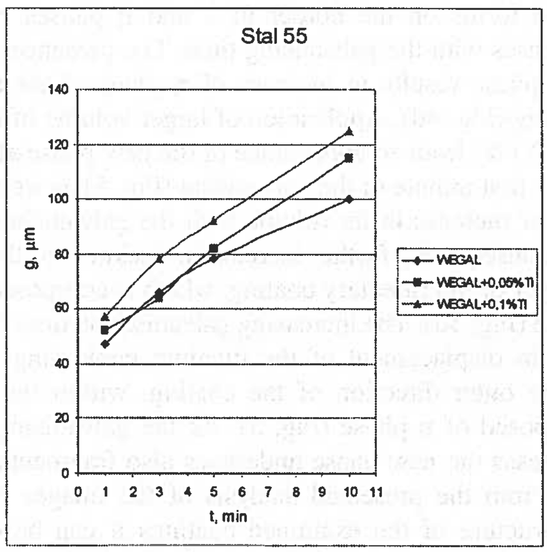

Fig. 3. Relation between the obtained in the examined galvanising baths thickness of coatings and galvanisation time (440°C, steel 55)

The increasing with time thickness of a coating, which runs along a parabolic curve, is a characteristic feature for all baths and all galvanised steels, irrespective of their reactivity (St3S, 55) – Fig. 2, 3. For the 55 steel (larger silicon content than in St3S steel) the range of thickness increment is smaller and on the average ranges from 52 μm for 1 min galvanising up to 113 μm for 10 min immersion in zinc. In the case of St3S steel, of chemical composition closer to the Sandelin effect, the thickness increment was on the average from 46 μm (1 min) to 132 μm for 10 min immersion of the samples in the bath.

The titanium additions had no influence on kinetics of coating growth on both examined steels. In the case of St3S steel, the addition of titanium to the WEGAL bath resulted in decrease of the coating thickness, however in the case of 55 steel an opposite tendency was observed. In the whole range of the examined galvanising time, the more titanium was contained in the galvanising bath the growth of coatings thickness becomes larger. On that basis it can be established that supplementing the WEGAL alloy with addition of titanium component does not bring expected results of reduction of coatings thickness on reactive steels.

After addition of titanium to the Zn-Al-Ni-Mn-Sn alloy and formation of coatings, presence of a new phase in their microstructure was observed – Fig. 4, 5. After addition of 0.05% of Ti to the bath (Fig. 4) a multilayer coating formed on the St3S steel, with clearly marked intermediary layers composed of δ_1, ζ and η phases, as viewed from the steel basis. The share of the mentioned intermetallic phases is proportional to the applied galvanising time. In the third minute, already, after immersing the steel samples in the galvanising bath a new phase forms on the border of ζ and η phases, which increases with the galvanising time. The presence of the new phase results in increase of η phase share in the coating (Fig. 4d). Application of larger volume of titanium (0.1%) leads to appearance of the new phase already in the first minute of the galvanising (Fig. 5) as well as to further increase in its volume with the galvanising time and consequently further increase in thickness of the outer layer of intermediary coating, which is composed of η phase (Fig. 5d). The increasing galvanisation time results also in displacement of the titanium containing phase in the outer direction of the coating, within the layer composed of η phase (Fig. 5). As the galvanising time increases the new phase undergoes also fragmentation.

From the presented analysis of the images of microstructure of the examined coatings it can be established that presence of titanium in the bath results in formation of an additional phase, of location and morphology which can not have any inhibiting influence on the process of reactive diffusion between its the two main components; iron and zinc.

For qualitative examination of chemical composition of the new – titanium-containing – phase investigation was performed with a use of X-ray microanalyser [16]. It was established that directly on the surface of the ζ phase, already in the region of η phase, precipitations of a new, five-component phase occurs. The basis for that intermetallic compound is, of course, zinc, and beside titanium there are also additions of: iron, aluminium and nickel (Zn-Fe-Al-Ni-Ti). It was established that in the case of long galvanising time (10 min) the examined titanium-containing phase contains also some small addition of tin.

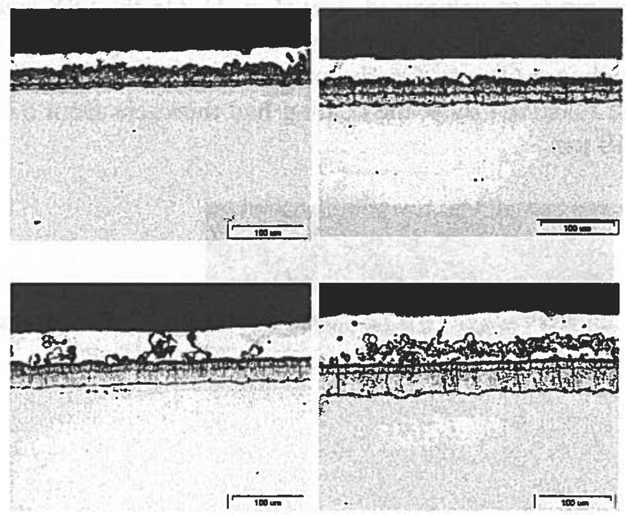

Fig. 4. Microstructure of zinc coatings obtained in WEGAL bath with addition of 0.05% of Ti on reactive steel St3S (440°C); a – 1 min, b – 3 min, c – 5 min, d – 10 min

