

Study of the structure of hot-dip galvanizing byproducts

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In galvanizing process several byproducts are formed. Among them solid materials composed by different compounds are grown in the galvanizing kettle. The present work examines the structure of the bottom dross and the blowing waste using X-ray and electron microscopical techniques. From this research it was deduced that bottom dross is composed by crystallites of the ζ -phase of the Fe-Zn phase diagram scattered in a matrix of pure Zn, while blowing waste, which is granular, is composed by spheres, whose core is of pure Zn covered with a layer of ZnO. Mixed Fe-Zn oxides were also detected in bottom dross. Hence these byproducts are mainly composed by pure Zn and different zinc compounds, while a large amount of iron in the form of Fe-Zn intermetallics and Fe oxides is present in bottom dross. In any case, this composition implies that the examined materials are suitable for zinc recovery.

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1. Introduction

Hot dip galvanizing is one of the most effective corrosion protection methods for steel and iron substrates [1]. However, although the anticorrosive performance of the hot dip galvanized products is undisputable and as a result this method is very advantageous, the production of galvanized objects involves the generation of several byproducts. Among them, the galvanizing dross, which amounts to 5-7% of the zinc consumed by the coating formation [2], is one of the most important. Galvanizing dross is formed inside or on top of the molten zinc [1]. Therefore, it can be classified as floating or bottom dross. The floating dross (also known as "galvanizing ashes") consists mainly of zinc and/or aluminum oxides and chlorides [1], while the bottom dross consists exclusively of intermetallic compounds, such as aluminum saturated δ (FeZn_7) phase [1]. Intermetallic compounds were also identified in the floating byproduct, but in this case the main component, which was reported, is $\text{Fe}_2\text{Al}_5\text{Zn}_x$ [1]. Both floating and bottom dross contain also a large amount of solidified zinc, which is trapped in liquid form in the device used for their removal from the zinc bath. The intermetallics of the floating and bottom dross are formed when the concentration of Al and Fe in the zinc kettle is above their solubility limits at a certain temperature. As a result their formation is unavoidable even in the case of perfect management of the zinc bath, because the deliberate Al additions, the Fe dissolution from the immersed objects and the kettle walls and the temperature uniformity are very difficult to be controlled [1]. This phenomenon is also enhanced by the Ni addition [3-4], which is used as a medium to inhibit the Sandelin effect (the formation of Fe-Zn alloys up to the surface of the galvanized coating [5]). Also, the formation of the surface oxides, which are present in the ashes, is also impossible to be inhibited, since both Zn and Al are

reactive metals and at the temperature of the zinc bath (about 450 °C [1]) their reactivity is extremely high. Consequently their reaction with the atmospheric oxygen is inevitable.

The presence of ashes and bottom dross in the molten zinc is undesirable because, as their particles float or suspend inside the liquid metal, they could be trapped inside the coating and cause a common fault known as "coating pimples" [6], resulting to a low quality coating. Therefore it is necessary to be regularly removed from the kettle. Especially the oxides formed on top of the bath are removed every time an object is immersed in the molten zinc.

Another byproduct, formed only at the tube galvanizing facilities during the finishing of the galvanized coating, is the blowing waste. After a tube emerges from the galvanizing bath, its inner surface is subjected to a compressed air wiping, in order to diminish its roughness and consequently lower the flow resistance. This way, a very thin powder is produced, which is mainly composed by Zn and ZnO [7].

However, these byproducts are not useless. By contrast, Zn is possible to be recovered from them thanks to its high concentration [2, 7-8]. Consequently they are a valuable raw material. Therefore it is very important to be fully characterized, so as to collect useful data. Furthermore their characterization could lead to a better understanding of the galvanizing process, resulting to its optimization and the minimization of their production.

