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RESEARCH ON THE COMPLEX MICROALLOYED ZINC MELTS

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ABSTRACT

Microalloyed zinc melts are used in hot dip galvanized processes in order to improve products quality. Experiments aimed at obtaining zinc coatings with increased resistance to corrosion, which adhere very well to steel support, which are not conducive Fe-Zn reactions, don't have negative environmental impacts and present uniformly dispersed phase structure in zinc matrix. To achieve these targets were chosen microalloying elements: nickel, tin, bismuth (compared to lead) and aluminium. There were made various degrees of microalloyed zinc to determine the influence of these factors on the characteristics of the melt and obtained layers. The degree of assimilation of elements in melted zinc was determined by spectrophotometer of samples alloy, taken from melt at different time intervals. There was also presented evidence of elements influence on alloy microstructure.

KEYWORDS: zinc melts, coatings, microalloyed process, microstructure.

1. Introduction

Improvement of characteristics for the use of hot-dip galvanised products is a primary objective of the producers.

To increase the resistance to corrosion, adherence, limiting pollution and zinc-iron reaction, are used more and more microalloyed zinc melts with various elements: aluminium, nickel, titanium, copper, tin, bismuth, etc. Microalloyed zinc melts in galvanising are important in the case of Sandelin steel zincking. It is characterized by the formation of thick layers and which can be hot - dip galvanised only in microalloyed zinc melts. There is a great interest in carrying out research which explores the influence of the alloying elements in zinc melts on coating layers characteristics and the characteristics of the melts [1, 2, 3, and 4]. The paper aims at analysis the effect of small quantities of nickel, tin, bismuth and aluminium on the zinc melts.

High purity SHG zinc it was microalloyed and the level of impurities is shown in Table 1.

Table 1. *The chemical composition of zinc used in experiments, in %*

Zn	Pb	Cu	Fe	Sn	Al	Cd
99.996	0.0014	0.0004	0.0005	0.0005	0.0005	0.0004

2. Experimental researches

In the framework of the research were analysed four different zinc melts microalloyed with nickel, tin, bismuth, lead and aluminium whose chemical composition is presented in Table 2.

Table 2. *The chemical composition of microalloyed Zn melts, in %*

Alloy	Ni	Bi	Sn	Pb	Al	Zn
Zn-Ni-Bi-Sn	0.16	0.71	2.95	0	0	96.18
Zn-Ni-Pb-Sn	0.16	0	2.88	0.72	0	96.24
Zn-Ni-Pb-Bi-Sn	0.16	0.41	3.49	0.43	0	95.51
Zn-Sn-Bi-Al	0	0.44	0.86	0	0.33	98.37

2.1. Microalloying with nickel

According to Zn - Ni phase diagram, nickel and zinc form intermetalic compounds and solid solutions - based compounds. Nickel is insoluble in zinc and at 418^{o}C and 94.8%Zn forms the (σ + Zn) eutectic. Alloying with Ni was made directly through the use of finely crushed Ni, (fine pieces < 1mm) and mechanical stirring. Microalloyed process is longer, lasting for at least one hour at the temperature of 700^{0}C. Assimilation efficiency is low because nickel was lost in slag and dross. Assimilation efficiency of the direct alloying experiments was found in 77%, measured three hours after the introduction of nickel (to calculate a concentration of 0.21%Ni and 0.16%Ni was obtained). In the literature, it is recommended both direct alloying with metallic nickel and the use of alloys with a maximum of 5% nickel.

2.2. Microalloying with bismuth

In the equilibrium diagrams of Zn-Bi, there is an insolubility of the two metals which form a eutectic at 97.3% Bi and 254.5 ^{0}C. Given the low melting temperature of bismuth (271^{0}C) microalloying was made with metallic bismuth, grinding and mixing in the melt by mechanical stirring.

Assimilation process of bismuth in the melt was stable, maximum efficiency is obtained. Bismuth is a micro alloying element used to replace lead, the same effect of melt fluidity and reduction of surface tension without being toxic.

Microalloying the melt with 0.1%Bi, influences surface tension and fluidity similarly using a Pb content of ~ 1% [2]. Although bismuth is more expensive, the quantity needed for alloying bath is much lower, costs are compensated. Bismuth is also very stable in the melt and requires replenishment of the proportional added zinc.

2.3. Microalloying with lead

Lead is the main impurity in zinc. The diagram of equilibrium Pb – Zn shows that these two elements are insoluble in liquid and solid state.

Present in zinc, lead influence on the characteristics is shown in Figures 1 and 2, lead decreases surface tension and increases the zinc melts fluidity.