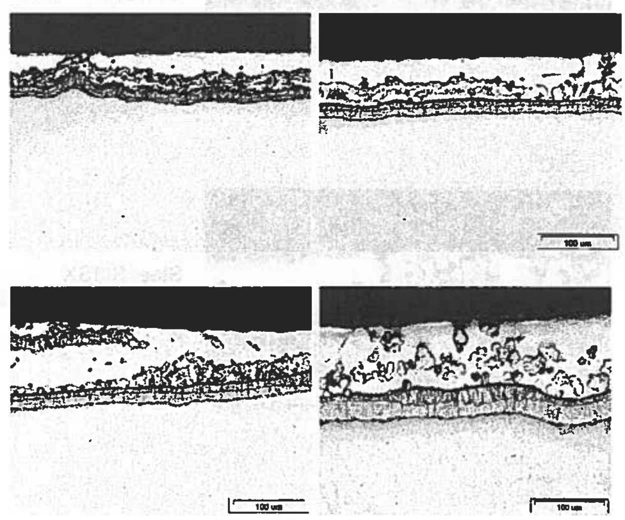

Fig. 5. Microstructure of zinc coatings obtained in WEGAL bath with addition of 0.1% of Ti on reactive steel 55 (440°C); a – 1 min, b – 3 min, c – 5 min, d – 10 min

For determination of plastic properties and adherence of the coatings to the steel basis a test for their bending was conducted. In all examined samples the coatings showed no cracking after the bending tests. Very small cracks on the bending surface in some of the samples does not change the results of very high plastic properties and good diffusion adherence to the steel basis of the fabricated coatings.

The visual inspection showed that the examined coatings had smooth, bright and shiny appearance. Such appearance of the galvanised coatings, supplemented with so called flower-shape image of various sizes, generally is approved by users as a standard. The obtained universality of the coatings causes the steel products, often manufactured from various grades of steel, to take advantageous, uniform appearance after galvanising.

The galvanising which was conducted in industrial conditions confirmed the results obtained during the examination of Zn-Al-Ni-Mn-Sn (WEGAL) alloy with respect to proper and economical galvanising of steel products (over 20% cut-off in alloy consumption when compared to the initial zinc consumption – about 80 kg per ton of galvanised products in a period of one year) with simultaneous increase in quality of the produced coatings, including corrosion resistance increase, especially on reactive steels [17].

4. Conclusions

The conducted studies into hot dip galvanising of low silicon steel, interstitial free steel 08X, steel killed with silicon 20 and 55 as well as reactive steel St3SX and St3S, proved the positive influence of the developed chemical composition of the Zn-Al-Ni-Mn-Sn (WEGAL) alloy on thickness and properties of the applied zinc coatings. The main advantage resulting from application of the new, lead-free bath is – besides the ecological aspect – limitation of the thickness increase and obtaining of a proper structure of the coating, especially on the reactive St3SX and St3S steels and on the steels killed with silicon, of the grade 20 and 55.

The presented zinc coatings show multilayer structure, formed by intermetallic Fe-Zn phases: δ_1, ζ and η. Such a type of the coating, regardless of the galvanised steel grade (universal), has very good diffusive adherence to the steel basis and very good plastic properties, as confirmed in the test of bending. Thanks to the outer layer, composed of η phase, the coatings are smooth, bright and shiny which was not possible to be obtained on reactive steels (Sandelin effect) and on the steels killed with silicon.

The developed and applied zinc alloy with additions of aluminium, nickel, manganese and tin gives possibility for formation and existence, during the period of galvanising, of a stable reactive diffusion stream of all components of steel and the bath in every formed intermediary layer of the coating.

The increase of the coating thickness with galvanising time, which runs according to the advantageous parabolic curve, can be seen as a confirmation of the obtained results, and the values of the curve in the whole period of galvanising time (from 1 to 10 min) as well as volumes of silicon in the steel are, at the very most, close to the double thickness of a coating which can be found on the steel preferred for galvanising, of the grade 08X.

The applied alloy additions of titanium introduced no significant changes in the kinetics of growth of coatings on the examined steels. Although the addition of titanium into the WEGAL bath in the case of St3S steel resulted in general decrease of coatings thickness but for the 55 steel the tendency was opposite. It can established that supplementing the Zn-Al-Ni-Mn-Sn alloy with additional titanium component does not explicitly result in decrease in the thickness of coatings on reactive steels. It results however in formation of a new multicomponent intermetallic phase Zn-Fe-Al-Ni-Ti, which contains also tin when the galvanising is conducted for a longer period (e.g. 10 min). The volume of the new phase, its location and morphology change with prolongation of the galvanising time. The new phase, located in the outer layer of the coating and composed of η phase, undergoes displacement in the outer direction of the coatings, fragmentation and spheroidisation when the galvanising time is increased.

During the performed galvanising on industrial scale, 60 kg of the WEGAL alloy for 1 t of the galvanised steel products was on the average used per year. The saving thus reached over 20% of the alloy when compared to the initial zinc consumption before application of the subject alloy. At the same time the quality of the produced coating was improved, also with relation to corrosion resistance.

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