The above-mentioned researches [2, 7-8] focus only on Zn recovery process. Apart from a brief characterization consisting of a rough chemical analysis of each byproduct, nothing else is reported. On the other hand, other studies [1 and references herein], that examine hot-dip galvanizing very thoroughly, offer only little information on the compounds that compose floating and bottom dross, without going into details. A more detailed

research was recently published [9] which was focused on the floating dross with a little reference to its effect on the galvanizing process.

In the present work a detailed analysis of the structure of bottom dross and blowing waste is attempted. In order to fulfill this work bottom dross samples were collected from a local galvanizing facility and blowing waste from a local tube mill. Also samples were taken from the clean zinc bath and the pure zinc ingots, as they are provided to the galvanizing industry, in order to be compared with the byproduct specimens.

2. Experimental

A rough flow sheet of a typical hot-dip galvanizing line is presented in Fig. 1. Bottom dross samples were provided by a batch hot-dip galvanizing facility. These samples were collected right after being removed from the zinc kettle. A tube mill provided the blowing waste. The samples of the clean zinc bath and the pure zinc ingots were provided by both industries. The zinc bath was considered "clean" right after the usual removal of the bottom and floating dross, as it is performed in the industry (mechanically with the usage of suitable shovels). The samples of the clean bath were collected with a special device from three different depths (10, 100 and 150 cm below the zinc surface).

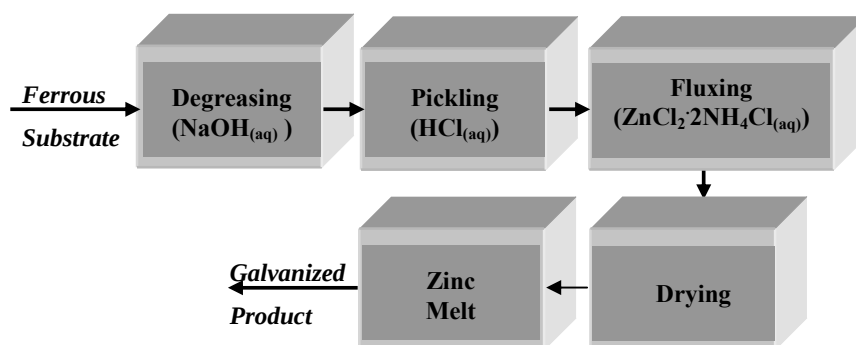


Fig. 1. Schematic diagram of a typical batch hot-dip galvanizing line. The chemical substances used in every step are pre-sented in the brackets. The index (aq) implies aqueous solution.

The examination of the samples took place with X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Conventional Transmission Electron Microscopy (CTEM). For the examination with XRD a two-cycle SEIFERT 3003 TT diffractometer was used with $\text{FeK}\alpha$ radiation ($\lambda=1.936\text{\AA}$). The examination with SEM took place in a 20 kV JEOL 840A SEM equipped with an EDAX analyzer (OXFORD ISIS 300) and the necessary software to perform linear microanalysis and chemical mapping of the examined substrate.

For the examination with TEM part of the blowing waste samples, which were powder-like, were captured between silicon tiles, polished up to about $40\text{ }\mu\text{m}$ and afterwards thinned with ion bombardment. For the bulk samples (bottom dross and pure zinc bath) only polishing and ion bombardment took place. The examination was accomplished in a 100 kV JEOL100CX TEM.

3. Results and discussion

3.1. Characterization of the zinc ingot and the clean zinc bath

The first step of the present work was the characterization of the pure zinc ingots used in the galvanizing process. Therefore one of them was cut in four pieces and about 50 particles in total were scratched from every surface of these pieces. These particles contain in

average 99.89 wt.% Zn, as it was determined with EDS. No impurities were detected with this method because of its low sensitivity, although the chemical analysis of the product, which was provided by its producer, mentions also the presence of Pb, Cd, Fe, Cu and Sn at a total concentration of about 0.014 wt.%. In any case, impurities of this concentration, although they are dissolved in the molten Zn bath, they do not affect significantly the structure of the coating [10-11]. Hence the zinc ingot composition has no effect on the formation of the different byproducts.

