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Preliminary communication

CHARACTERIZATION OF THE HARD ZINC ORIGINATED FROM THE HOT-DIP GALVANIZING

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The aim of the present paper is to refine hard zinc from the iron presented in the form of intermetallic compounds. During hot-dip galvanizing steel parts are galvanized to ensure corrosion protection. Due to the process zinc coatings create. Hard zinc originates in the hot-dip galvanizing process as a result of exceeding of maximum iron solubility in the molten zinc bath. The maximum iron solubility in the molten zinc is 0.03 %. Iron segregates in the form of $FeZn_{13}$, which has a higher density than molten zinc and thus accumulates on the bottom of the kettle. Such intermetallic compound is called hard zinc or bottom dross. This hard zinc is drawn from the bottom of the kettle in regular intervals. Due to the high metal content up to 94 % of Zn, hard zinc should be treated in order to zinc recovery. The present paper is focused on zinc recovery by pyrometallurgy due to its high metal content.
Key words: hard zinc, zinc refining, recycling, waste.

Karakterizacija tvrdog cinka nastalog u postupku vruće galvanizacije. Cilj ovog rada je pročistiti tvrdi cink iz željeza prisutnog u obliku intermetalnih spojeva. Tijekom postupka vrućeg pocinčavanja čelični dijelovi se galvaniziraju kako bi se osigurala zaštita od korozije pri čemu se formiraju prevlake od cinka. Tvrdi cink nastaje u procesu vruće galvanizacije kao rezultat prekoračenja maksimalne topljivosti željeza u kupki rastaljenog cinka. Maksimalna topljivost željeza u rastaljenom cinku iznosi 0.03 %. Željezo segregira u obliku $FeZn_{13}$ koji ima veću gustoću od rastaljenog cinka i tako se akumulira na dnu kade za pocinčavanje. Takav intermetalni spoj se naziva tvrdi cink ili otpad. Ovaj tvrdi cink se izvlači s dna kade u pravilnim intervalima. Zahvaljujući visokom udjelu metala do 94% Zn, tvrdi cink treba tretirati kako bi se cink regenerirao. Fokus ovog rada je na regeneraciji cinka pirometalurgijom zbog visokog udjela metala.
Ključne riječi: tvrdi cink, pročišćavanje, recikliranje, otpad.

INTRODUCTION

Steel components should provide a long period service in constructions, buildings, vehicles and other products. To ensure this requirement a corrosion protection is required on the steel products. Zinc coating are the most common used corrosion protection coatings. Zinc coating can be made by various methods as hot-dip galvanizing, zinc spraying, mechanical plating and so on. Hot-dip galvanizing process is used for this purpose the most. Process consists of several pre-treatment steps followed by dipping of steel parts in the molten zinc under the certain temperature (usually about 465 °C). The zinc bath contains more than 99 % of zinc. Process of hot-dip galvanizing can be divided according to the steel material to be coated into continual and batch process. The classification of batch process is dependent on the pre-treatment methods. Process with pre-treatment step using fluxing and further drying is called dry batch process and without this step, where the flux agent (consists of NH_4Cl) is put directly into one part of zinc bath, is called a wet batch process. During batch hot-dip galvanizing process in the zinc bath itself, there creates a by-product known as bottom dross or hard zinc. This so called by-product creates due to exceeds of maximum iron solubility (0.03 %) in the molten zinc under the given temperature. After exceeding of this solubility iron starts to precipitate into intermetallic compound in the form of $FeZn_{13}$. Due to its higher density than molten zinc, these compounds settle on the bottom of the zinc kettle and regularly are withdrawn by special mechanical hands. During withdrawal of the intermetallic compounds the pure zinc is also catch and thank to this the hard zinc contains up to 94 % of zinc. With such high zinc content, the possibilities of zinc recycling from this "waste" are put under investigation. In the work, there are possibilities of zinc refining from the iron impurity presented in the intermetallic compound as $FeZn_{13}$ phase studied. With problematic of hard zinc characterization and treating also deals work. [1-5]

MATERIAL CHARACTERIZATION

In the first step, the characterization of the sample 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 a light microscopy (LM). For LM analysis the microscope OLYMPUS XC50 was used.

