

CHARACTERIZATION OF THE BOTTOM DROSS FORMED DURING BATCH HOT-DIP GALVANIZING AND ITS REFINING

J. Trpčevská¹, B. Hlucháňová¹, T. Vindt,¹ W. Zorawski², D. Jakubéczyová³

¹Department of Non-ferrous Metals and Waste Treatment, Faculty of Metallurgy, Technical University of Košice, Letná 9, 042 00 Košice, Slovakia

²Faculty of Mechatronics and Machine Building, Kielce University of Technology, Al. T. Państwa Polskiego 7, 25-314 Kielce, Poland

³Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 043 53 Košice, Slovakia

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Corresponding author: J. Trpčevská, Tel: +421-55 602 2409, Fax: + 421 55-602 2428, E-mail address: jarmila.trpcevska@tuke.sk, Department of Nonferrous Metals and Waste Treatment, Faculty of Metallurgy, Technical University of Košice, Letná 9, 042 00 Košice, Slovakia

Abstract

During the process of hot-dip galvanizing some byproducts are formed. The present work is aimed at the characterization of bottom dross formed during batch hot-dip galvanizing process and its refining. Atomic Absorption Spectroscopy (AAS) provided chemical analysis. Microstructure of the bottom dross was characterized using light microscopy and Scanning Electron Microscopy (SEM) in combination with Energy Dispersive X-ray analysis (EDX). Phase composition was studied by X-Ray Diffraction (XRD) method. Refinement of the bottom dross was performed in order to iron removing by aluminium addition at selected processing parameters (amount of aluminium addition and refining duration). Experiments revealed significant decrease of iron in the bottom parts of refined samples. Aluminium abundance and increasing of refining duration showed no positive effect on refining efficiency.

Keywords: galvanization, microstructure, intermetallics, X-ray diffraction, dross formation, refining

1 Introduction

Hot-dip galvanizing is one of the oldest methods of zinc coating. It involves immersion of steel parts in molten zinc to provide a corrosion protecting coatings. There are two different processes for applying a zinc coating to steel by this method. One process involves the application of zinc onto a continuous passing steel sheet through a bath of molten zinc at high speeds, known as “continuous” hot-dip galvanizing. The second hot-dip process involves the application of zinc onto various constructions, a large diameter pipes, screws, frames, fasteners, etc. These items are coated either one at a time or, in the case of small parts, as a number of parts placed in a basket. This process is known as “batch” (or “general”) hot-dip galvanizing. Both processes are accompanied by formation of several byproducts. The galvanizing dross is one of the most important. Dross is defined as a byproduct of galvanizing process that forms as a result of intermetallic reactions with the iron in the bath that has been introduced by the steel parts being coated. Iron solubility in molten zinc is affected by element additions to the bath and to a greater degree by temperature changes. The zinc bath can contain variable amounts of aluminium (0-

0,05wt%Al at batch galvanizing and 0,12-0,3wt%Al at continuous galvanizing) resulting in different dross compounds being formed [1-5]. Galvanizing dross is formed inside or on the top of the molten zinc. Top dross in continuous galvanizing is $\text{Fe}_2\text{Al}_5\text{Zn}_x$ (η) and the bottom dross is FeZn_{10} (δ) [6]. In batch galvanizing process zinc ash is formed on the surface of the galvanizing bath and consists primarily of ZnO with varying amounts of $\text{Zn}_5(\text{OH})_8\text{Cl}_2$. The dross on the bottom of the kettle is FeZn_{13} (ζ) and is known as “hard zinc”. Hard zinc is denser than zinc and settles at the bottom of the bath of liquid zinc during galvanization. Both top and bottom dross contain also a large amount of solidified zinc, which is trapped in liquid form during their removing from the zinc bath [7]. Although hard zinc is rich in zinc it can not be reused in the galvanization processes. There are several methods for hard zinc processing [8,9]. Bottom dross processing in order to ZnO powder production in Slovakia is realized in firm SlovZink, a.s. Košeca [10].