Afterwards the clean Zn bath was examined. For this investigation about 15 samples (from each sampling depth as it was previously explained) were examined with EDS in order to determine their chemical composition. The average results are presented in Table 1, from which it is obvious that the concentration of the impurities is much higher than in the ingot.

Al is deliberately added to the zinc bath in order to improve the appearance of the final product [1], while Fe and Cl are transferred by the ferrous substrate during its immersion in the liquid metal. Fe is also dissolved from the kettle walls. However, as it was mentioned earlier, impurities of so low concentration do not have significant effect on the coating structure. Furthermore the Zn concentration in the bath remains high enough, so as to be close to the necessary concentration for the production of a

good quality coating [12]. No nickel addition takes place at the industries that provided the samples, as it was stated by their chief engineers and consequently this metal was not detected. Other elements such as Sn, Cu and Cd that originate from the zinc ores were not detected because of the low sensitivity of EDS.

The examination with XRD is in accordance with the EDS results. As a matter of fact, it verifies the presence of zinc, iron and amorphous zinc and iron chlorides (Fig. 2). TEM also detected pure Zn (PDF#040831 [13]), as it was expected. However, the diffraction patterns of Fig. 3a and 3b prove that, apart from pure Zn, Fe-Zn solid solutions and Fe-Zn phases (PDF#320478 and PDF#341314 [13]) are present in the examined sample.

Table 1. Results of EDS microanalysis (average values) of pure zinc bath.

Element	Concentration (wt.%)
Zn	98.70
Fe	0.5
Cl	0.4
Al	0.4

The presence of Fe-Zn solid solutions is indicated by the broadness of the zinc diffraction rings relatively to the position of the rings of pure Zn. These compounds are most probably formed during the solidification of the liquid sample, which was taken from the kettle, since the Zn bath contains a small concentration of dissolved Fe. They are not visible with XRD due to their low concentration.

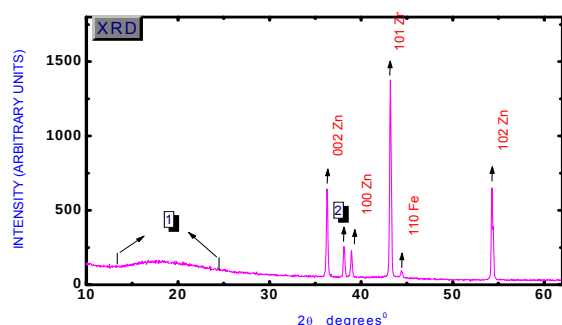


Fig. 2. XRD pattern of the pure zinc bath (1: amorphous Zn and Fe phases, 2: ZnCl_2).

By contrast, Fe-Zn phases are likely to have been already present in the liquid when it was collected from the kettle and not formed during its solidification, because these phases are insoluble in molten Zn and their melting point is higher than the temperature of the Zn bath [1]. This fact indicates that the cleaning of the zinc bath is incomplete since the perfect purification of a liquid metal in a large-scale industrial facility is very difficult. So, their presence is not peculiar.

However, if we take into account that TEM is a very sensitive method and the fact that the XRD patterns do not include any peaks referring to these phases, it could be deduced that in this case their concentration is very low and consequently their effect is seemingly unimportant, at least when the Zn melt is clean.

In any case from the above examination it is obvious that the zinc bath always contains a small amount of Fe-Zn phases. Furthermore it is likely to be saturated in Fe, if we take into account the maximum Fe solubility in liquid Zn as it is determined in the Fe-Zn phase diagram [1]. From this observation it could be deduced that the formation of bottom or floating is unavoidable, since the formation of Fe-Zn intermetallics is favored by the zinc bath composition.