In order to observe 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 was used NETZSCH STA 449F3 STA449F3A-0861-M. DTA curve provides data on the transformations that have occurred, 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. [6]

RESULTS OF ANALYSIS

From the conducted investigation of sample by AAS the chemical analysis is given. The hard zinc contains 2.68 - 3 % of iron and the rest is zinc. This kind of waste does not contain any other impurities or elements.

The phase analysis of sample can be seen in the Fig. 1.

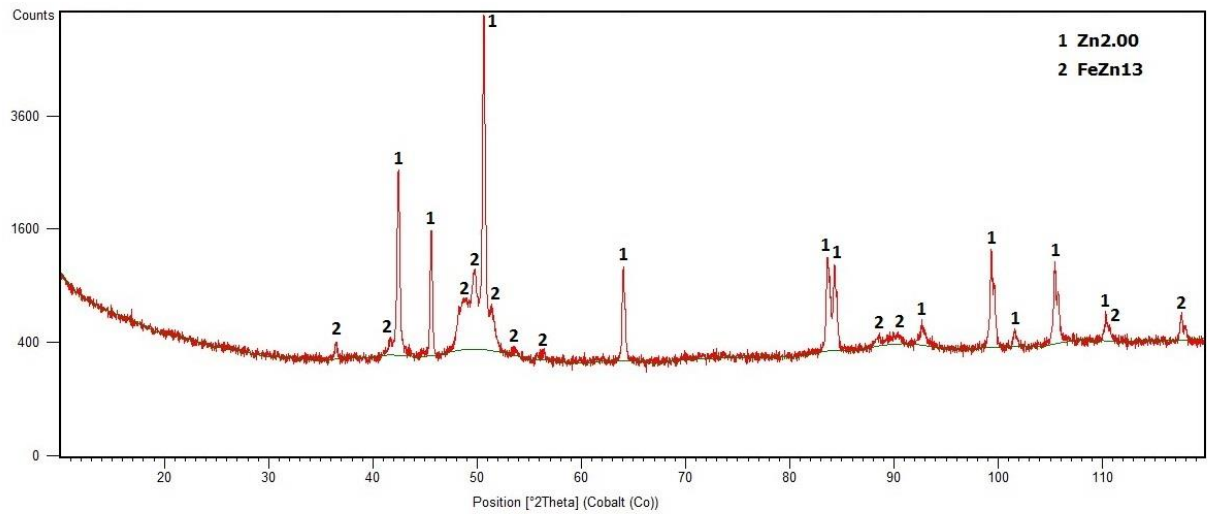

Figure 1. The XRD pattern of the phase analysis
Slika 1. XRD difraktogram uzorka

The result of the phase analysis of given sample shows that iron is bonded to the zinc into the intermetallic compound $FeZn_{13}$ phase and beside the phase there is pure metal zinc presented as a matrix. The observation of intermetallic compounds and zinc matrix can be seen in the Fig. 2.

