GDMB News inside

ERZMETALL

World of Metallurgy

GDMB

70/2017 No. 4 · July/August
GDMB Verlag GmbH
ISSN 1613 - 2394 · www.GDMB.de

4/2017

Internationale Fachzeitschrift für Metallurgie
International Journal of Metallurgy

Zinc Waste Treatment Originated During Hot-Dip Galvanizing

Katarína Blašková, Jarmila Trpčevská, Jana Pirošková, Martina Laubertová

The present paper is focused on the research of the hard zinc and top dross treatment possibilities. Hard zinc or bottom dross originates during the hot-dip galvanizing process in the zinc bath and top dross is produced in the continuous process. In this paper wastes are characterized and the attention is paid to chosen kinds of solid wastes. Hard zinc contains 91 to 96 % of zinc. Iron represents an impurity with content of 1 to 6 %. Top dross contains about 1 % Fe and Al and the rest represents zinc. In every case the iron is an unwanted element in drosses. Therefore, the possibilities of hard zinc and top dross treatment with the aim of iron removal are studied in this work.

Keywords:

Hot-dip galvanizing – Waste – Drosses – Iron – Recycling

Behandlung von zinkhaltigen Rückständen der Tauchfeuerverzinkung

Diese Arbeit untersucht die Möglichkeiten der Behandlung von Hartzink und Oberflächenkrätze. Hartzink oder Bodenkrätze entsteht bei der Tauchfeuerverzinkung, Oberflächenkrätze bei der kontinuierlichen Bandfeuerverzinkung. Rückstände werden charakterisiert und ausgewählte Arten fester Rückstände werden untersucht. Hartzink enthält 91 bis 96 % Zink und als Verunreinigung Eisen mit einem Gehalt von 1 bis 6 %. Oberflächenkrätze enthält ungefähr 1 % Eisen und Aluminium, der Rest besteht aus Zink. In allen Fällen stellt Eisen ein unerwünschtes Element in den Krätzen dar. Aus diesem Grund werden die Möglichkeiten der Behandlung von Hartzink und Oberflächenkrätze mit dem Ziel, das Eisen zu entfernen, untersucht.

Schlüsselwörter:

Tauchfeuerverzinkung – Rückstand – Krätze – Eisen – Rückgewinnung

Traitement des déchets de zinc produits lors de la galvanisation à chaud

Tratamiento de residuos de zinc proveniente de la galvanización en caliente por inmersión

1 Introduction

The hot-dip galvanizing process is one of the most commonly used processes of steel coatings to avoid corrosion of steel parts. As corrosion protection the metal zinc is used. Regarding to the kind of steel to be coated, there are several types of hot-dip galvanizing. Steel sheets are coated through continuous galvanizing, whereas steel parts and single components are coated in batch galvanizing process. The process of zinc galvanizing consists of several pre-treatment steps to ensure complete impurities removal followed by dipping particles in the molten zinc at a temperature of about 465 °C. In the pre-treatment steps that consist of cleaning, degreasing, pickling and fluxing, the liquid waste develops. In the molten zinc bath where the pre-treated steel particle is dipped in order to gain a zinc coating, several kinds of waste are produced. In continual galvanizing the bottom dross forms on the bottom of the zinc kettle due to exceeding the maximum iron solubility in the molten zinc at the given temperature (at 465 °C the maximum iron solubility is 0.03 %). After exceeding the maximum iron solubility, iron starts to precipitate with zinc into the intermetallic phase $FeZn_7$. In this process aluminium in amount of 0.11 to 0.20 % is added. In that moment due to the higher affinity of iron to aluminium, iron starts to bond to the aluminium and creates an intermetallic phase Fe_2Al_5 which has lower density than molten zinc and thus accumulates on the surface of the zinc bath. Such dross is called zinc top dross. In the dry batch galvanizing (without aluminium addition) bottom dross or so called hard zinc forms on the bottom of the kettle similarly as in the previous process. This bottom dross is basically an intermetallic compound $FeZn_{13}$. On the surface of the kettle zinc ash is also produced. In the batch process sal-ammoniac flux develops on the surface of the zinc bath due to the process characteristic. Hard zinc from the batch process and zinc top dross from the continuous process are investigated in this study. In the present time, those kinds of wastes are sold to further processing. In the Slovak Republic over 2000 t of those wastes are generated every year. The price for hard zinc is multiplied by coefficient 0.7 to 0.4 and top dross 0.71 to 0.75 approximately according to current demand and purity [1-4].