3.2. Characterization of bottom dross

As it was mentioned earlier, bottom dross is usually removed from the Zn kettle by mechanical means (special shovels). This method results to the simultaneous removal of an important Zn quantity during the cleaning of this by-product. This phenomenon is obvious at the SEM micrographs, which were recorded (Fig. 4a and 4b).

Three phases are observed in these micrographs. One of them is lighter and appears like "islands" inside the second phase, which looks like a darker "sea". Many white spots are also scattered in the second phase. Also, in both micrographs dark spots are present, which refer to voids, probably formed because of the slow solidification process of the liquid metal after its removal from the zinc kettle. Furthermore, in both micrographs there are straight lines formed because of the imperfect polishing of the specimens prior to the SEM observation.

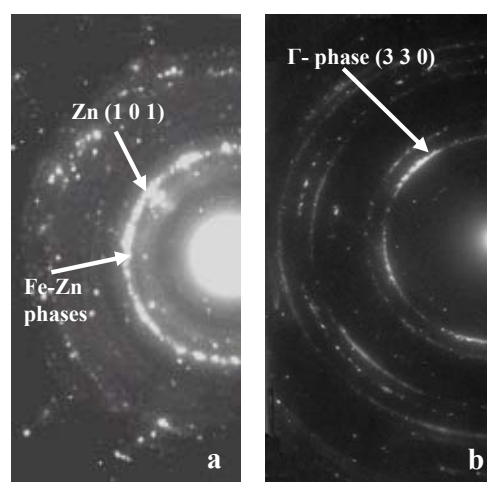


Fig. 3. Diffraction pattern of the zinc bath (a: Zn and Fe-Zn solid solutions, b: Γ -phase).

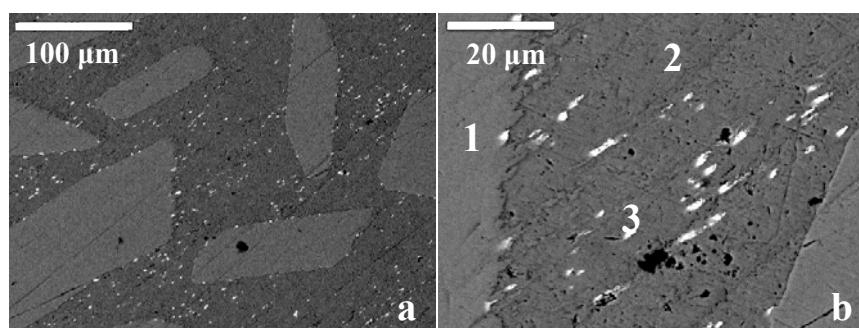


Fig. 4. SEM micrograph of the bottom dross (a: x450, b: x2000, focused on the darker area between the lighter fragments).

Table 2. Results of EDS microanalysis (average values) of bottom dross. The numbers of the phases refer to Fig. 4b.

Phase Number	Concentration (wt. %)		
	Zn	Fe	Pb
1	99.7	0.3	0
2	93.8	6.2	0
3	33.2	42.8	24.0

The results of the microanalysis of the above-mentioned phases are summarized in Table 2, where the average of the data recorded from 20 points from each one of these phases is presented. This table shows that the darker area between the lighter fragments (phase #1 in Fig. 4b) is composed almost exclusively by Zn. This is the liquid Zn trapped in the device used for the cleaning of the kettle. The lighter areas of the dross (phase #2 in Fig. 4b) are mainly composed by Zn, while they contain also about 6 wt.% Fe. This composition is typical for the ζ (zeta) phase of the Fe-Zn phase diagram [1]. The presence of Zn and the ζ -phase was also identified with XRD (Fig. 5). In any case ζ -phase is insoluble in molten Zn and its melting point (about 530 °C [1]) is higher than the kettle temperature (about 450 °C). Consequently, particles of this phase, formed when the Fe concentration in the kettle is above its solubility, precipitate at the bottom of the liquid Zn.