In the present work a detailed analysis of the structure of bottom dross (hard zinc) formed during batch galvanizing is attempted. Also refining of hard zinc through removal of iron has been investigated. Basis for refining process of hard zinc with Al is formation of Al_nFe_m intermetallic compounds lighter than zinc. They are coming to metal surface and refine the zinc [8].

2 Material and methods

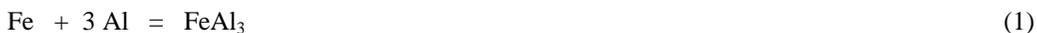
Bottom dross samples were provided by three local batch hot-dip galvanizing facilities. The first step of the present work was the characterization of provided samples of the bottom dross using particular identification methods (chemical analysis, metallographic analysis, image analysis, EDX microanalysis, X-Ray diffraction) and subsequently verification of the possibility of hard zinc refining by aluminium addition.

Metallographic analysis was performed on light microscope Olympus GX71 with digital camera DP71. The etchant used in metallographic examination was solution of distilled water (100 ml) + hydrochloric acid (5 ml), etching time 5 minutes.

Elemental composition of individual phases being analyzed by Energy dispersive X-ray analysis (EDX) Link 860 connected with scanning electron microscope JSM-35 CF. Presence of zinc matrix and the FeZn_{13} type ζ (zeta) phase was also identified with X-Ray diffraction analysis (XRD) using diffractometer DRON with Cu radiation.

Program ImageJ was used for image processing and analysis of microstructural images of individual bottom dross samples. Digital images of the microstructures were processed to remove the noise. The next step was thresholding as a key step of image analysis. Filtering procedure “fill hole” and Gauss filter for removing additive noise were applied [11]. In automatic mode in a binary image analyses were realized. Area fraction of intermetallic particles was evaluated.

Refining process of hard zinc was carried out on a laboratory scale. Effect of two parameters was studied: amount of aluminum content and refining duration. Experiments were carried out in graphitic crucibles. Sample with the highest iron content (facility 1) was chosen for experiments. The samples of bottom dross with aluminum addition were placed in an electric furnace. Aluminum was in the form of wire chopped on 20 mm pieces in length. At first aluminum pieces were placed into two crucibles and then bottom dross pieces put on them (**Fig. 1**). Refining temperature was 700°C. Duration of heat processing was 30 minutes for samples A and B and 60 minutes for samples C and D. Calculation of stoichiometric amount of aluminum needed for refining has issued from (1).



In bigger crucible (samples A, C) 1000 g of bottom dross and 50 g of aluminium were used. In smaller crucible (samples B, D) 400 g of hard zinc and 100% surplus of Al, i.e. 40 g were used. Alloys solidification took place after refining. Crucibles with cover were put on cold metal bed for regulated solidification. Solidified samples were getting out from crucibles and subsequently lengthways cut. Three samples from each alloy were taken from top, middle and bottom part, respectively (**Fig. 2**). These samples were subjected to chemical analysis using AAS. Microstructure of samples taken from top and bottom part was studied, too.



Fig.1 Bottom dross before refining



Fig.2 Bottom dross after refining

3 Results and discussion

Table 1 shows the chemical composition of the used bottom dross samples determined by Atomic Absorption Spectroscopy. The samples contained minimum 2,19 wt% Fe, maximum 2,9 wt% Fe (on the average 2,54 wt%) and the presence of Pb and Sn. Residue is zinc.

Table 1 Chemical Analysis of the Bottom Dross Samples (AAS Analysis)

Facilities	Elements [wt %]		
	Fe	Pb	Sn
1.	2,9	-	0,24
2.	2,52	0,3	-
3.	2,19	0,44	0,03

Microstructure of samples is shown in **Fig. 3-4**. Microstructure of bottom dross is two-phases: intermetallic particles of Fe/Zn of various geometric shapes and zinc matrix, which is result of simultaneous removing of zinc from bath during standard cleaning procedure. On the literature review it is supposed that intermetallic particles represent FeZn₁₃ type ζ (zeta) [1,2].