2 Experimental

2.1 Material and methods

In the first step, the characterization of samples was conducted. Chemical composition was determined by AAS (Atomic absorption spectrometry), phase analysis by XRD (X-ray diffraction) using analyzer (X-ray diffractometer PANalytical X'pert PRO MPD).

The sample of hard zinc was further investigated by metallographic analysis. Microstructure was evaluated using light microscopy (LM). For LM analysis the microscope Olympus XC50 was used. The scanning microscope Tescan Mira 3 FE was used for SEM analysis.

In order to observe the behaviour of hard zinc during heating, its changes, either exothermic or endothermic, the DTA analysis (Differential Thermal Analysis) was conducted. For DTA analysis and evaluation Netzsch STA-449F3A-0861-M was used. The DTA curve provides data on the transformations that occur, such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak is the enthalpy change and is not affected by the heat capacity of the sample [5].

In Figure 1, there can be seen the samples of hard zinc and zinc dross.

3 Results and discussion

From the conducted investigation of samples by AAS the chemical analysis is given in Table 1.

From Table 1 it can be seen that the hard zinc contains 2.55 to 2.81 % iron and the rest is zinc. Zinc top dross contains besides iron in range of 0.34 to 0.41 % also aluminium in amount of 0.6 to 0.69 % and the rest is zinc. The phase analysis of the samples can be seen in Figures 2 and 3 and Tables 2 and 3.

Table 1: Results of the chemical analysis

	Element	Chemical compositon [%]		
Hard zinc	Fe	2.81	2.55	2.67
	Zn	rest	rest	rest
Zinc dross	Fe	0.37	0.41	0.34
	Al	0.60	0.64	0.69
	Zn	rest	rest	rest

Table 2: Result of the hard zinc phase analysis

Ref. Code	Name of compound	Chemical formula
96-900-8523	Zinc	Zn
03-065-1238	Iron zinc	$FeZn_{13}$

Table 3: Result of the zinc top dross phase analysis

Ref. Code	Name of compound	Chemical formula
96-900-8523	Zinc	Zn
00-001-1265	Iron aluminium	$FeAl_3$
00-001-1228	Aluminium iron	Fe_2Al_5

Fig. 1:
Sample of hard zinc (left) and zinc dross (right)

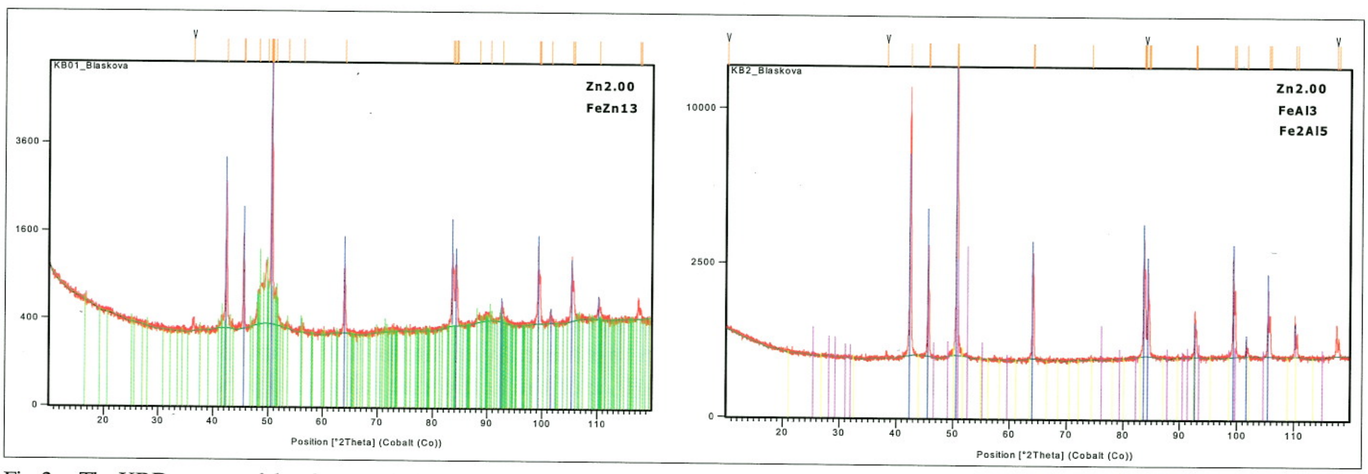

Fig. 2: The XRD pattern of the phase analysis: hard zinc (left) and zinc dross (right)