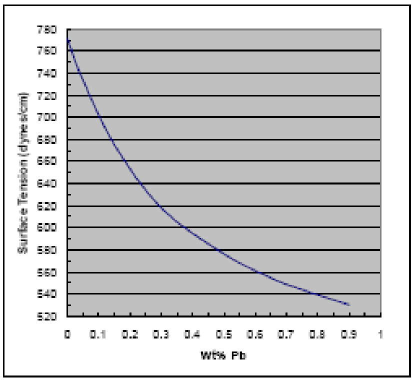

Fig.1. *The effect of lead on surface tension of zinc melts, [3]*

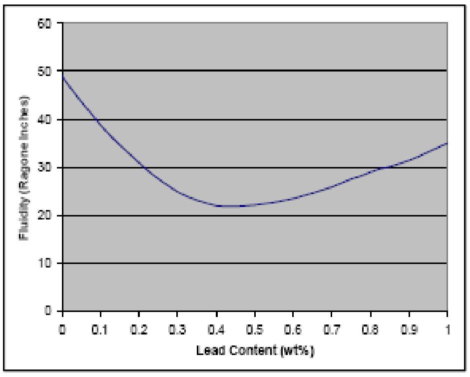

Fig. 2. *The effect of lead on fluidity of zinc melts, [3]*

2.4. Microalloying with tin

In the experiments, microalloying with tin was made with metallic tin. Sn-Zn equilibrium diagram shows a total insolubility of this element in zinc with the formation of a eutectic at 198.5^{0}C and 91.2% Sn. Tin, like most analyzed elements, forms intermetallic compounds with nickel.

2.5. Microalloying with cadmium

Cadmium is often present in zinc and can be considered an impurity. He is among the few elements which are soluble in zinc at room temperature and 0.1%Cd. Under 0.6%Cd does not affect coating structure being present in the dissolved layer foil which gives it greater resistance to corrosion. Microalloying with cadmium was made with metallic cadmium. Assimilation efficiency was achieved by 96% (addition of alloying was calculated for a concentration of 3% and 0.26% was obtained.

2.6. Microalloying with aluminium

In galvanizing melts aluminium has a major influence on slag formation, in decreasing its quantity, favouring a clean and shiny surface. Zinc melts density decreases by adding aluminium (aluminium has a density of approximately 2.5 times lower than zinc), Fig.3.

By increasing aluminium content in the melt, surface tension increases (Fig. 4).

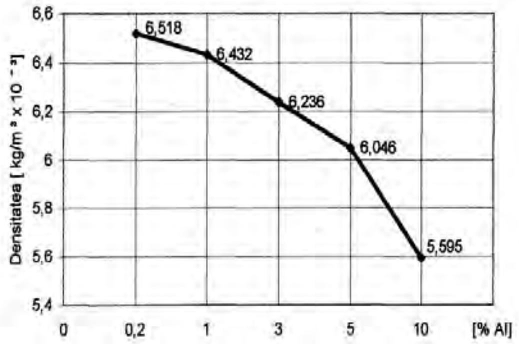

Fig. 3. *The effect of aluminium on the density of zinc melts.*

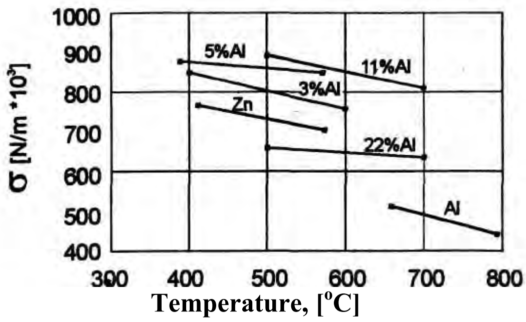

Fig. 4. *The effect of aluminium on surface tension of zinc melts.*

Given the differences in specific gravity between the two metals and the high reactivity of aluminium, microalloying with this item is recommended to be made with Zn-Al alloy. In the experiment was used commercial alloy (Zn + 4% Al). Equilibrium diagram Zn – Al shows an insolubility of Al in zinc at room temperature and solubility of 0.1% Zn in aluminium.

Zinc solubility in aluminium increases significantly with temperature. At 227 °C and 77.7% formed the eutectic (α + Zn).

3. Microstructure analysis of microalloyed zinc melts

At microalloying zinc with nickel, composite structure is obtained, consisting of intermetallic compounds (Zn-Ni, Zn-Ni-Sn, Ni-Sn) finely dispersed in zinc matrix (Fig. 5, Fig. 6).

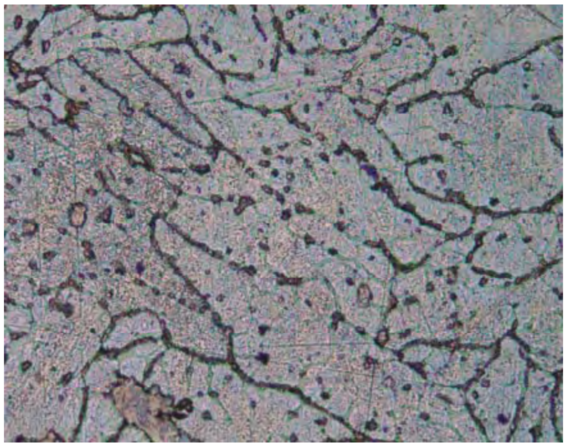

Fig. 6. *Microstructure of zinc microalloyed with Ni-Sn- Pb, X400*

Simultaneous use of lead and bismuth, and increasing the amount of tin finish striking structure, with the growing amount of intermetallic compounds. (Fig. 7)