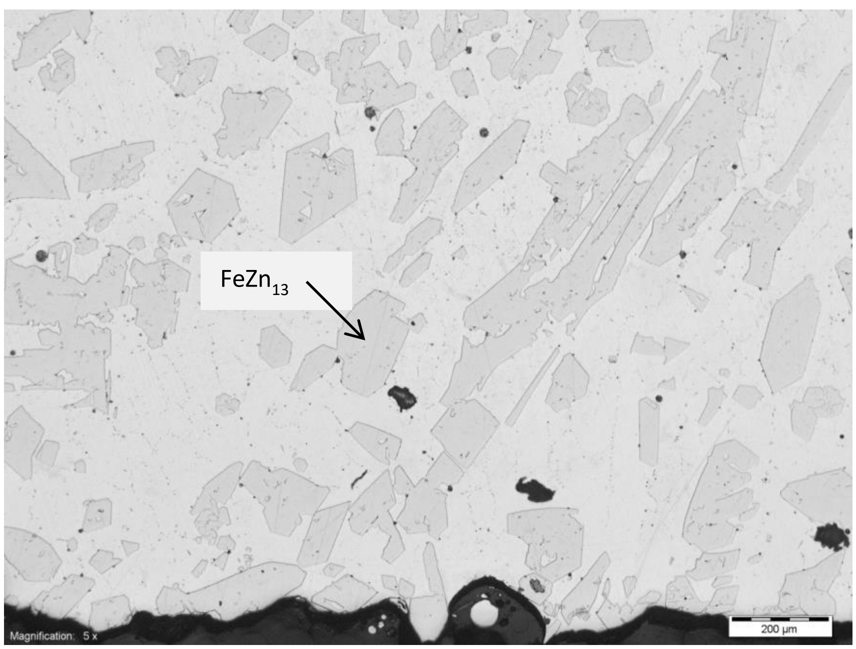

Figure 2. Metallographic observation of hard zinc (200x magnification)
Slika 2. Metalografsko promatranje tvrdog cinka (povećanje 200x)

The darker objects in the Fig. 2 represent intermetallic compounds whereas the lighter areas or surrounded area represents the zinc matrix. According to the magnification it can be seen that the size of the $FeZn_{13}$ phase varies in range of 50 – 200 μm. The result of the DTA analysis is given in the fig. 3.

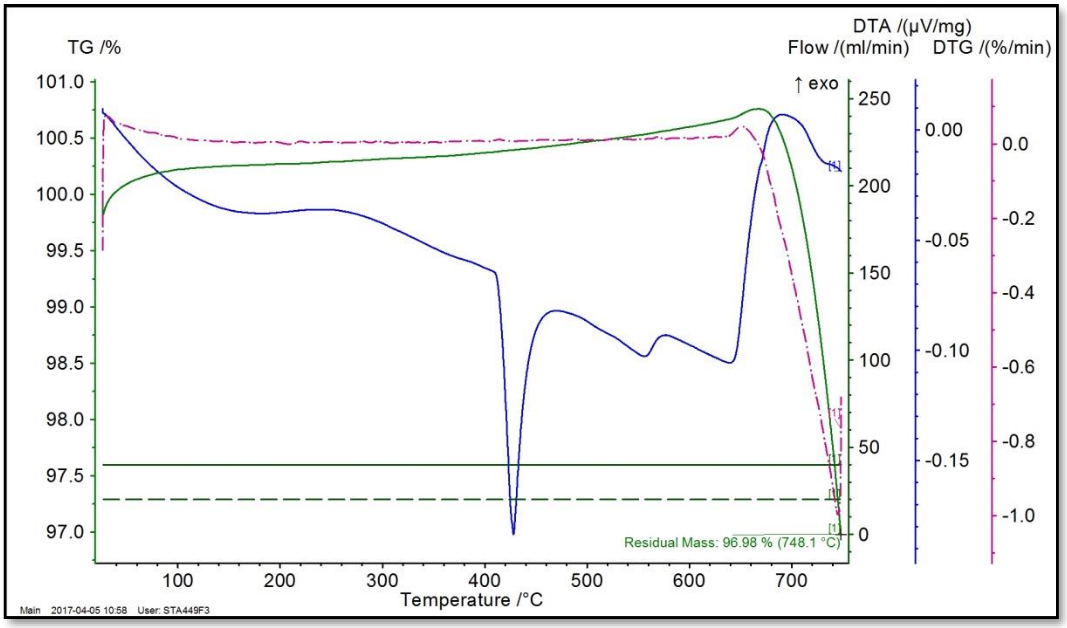

Figure 3. The result of the DTA analysis of hard zinc
Slika 3. Rezultat DTA analize tvrdog cinka