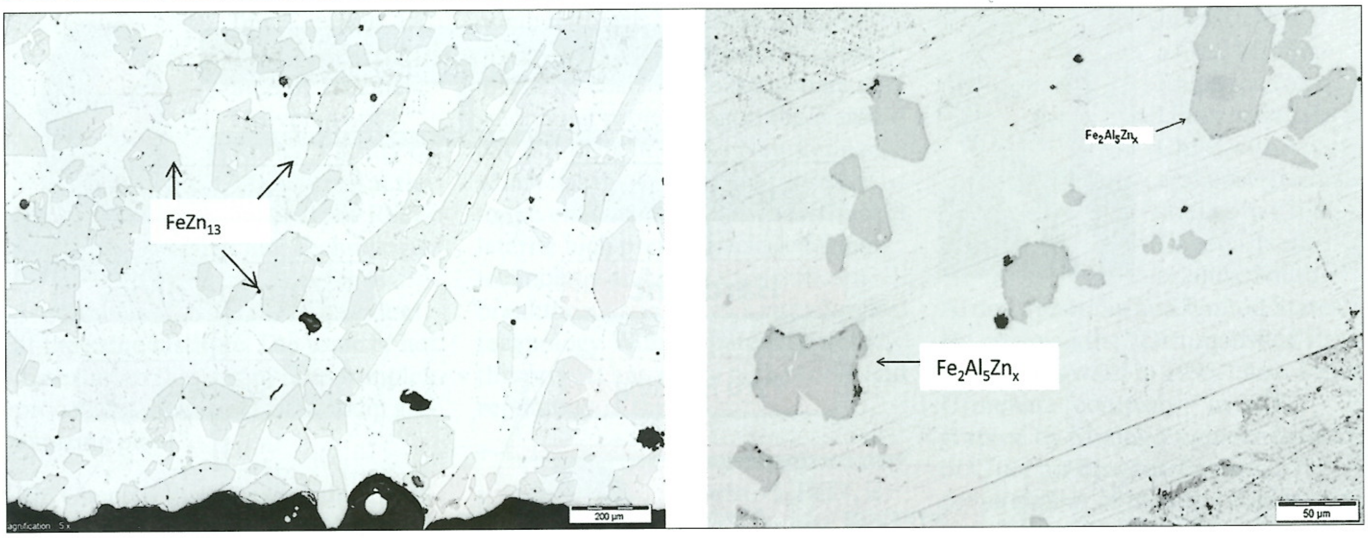

Fig. 3: Metallographic observation of hard zinc (magnification 5×) (left) and zinc dross (magnification 20×) (right)

The result of the phase analysis of hard zinc shows that iron is bonded to the zinc into the intermetallic compound $FeZn_{13}$ phase and beside the phase there is metallic zinc presented as a matrix.

The result of the phase analysis of zinc dross shows that iron is bonded to the aluminium into the intermetallic compound Fe_2Al_5, and $FeAl_3$, respectively. Beside those phases there is metallic zinc present as a matrix.

The darker objects in Figure 3 represent intermetallic compounds whereas the lighter areas or surrounded area represent zinc matrix. According to the magnification it can be seen that the size of the $FeZn_{13}$ phase varies in range of 50 to 200 µm. The size of the Fe_2Al_5 phase varies in range of 20 to 100 µm.

In Figure 4, there can be seen the result of the DTA analysis of the hard zinc.

