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A negative effect of the insoluble particles of dross on the quality of the galvanized coatings

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Abstract

In continuous galvanizing process several byproducts are formed. Amongst these byproducts insoluble particles composed by different compounds are grown. The most problematic seems to be a complex oxide of a $ZnAl_{2-x}Fe_yO_4$ stoichiometry (spinels) with variable lattice parameters, which is formed at the zinc/substrate interface. This oxide accelerates the breakdown of Fe–Al passive layer, resulting in the formation of a series of Fe–Zn intermetallic phases by an outburst growth. The samples used in this study were industrially galvanized wires and byproducts, which were studied by different methods, i.e., Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-Rays-Diffraction (XRD).

Keywords: Hot-dip galvanizing; Zinc coating; Outburst; Spinel; XRD; SEM; TEM

1. Introduction

The production of galvanized objects involves the generation of several byproducts. Amongst them, the galvanizing dross is the most important. Galvanizing dross is formed inside or on top of the molten zinc and it is classified as floating or bottom dross [1]. The floating dross (also known as "galvanizing ashes") consists mainly of a mixture of oxides and chlorides [2], while the bottom dross consists exclusively of intermetallic compounds. Intermetallic compounds were also found in the floating byproducts, but in this case the $Fe_2Al_5Zn_x$ was reported to be the main component [3].

The intermetallic compounds of the floating and bottom dross are formed when the concentration of some elements in the zinc kettle exceeds their solubility limits. Even in the case of a perfect management of the zinc bath, the deliberate elements additions, the Fe dissolution from the immersed objects, in combination with the variable gradient of temperature lead to the crystallization of the above-mentioned byproducts [4].

It was found [5] that impurities or insoluble particles of byproducts, even in usual levels incite diffusional interface instabilities of catastrophic proportions with a consequent breakdown of a thin iron–aluminum layer which temporary protects the iron from excessive attack. Once the protective Fe–Al layer is destroyed, iron–zinc compound outbursts are formed leading to a degradation of the quality of the zinc coatings. On the other hand, insoluble particles and undesirable intermetallic phases could be trapped inside the coating thus causing a common fault known as "coating pimples" [6], which consists of the formation of swells on the galvanizing surface.

In spite of persistent efforts to elucidate the role of the insoluble particles at the continuous galvanizing process, their influence on the diffusional interface instabilities remains somewhat obscure.

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Till now relevant studies mainly focus on the Zn recovery process [1,7]. Apart from a brief characterization few information are available on the procedure of the formation of the compounds that compose the different particles found in the drosses.

Consequently a detailed analysis of the composition of every byproduct and the way they influence the galvanizing process seems to be necessary. For comparison reasons samples taken from the "clean" zinc bath and from the pure zinc ingots were analyzed. In all cases products were carefully examined by means of SEM, TEM and XRD measurements.

In this work we mainly focus on the destabilization of the protective layer formed at the interface between zinc bath/substrate induced by the insoluble particles of the byproducts.

2. Experimental

Both dross samples and coated specimens were provided by a continuous wire hot-dip galvanizing facility, where galvanization takes place following the Cook–Norteman line [2]. These samples were collected right after being removed from the zinc kettle. The same industry provided the samples of the clean zinc bath and the pure zinc ingots. The zinc bath was considered "clean" right after the usual removal of the bottom and floating dross.

The examination of the samples was performed using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). For the examination with XRD a two-cycles SEIFERT 3003 TT diffractometer was used with FeKα radiation ($\lambda = 1.936$ Å). The examination SEM took place in a JEOL 840A (operated at 20 kV), equipped with an EDAX analyzer (OXFORD ISIS 300) and the necessary software to perform linear microanalysis and chemical mapping of the examined substrate.

To examine the byproducts with TEM, materials, which were powder-like, were captured between silicon tiles, polished up to about 40 μm thickness and thinned with ion bombardment. In the case of bulk samples only polishing and ion bombardment took place. The examination was accomplished in a JEOL100CX TEM, operated at 100 kV.

3. Results and discussion

The ingots of the zinc used in the galvanizing process were found to be practically free from impurities as detailed SEM analysis showed that they contain 99.89 wt% Zn. Some impurities of Pb, Cd, Fe, Cu and Sn of a total concentration less than 0.1 wt% seem not to affect the structure of the coatings as it was elsewhere established [8,9]. The concentration of the impurities was below the detection limit of SEM and as a result it is not presented in Table 1.

Situation was changed when samples from the zinc bath were examined. Due to an accumulation of impurities the so-

Table 1
Results of the SEM microanalysis of the pure zinc bath

Element	Zn ingot	Pure Zn bath
	Concentration (wt%)	Concentration (wt%)
Zn	99.89	98.45
Fe	Non detected	0.33
Sn	Non detected	0.35
Cl	Non detected	0.25
Pb	Non detected	0.15
Al	Non detected	0.30
Cu	Non detected	0.10
Cd	Non detected	0.12

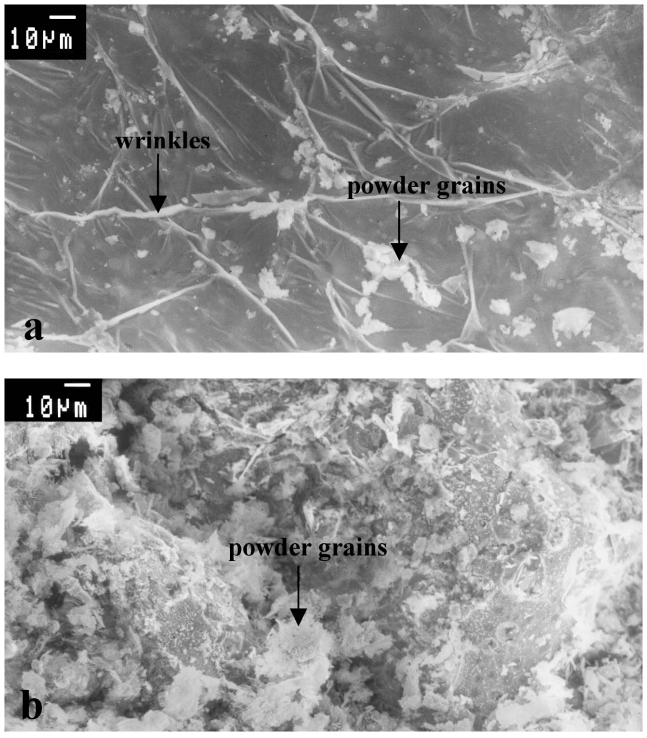

Fig. 1. SEM micrographs of the floating dross (a: thin film, b: thick layer).

Table 2
Results of the SEM microanalysis of the floating dross samples

Element	(a)	(b)
	Concentration (wt%)	
C	0.35	0.45
O	45.60	25.50
Al	16.20	17.00
Cl	5.10	7.60
Zn	28.20	41.30
Pb	1.25	0.80
Fe	2.10	1.65
Ti	1.20	5.70