From the fig. 3, it can be seen that under the temperature approximately 420 °C the zinc starts melting as it is presented by endothermic peak. Reaching the temperature 530 °C the intermetallic phase $FeZn_{13}$ starts to transform into intermetallic phase $FeZn_{10}$, whereas the transformation is finished reaching 560 °C (presented as second smaller endothermic peak). Under the temperature over 640 °C this phase dissolves completely in the molten zinc (the third endothermic peak). Evaluation of this DTA result was conducted in connection with binary Fe-Zn diagram. The result of analysis showed residual mass in amount of 96.98 % under the 748.1 °C. That means about 3 % of sample vaporized at temperature of 748.1 °C. This phenomenon can be argued through higher partial zinc pressure during analysing and thus zinc started slowly vaporizes. The partial zinc pressure can be count as follows:

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

$$\Delta G0 = R.T.\ln\frac{pZn}{p0} \quad (1)$$

PROPOSAL OF HARD ZINC TREATMENT ACCORDING TO ITS CHARACTER

Because the melting point of the pure zinc is 419 °C and the melting temperature of the $FeZn_{13}$ phase is 530 °C the pure molten zinc under the particular temperature could be separated from the present intermetallic phase. Furthermore, the density of the pure molten zinc and the intermetallic phase is slight different. Due to the higher intermetallic compound's density the $FeZn_{13}$ (ρ= 7.3 g/cm^3) particles should separate from the molten zinc (ρ= 7.14 g/cm^3) on the bottom of the crucible. In order to ensure a heat zone with a different temperature in the crucible during treatment the temperature gradient (Fig. 3) was proposed in the process.

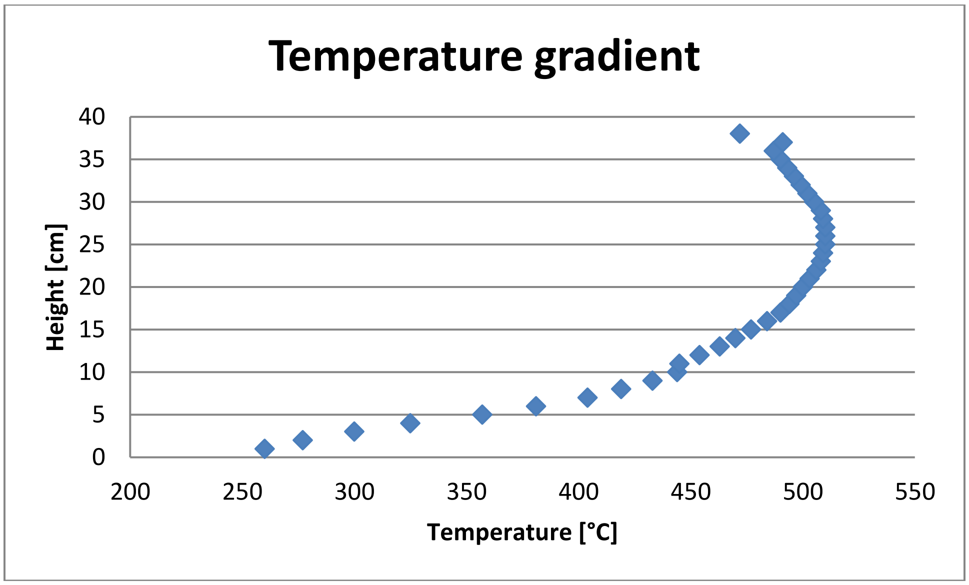

Figure 4. Measurement of the temperature gradient in the heat aggregate
Slika 4. Mjerenje temperaturnog gradijenta u toplinskom agregatu

From the figure 4, it can be seen that in the furnace there is ensure a certain temperature gradient. The furnace is able to work up to 1 000 °C. In the figure, there is given an example of temperature arrangement, while during the pilot experiments the highest temperature in the furnace should be at 510 °C to ensure the intermetallic compounds won't be dissolved.

Authors Kechin [7] and Begunov [8] studied the refinery of zinc from the iron. From those studies it can be deduced that intermetallic compounds present in the hard zinc could be treated in the furnace by melting with chosen additives. Particular additives can rebound iron from the zinc into different intermetallic compounds with different characteristics to zinc and thus separate them from the metal zinc. As appropriate additives the silicon and aluminium are put under the consideration. Silicon does not dissolve in the molten zinc and creates several phases with iron. Aluminium creates also several phases with iron with different characteristic to molten zinc. However, aluminium dissolves in the molten zinc and thus it could be used in the zinc as alloying element. The experimental proposition is pictured in the fig. 5.