Under the temperature of approximately 420 °C the zinc starts melting as it is displayed by the endothermic peak. Reaching the temperature of 530 °C the intermetallic phase $FeZn_{13}$ transforms into the intermetallic phase $FeZn_{10}$ (presented as second smaller endothermic peak). At a temperature over 630 °C this phase dissolves completely in the molten zinc (the third endothermic peak). The evaluation of this DTA result was conducted in connection with the binary Fe-Zn diagram. The result of analysis showed residual mass in amount of 96.98 % at 748.1 °C. That means about 3 % of the sample vaporized at the temperature of 748.1 °C. This phenomenon can be explained by higher partial zinc pressure during analysing and thus zinc started slowly to vaporize. The partial zinc pressure can be calculated as follows:

From the HSC Chemistry the standard Gibbs free energy was calculated. Expectation that zinc as liquid passes to the gaseous form at the temperature 750 °C resulted in ΔG^0 = 15,305 J. By the given formula (equation 1) the partial zinc pressure was set up as p_{Zn}= 16,757 Pa.

$$\Delta G^0 = R \cdot T \cdot \ln \frac{p_{Zn}}{p_0} \quad (1)$$

Based on a research about treatment possibilities, the experimental proceedings have been built and proposed treatment methods are displayed in the scheme in Figure 5.