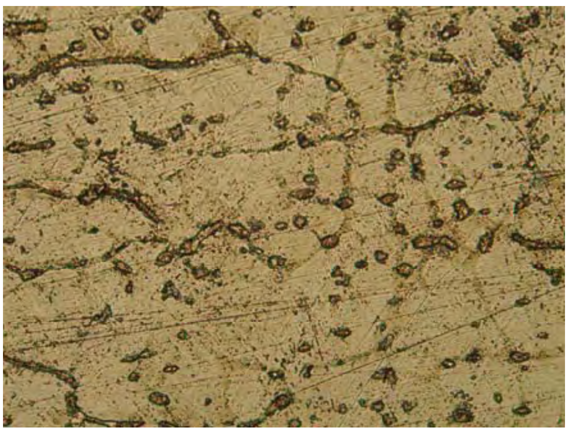

Fig. 5. *Microstructure of zinc microalloyed with Ni-Sn- Bi, X400.*

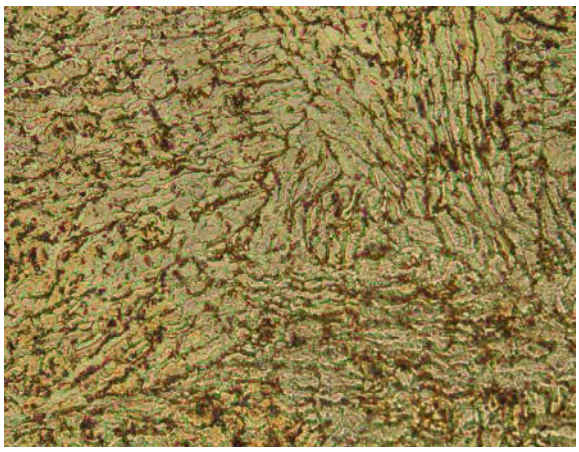

Fig. 7. *Microstructure of zinc microalloyed with Ni-Sn- Pb-Bi, X400.*

Metallographic analysis of microalloyed zinc with tin, bismuth and aluminium also reveals changes in microstructure, appearance of zinc-tin eutectic and bismuth crystals insertion (insoluble zinc) in the interdendritical space, as shown in Fig. 8.

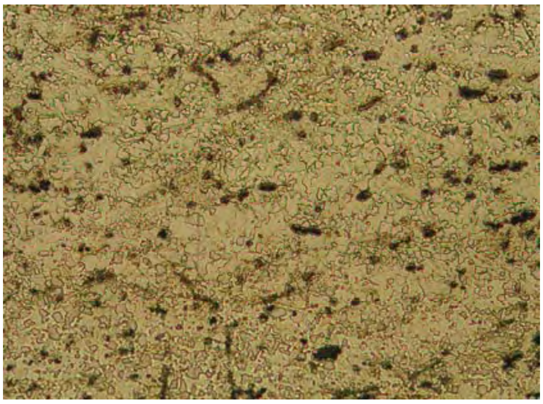

Fig. 8. *Microstructure of zinc microalloyed with Sn-Bi-Al, X400.*

4. Conclusions

1. Microalloying was made directly, using metallic elements, finely crushed, followed by mechanical mixing. At microalloyingwith nickel, was applied a maintenance at 700^0C.

2. All equilibrium diagrams of microalloying element and zinc have insolubility in the solid state, with formation of eutectic. Nickel forms intermetallic compounds with zinc and other studied elements.

3. The degree of assimilation of microalloyed element in the melt (calculated as the difference between the introduced metal content in the melt and the chemical composition analysis results) was different, depending on the element:

- Bismuth is assimilated 100% and it is stable in the melt, replenishment is required only when is made addition of zinc;
- Nickel is assimilated in proportion of 77%, it is lost in dross and slag;
- Tin and cadmium are assimilated at a rate of about 96% and are stable in the melts;
- Aluminium is well assimilated only using zinc-aluminium alloy, because it is lighter than zinc and has high affinity for oxygen. Aluminium is very reactive, it is consumed quickly and must be periodically added to zinc melts.

4. Bismuth is a novelty element for microalloying zinc melts, used to replace lead, having the same effect on melt fluidity and reduction of surface tension without being toxic.

5. At microalloying zinc melt with nickel composite structure is obtained consisting of intermetallic compounds (Zn, Ni, Zn-Ni-Sn, Ni-Sn) finely dispersed in the matrix of zinc.

6. Metallographic analysis of microalloyed zinc with tin, bismuth and aluminium also reveals changes in microstructure, appearance of zinc-tin eutectic and bismuth crystals insertion in the interdendritical space.

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