The white spots (phase #3 in Fig. 4b) observed in this phase contain a large amount of Pb. Lead is added in the

molten Zn in order to diminish the surface tension of the liquid and consequently reduce the coating thickness [11]. However the Pb solubility in liquid Zn is low, therefore a layer of molten Pb with an average thickness of a few centimeters precipitates at the bottom of the Zn kettle. It is likely that this layer is the source of Pb in the examined specimen because, as it was already mentioned, ζ -phase is denser than liquid zinc and settles at the bottom of the zinc kettle. However it is not denser than liquid lead and as a result the dross crystals float on its surface. Hence during their removal Pb is also drifted by the tool used.

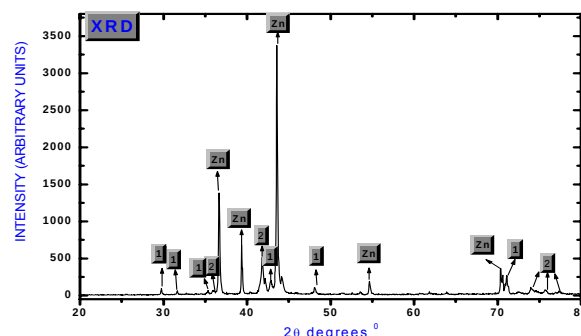


Fig. 5. XRD pattern of the bottom dross. Peaks noted with #1 refer to the ζ -phase of the Fe-Zn phase diagram and peaks noted with #2 refer to mixed Fe-Zn oxides.

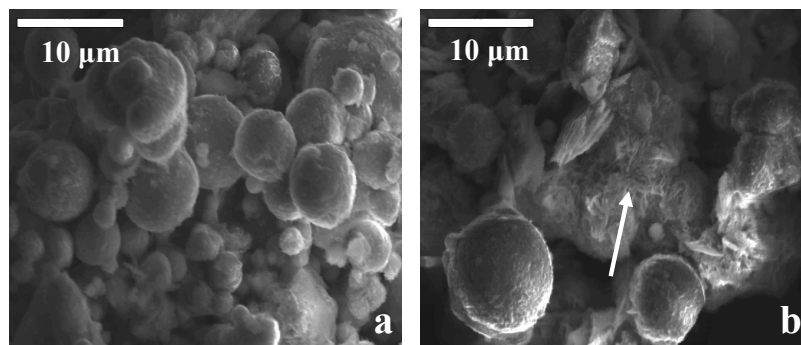


Fig. 6. SEM micro-graphs of two different grains of the blowing waste. In Fig. 6b the arrow points the needle-like crystals that were observed.

In any case from the above examination it could be deduced that ζ -phase is the main byproduct, while Zn and Pb are removed because of the imperfect method applied for the cleaning process. The XRD pattern reveals also the presence of mixed Fe-Zn oxides which were not detected with EDS. Their formation is probably due to the superficial oxidation of the bottom dross when removed from the zinc kettle. By that time zinc is still liquid, while the ζ -particles are hot. As a result they are very vulnerable to corrosion. If we take into account that these materials usually remained stored for several months the oxide formation is not peculiar. EDS did not detect any oxygen because the cross-section of the sample was examined after polishing. Hence since plain view was not analyzed oxygen was not reported. XRD by contrast examined the surface of the as-received sample, where oxide concentration was rather high.

3.3. Characterization of the blowing waste

As it was mentioned before, the blowing waste is a

byproduct formed only in tube galvanizing after hot-dipping. By contrast to the bottom dross whose specimens are bulk, the blowing waste is powder-like and it is mainly composed by spheres as it can be seen at the SEM micrographs of Fig. 6. Moreover some needle-like crystals are also observed (Fig. 7) in a higher magnification. The spheres are formed through the solidification of Zn droplets during blowing. As their microanalysis shows (Table 3) only Zn and O are present in them. Consequently, they are probably composed by a core of pure Zn covered with a layer of ZnO. The data of Table 3 is the average of the microanalysis 20 different spheres.