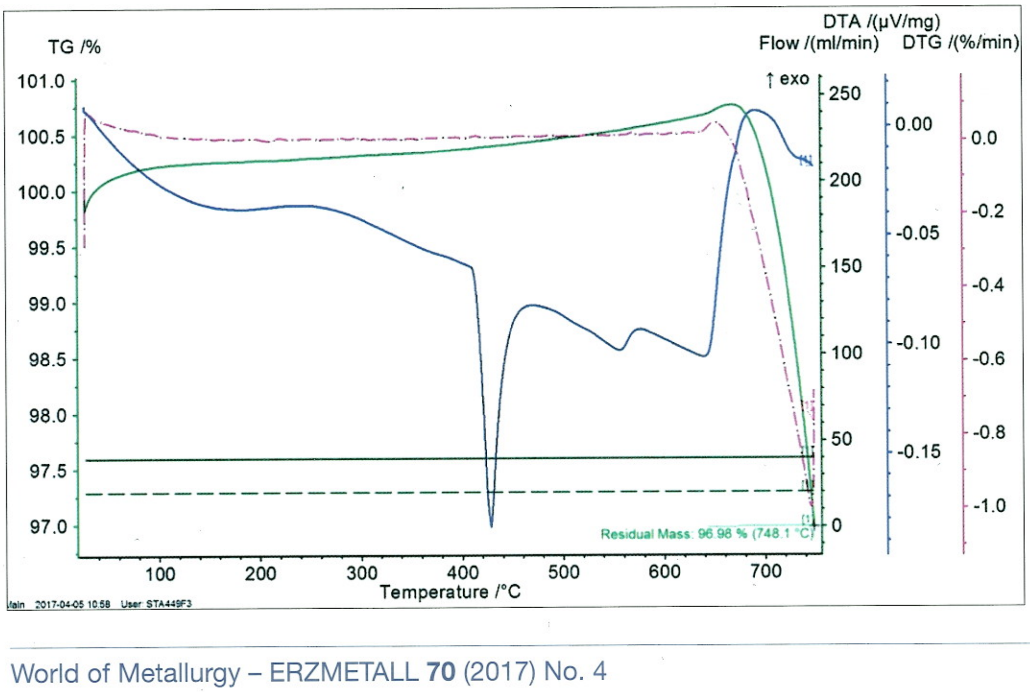

Fig. 4: Result of the DTA analysis of hard zinc

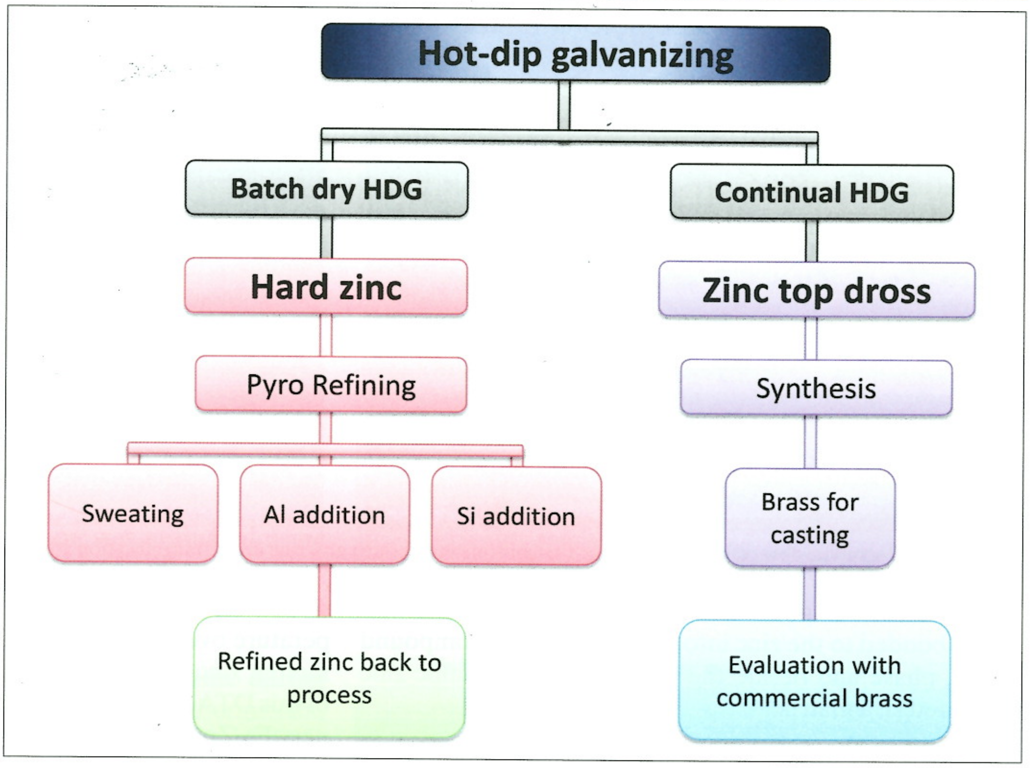

Fig. 5:
Proposal of waste treatment

4 Conclusions

The present paper characterizes the chosen solid waste hard zinc and zinc top dross. The only impurity in those wastes is iron that is bonded into intermetallic compounds. The only possible way how to treat such kinds of waste is by pyrometallurgy due to its high zinc content. In the first stage the characterization of both kinds of waste were conducted by chemical analysis, phase analysis and the hard zinc was submitted also for DTA analysis. Proposed way of hard zinc treatment is by flame refining using sweating in a furnace with temperature gradient. Addition of chosen elements such as Si and Al will be investigated, too. The top dross will be used for synthesis of brass for casting and its characteristics will be investigated.

Acknowledgement

This work was supported by a grant from the Slovak National Grant Agency under the VEGA Project 1/0442/17.

References

[1] Maass, P. & Peissker, P. (2011): Handbook of Hot-dip Galvanization. – Wiley-VCH; 1 edition, ISBN-10: 3527323244.

[2] Marder, A.R. (2000): The metalurgy of zinc-coated steel. – Progress in Materials Science 45: 191-271.

[3] Kuklík, V. & Kudláček, J.: Žárové zinkování. – 208 pages, ISBN 978-80-905298-2-3.

[4] Bright, M. et al. (2007): The advantages of recycling metallic zinc from the processing wastes of industrial molten zinc applications. – Light Metals 2007, The Minerals, Metals and Materials Society.

[5] DTA analysis characteristic, online available on the internet> http://instrument-specialists.com/applications/differential-thermal-analysis-dta/> [Cited: 4.4.2017].

Katarína Blašková*
Jarmila Trpčevská
Jana Pirošková
Martina Laubertová
All:
Technical University of Košice
Faculty of Metallurgy, Institute of Recycling Technologies
Letná 9
042 00 Košice
Slovak Republic
* e-mail: katarina.blaskova@tuke.sk

Ing. Katarína Blašková graduated of Technical University of Kosice, Faculty of Metallurgy, at the Institute of Recycling Technologies in 2015. Since September 2016 she is PhD. student at the same institute. The topic of her dissertation thesis was "The complex processing of waste from hot dip galvanizing plant".