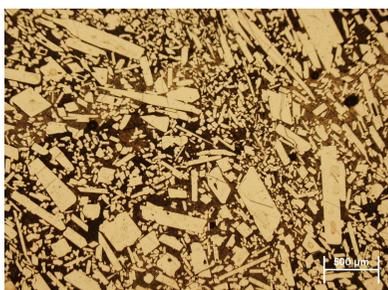


Fig.3 Microstructure of bottom dross



Fig.4 Microstructure of bottom dross, higher magnification

Realized EDX analysis has provided information about iron content 6,6 – 6,9 wt% and zinc content 93,1 – 93,4 % of intermetallic phase in sample (facility 1). These results are in accordance with results obtained on the calculation by means of atomic weight (atomic weight of iron is 55,847 and atomic weight of zinc is 65,38). On the base of this calculation iron content is 6,16% and zinc content is 93,65% in intermetallic compound of FeZn_{13} type. Zinc matrix is composed almost exclusively by Zn (99,7%).

XRD pattern of hard zinc is shown in **Fig.5**. This method has confirmed the presence of FeZn_{13} phase. ζ phase (FeZn_{13}) has been intensively studied by Liu et al. [12]. The results of X-Ray diffraction combined with Rietveld structure refinement indicated that the structure of FeZn_{13} is monoclinic and the lattice parameters are $a = 1,3408$ nm, $b = 0,7605$ nm, $c = 0,5074$ nm, and $\beta = 127,206^\circ$.

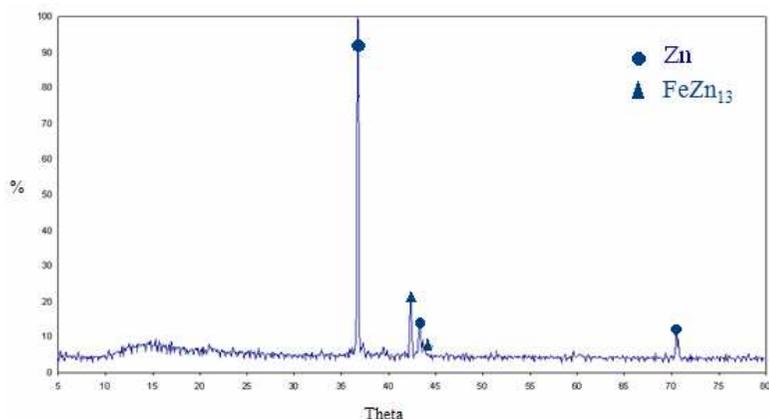


Fig.5 XRD pattern of hard zinc

Results of image analyses are shown in **Table 2**. Area fraction of intermetallic phase results represent average value determined from three measurements from each delivered bottom dross samples. Area fraction of FeZn_{13} phase is approximately 50% embedded in zinc matrix. Approximately 3 wt% Fe (on the base of the atomic weight calculation) corresponds to such fraction of FeZn_{13} phase. In this way determined iron content taking in responsibility area fraction of FeZn_{13} phase is in good agreement with results obtained by AAS.

Table 2 Image analyses of area fraction FeZn_{13} in zinc matrix

Facility	Area fraction of FeZn_{13} [%]	Calculated Fe content [wt %]
1.	58,46	3,6
2.	45,48	2,8
3.	51,71	3,18