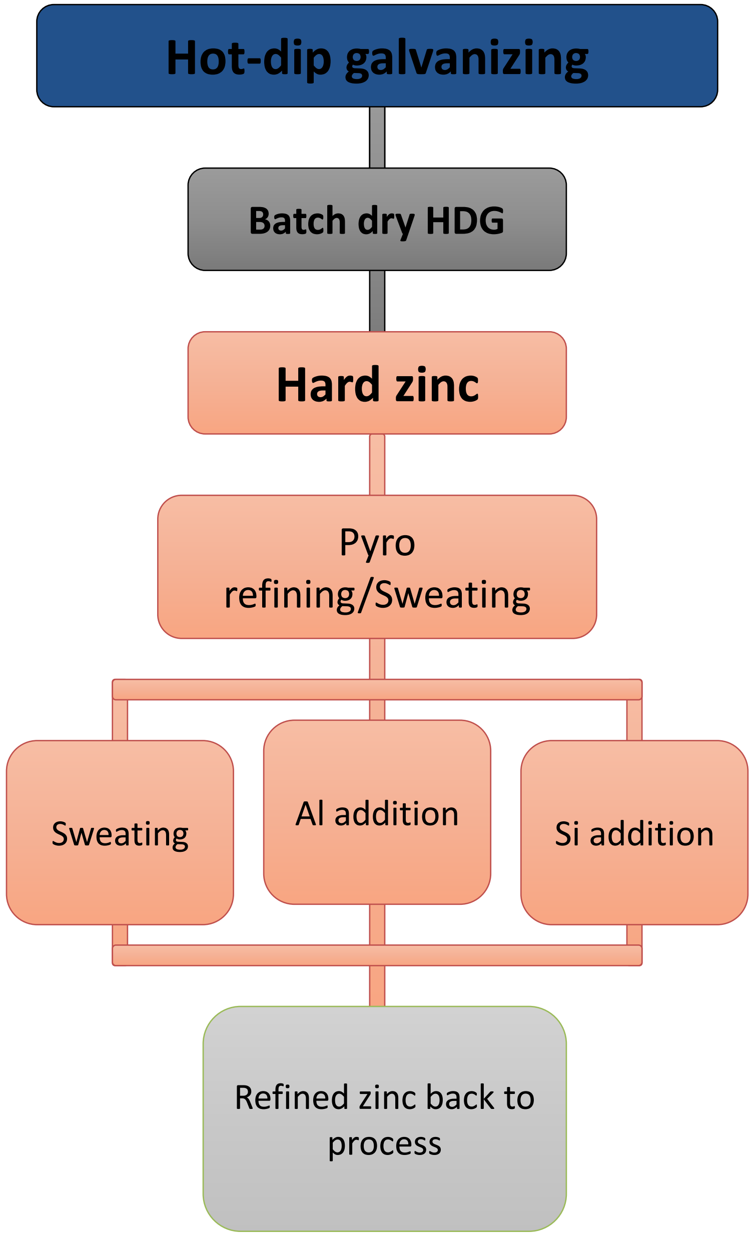

Figure 5. The proposal of the experimental part of zinc refining
Slika 5. Prijedlog eksperimentalnog dijela pročišćavanja cinka

CONCLUSION

In this paper the hard zinc from batch galvanizing was characterized in order to propose appropriate treatment. It was find out that hard zinc contains iron in amount of 2.68 - 3 % as impurity bonded to the zinc into intermetallic compound $FeZn_{13}$. Treatment should be consider in order to iron removal from the hard zinc. Intermetallic compound has different characteristics to zinc such as higher density and higher melting point. According to those differences the molten zinc could be separated from the intermetallic compound under the particular conditions. With this purpose the furnace with gradient temperature was constructed. Also addition of chosen additives can be beneficial to the intensification of the iron separation. In that case iron would bonded into different intermetallic compounds and thus separated from the pure metal zinc.

Acknowledgement

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