Liu Cheng is the Vice President and Chief Engineer of China ENFI Engineering Corporation (hereinafter referred to as ENFI). In July 1993, he was graduated from the Central South University of Technology, with non-ferrous metallurgy as his major. In the same year, he started his career in ENFI. Working at the non-ferrous metallurgy technical engineering development and engineering design all the way, he has been participated in and taken charge of several key technical research and development projects proposed in National Scientific Key Projects of the Eighth Five-Year Plan as well as engineering designs of several large scale non-ferrous hydrometallurgy projects like battery grade nickel sulfate project in Jinchuan. All those experiences have empowered him to have a good command of hydrometallurgy processes of metals like copper, lead, zinc, nickel, cobalt, gold, etc. He has led a team in launching the first nickel laterite HPAL commercial production project in China. Under his leadership, the high temperature pressure leaching technology was successfully developed. As an intellectual property owned by ENFI, this technology promotes the exploitation and utilization of complex and refractory resources as well as low grade resources at home and abroad, enhances our technical competitiveness in market development and ability in participating in the providing engineering technical service for the overseas non-ferrous mining projects. All those achievements have been successfully applied in a large scale overseas resource development project, that is the Ramu NiCo Project in Papua New Guinea, which has made great contributions to the enhancement of national nickel laterite high pressure acid-leaching technology and marks a significant breakthrough in China's metallurgical technology. With six patents granted, this project has won a high profile and reputation in the industry.

Ing. Martina Laubertová, PhD., is an Assistant Professor at the Institute of Recycling Technologies, Faculty of Metallurgy, Technical University of Kosice. She finished Ph.D. study in 2009. Her dissertation was focused on "Application of microwave energy in chalcopyrite leaching". Her research and development activities are focused on the processing and recycling of waste, mainly metals from electronic waste by hydrometallurgical methods and also on procedure of sampling solid materials. In the last five years she became author and co-author of 43 scientific papers and her publications has achieved 60 citations.

Ing. Jana Piroškova, PhD., graduated of Technical University of Kosice, Faculty of Metallurgy, at the Institute of Recycling Technologies in 2011. She graduated Ph.D. study in 2015. The topic of her dissertation thesis was "Processing of spent flux originated from wet hot dip galvanizing process". Since November 2015 she is working as an assistant profesor at the Institute of Recycling Technologies. She is an expert in the production of non-ferrous metals and processing of industrial wastes.

Juan Rayo is a Civil Mining Engineer, from Universidad de Chile, with several post-graduate studies in Chile, Canada, Netherlands, South Africa, Australia and United States. He received the "Distinguished Professional" award in 1995, "José Tomás Urmeneta (company)" in 2008, granted by Mining Engineer Institute of Chile for his contribution in the development of national engineering and "Fernando Riveri" for the value agreement in the mining innovation in 2012. "Outstanding Company in Innovation" award in 2014, granted by the Association of Exporters of Manufactures of Chile (ASEXMA), recognition to JRI as a company outstanding in innovation. Management award 2015, granted by the College of Engineers of Chile, in recognition of its innovative vision and business leadership. He has more than 40 years of professional experience in project development, academic activities, applied research projects, national leader in the development of "Confidence Commissions" (technical audits, validation studies, business profiles and strategic plans). He has led EPCM projects and managed larger projects (over 100 mill. US$). He has been Project Manager in more than 70 relevant projects and consultant-specialist in more than 200 studies and leader in the development of more than ten RD&I projects. Juan Rayo is the founder and main shareholder of the consulting firm JRI Ingeniería S.A., which employs more than 300 Chilean professionals. He was President of the Mining Specialty of the College of Engineers for eight years and President of the Association of Consulting Engineers for two years. He has been and/or is director of more than 12 companies of engineering, construction and operational services.

Doc. Ing. Jarmila Trpčevská, C.Sc., is currently working on Technical University of Košice, Faculty of Metallurgy at Institute of recycling technology as an assistant professor. During 1989 to 2002 she worked at the Institute of materials research at Slovak academy of Science as a scientific worker. In the scientific field she has experiences in the following areas: microscopic evaluation of materials, EDX microanalyses of materials, phase composition of materials, surface engineering and processing of metal waste. She has received certificate from Oxford Microanalysis Group resulting from application course of microanalytical methods. Processing of the waste originated during hot dip galvanizing is the main field of the research interest at the present time. She is leader of scientific project dealing with the processing of galvanizing wastes such as zinc ash, spent zinc flux and bottom and top dross. The main subject in the field of teaching is non-ferrous metals, processing of metallic waste and refining and alloys processing.