The microanalysis of the needle-like crystals indicates that these crystals are mainly composed also by Zn and O with a mole proportion equal to 1:1. Hence, these crystals are probably pure ZnO. The presence of Zn and ZnO was verified with XRD (Fig. 8, ZnO-PDF#211486, Zn-PDF#040831 [13]) and finally the presence of ZnO was also detected by electron diffraction (Fig. 9).

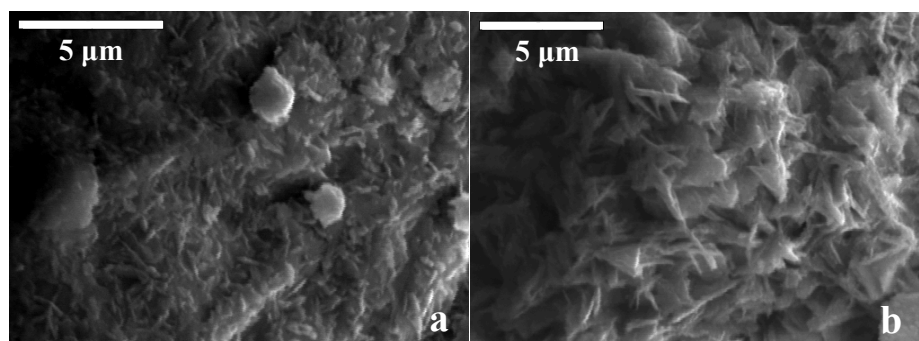


Fig. 7. SEM micrographs of the needle-like phase formed on the grains of the blowing waste.

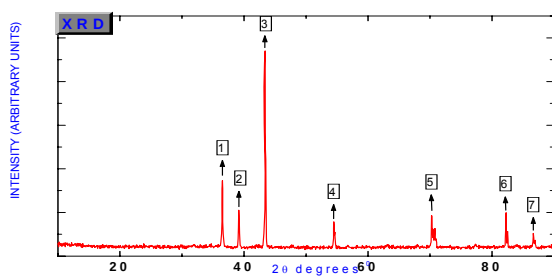


Fig. 8. XRD pattern of the blowing waste. Peaks #1 to #7 correspond to Zn (PDF# 040831 [13]) and peaks #1, #2, #4 and #6 correspond to ZnO (PDF#211486 [13]).

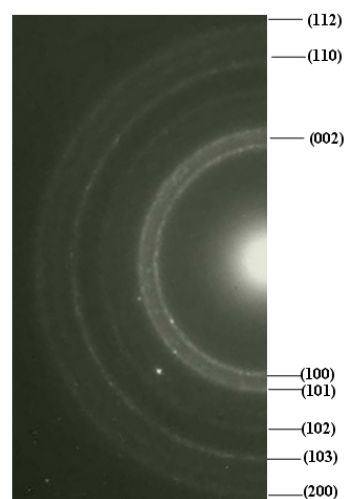


Fig. 9. ED patterns referring to ZnO (PDF#361451).

Table 3. Results of EDS microanalysis (average values) of blowing waste.

Phase	Concentration wt. %	
	Zn	O
Spheres	91.3	8.7
Needles	20.3	79.7

4. Conclusions

From the above investigation it was deduced that the composition of the pure zinc ingot does not contribute to the formation of galvanizing byproducts, while the zinc bath composition renders the formation of bottom dross unavoidable.

Furthermore, both bottom dross and blowing waste contain large amounts of zinc in different forms. In bottom dross mainly crystallites of the ζ -phase of the Fe-Zn phase diagram scattered in a matrix of pure Zn were detected, while in blowing waste, which is granular, is composed by spheres whose the core is of pure Zn covered with a layer of ZnO. Bottom dross contains also a small amount of Pb.

Finally these compounds could be used as raw materials for zinc recovery or for other processes for the production of different zinc compounds. However the large Fe concentration could be a certain drawback.

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