The effect of aluminum addition to the bottom dross on the iron removal during refining process is explained by formation of intermetallic compounds of Al_nFe_m type as the result of bigger chemical affinity of Al to Fe than to Zn. They are characterized by low solubility in zinc and easily remove Fe from zinc [8]. The aim of the research was to study the effect of aluminum amount addition and refining duration on the effectiveness of hard zinc refining. In Fe-Al system there are intermetallic compounds as follows: FeAl , FeAl_2 , FeAl_3 , Fe_2Al_5 and Fe_3Al . The probability of the formation the particular intermetallic compounds is given by ΔG^0 value. The

most negative value ΔG^0 has FeAl phase, thus its formation is from thermodynamic view-point the most probable [13]. Taking into account that intermetallic phase FeAl₃ has the highest Al content, computed stoichiometric amount of aluminium has derived just from this phase. Intermetallic particles Al_nFe_m formed during refining process are lighter than zinc and segregate onto the surface. The rate of their segregation in liquid zinc is related to the temperature of liquid zinc and refining time [8]. **Table 3** shows results of chemical analysis of samples after refining.

Table 3 Chemical composition of refined alloy

Elements [wt %]	A			B			C			D		
	1	2	3	1	2	3	1	2	3	1	2	3
Zn	95,62	97,26	86,38	81,25	84,48	77,92	90,3	83,18	74,47	87,2	78,6	76,21
Fe	0	0,7	3,9	0	2,82	3,79	0,037	2,03	7,04	0,073	3,51	4,95
Al	0,85	1,57	9,52	3,28	9,81	13,34	1,37	3,52	9,61	5,29	10,45	12,92

In the bottom part of alloy in all samples (A1, B1, C1, D1) decrease in the iron content of refined alloy is observed. Gradual increase in the iron content from bottom toward top of the sample is consequence of Al_nFe_m intermetallic compounds formation and their moving upward. Abundance of aluminium had no positive effect on the removal of iron, however increased Al content was observed in all parts of refined alloy. If sample A1 contained 0,85% Al, sample C1 1,37% Al, respectively. Likewise alloy B1 contained 3,28 % Al and alloy D1 5,29% Al, respectively. Aluminum content in refined zinc is higher then it is acceptable for the most common hot-dip galvanizing process and therefore it is possible to use it only in some portion in galvanizing bath. It would be desirable examine the effect of lower aluminium addition on the refining effectiveness.

It can be seen that the increase in refining duration from 30 minutes to 60 minutes at chosen conditions (aluminium content and temperature) had no positive effect on iron removing. Refining duration 30 minutes (samples A, B) has resulted in iron removing to the zero values in bottom parts of alloy. Barakat has observed the effect of duration on removal of iron from hard zinc by adding 0,4 wt% of Al and 10 wt% of Zn independently, at 650°C. In his experiments it had be seen that Fe concentration in refined zinc decreased as refining duration increased up to 2 hours. A further increase in duration (over 2 hours) had no positive effect on zinc refining [9]. It has to be noted, that Barakat has carried out his experiments at lower temperature and significantly lower aluminium content.

Because of pyrometallurgical process was conducted at air, formation of oxide layer was observed. As it is stated in [13] if process of zinc refining takes place at temperature conditions over 600°C is necessary to apply protective nitrogen atmosphere. The optimum temperature for zinc processing with Al is 700°C due to the fact that this temperature is just above the melting point of Al (660°C) [9].

4 Conclusions

On the basis of realized experiments on the delivered samples of bottom dross the following conclusions have been reached:

Samples of bottom dross delivered from three local facilities contained on an average 2,56 wt% of Fe. Microstructural evaluation has shown two phase structure of bottom dross. EDX analyses have determined elemental composition of individual phases. X-Ray diffraction method has confirmed the type of intermetallic compound FeZn₁₃ phase (ζ phase). Area fraction of FeZn₁₃ phase embedded in zinc matrix is approximately 50%. Iron content in bottom dross measured by AAS corresponds to iron content in area fraction of FeZn₁₃ phase determined by image analysis.

Refining of bottom dross by aluminum addition resulted in significant iron decrease in bottom parts of refined alloy. Aluminum abundance and extension of refining duration at chosen process parameter had no positive effect on refining effectiveness. Negative feature of the pyrometallurgical treatment in air was formation of oxide layer. Refining process is necessary conduct in protective nitrogen atmosphere with a view to minimizing its formation.

Acknowledgements

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