THE EFFECT OF ATMOSPHERIC CONDITIONS ON ZINC COATINGS

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The influence of the atmospheric conditions on the surface of zinc coatings of galvanized iron materials is studied by different methods. The samples used are industrial wires galvanized by hot-dip method, which were exposed to the open air under all weather conditions for one month, in a heavy industrially polluted environment. Several phases were detected either due to the certain procedure of the galvanization or due to the reaction of the atmospheric SO_2 and CO_2.

1. Introduction

Hot-dip galvanizing for coated steel products is widely used in the manufacture of materials for the automotive and home appliance industries [1]. During the process of hot-dip (immersing in molten metal) galvanization clean, oxide free iron or steel is immersed into molten zinc in order to form a zinc coating which is metallurgically bonded to the iron or to the steel surface [2]. The hot-dip galvanized coatings are used as a means of protecting steel from corrosion, through the action of the zinc coatings, which has a slower rate of corrosion and exhibits anodic behavior compared to the steel when the component is placed in a corrosive environment [1,3]. The aim of the present work is to study the influence of the environmental condition on the surface of zinc coatings as well as the complete description of the phases formed during the galvanization.

2. Experimental

The galvanized iron used for this study were wires and were produced industrially with the following process [4]: i) Dry degrading of wire by tension in various diameters, ii) Wire lubrication with special materials or reactors in order to remove impurities of surface, iii) Annealing at 900 °C for relaxation process, iv) Cooling with water, v) Hydrochloric acid pickling (removal of rust and impurities), vi) Water rinse for final cleaning before hot dipping, vii) Prefluxing in zinc ammonium chloride solution (surface conditioning), viii) Air drying, ix) Hot dip galvanizing in pure Zn bath (at 460-490 °C), x) Air drying, xi) Removal of excess Zn with different procedure, xii) Polishing with a solution of oil and perlite, xiii) Water cooling, xiv) Rolling of wire.

The wires were of various diameter (1600-2500 μm), the thickness of the coatings was not homogeneous varying from 5 μm to 40 μm and the zinc bath temperature ranged from 460 ^{0}C to 490 ^{0}C. The samples were let in the open air under all weather conditions for one month, in a heavy industrially polluted environment. The samples were studied by three different methods i.e. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-Rays Diffraction (XRD).

For the XRD study the specimens were prepared with cold rolling in sheet form. A 1-cycle diffractometer Philips -CuKα radiation (λ= 1.54406 Å) was used. For the TEM study the specimens were prepared by ion milling on thin cross-sections cutted vertical to the wire axes. The examination took place in a 120 kV TEM (JEOL-100-CX). For the SEM study cross-sections of wires with different diameters were examined as well as the outer surface of the galvanized wires. The examination took place in a 20 kV SEM (JEOL- JSM- 840 A) with EDAX analyzer (OXFORD ISIS 300).

3. Results and discussion

The mechanism of the diffusion is predominant during hot-dip process [1]. A number of different phases are formed during diffusion of the coating material on iron. The reaction between Fe and Zn during hot-dip galvanizing, which occurs by interdiffusion in the solid-solid condition, is difficult to control and the mechanism for the interactions between Fe and Zn are not well understood. As the bath of galvanization, is industrial, it contains also some impurities which affect [5] the diffusion and lead to non-equal distribution. The usual impurities are Al, Pd, Sn, P, Mg, Ca, Cd, S, Si, Mn, Cu and most of them are detected by the EDS (Energy Dispersion X-ray Fluorescence Spectroscopy) analysis.

SEM analysis detected differences both in the appearance of the coating surface and in its elemental analysis between the corroded and the non-corroded samples. Additionally, cross-sectional observation developed the inhomogeneity of the thickness of the coating layer. The results of the EDS analysis are presented in Table 1. The values written are mean values of 15 different measurements on different areas in the same sample or different samples. The impurities with a proportion less than 1% are omitted. The main findings are the presence of sulfur, carbon and oxygen on specific points in the surface of the corroded specimens. The significant increase of sulfur content in some areas is accompanied by the simultaneous increase of oxygen and carbon. The appearance of the corroded areas is difficult to identify only by observation (Fig. 1) as they appear, and not always, only darker than the surrounding area. This is because this contrast is common in such industrial materials due to other " defects " on the surface.

Table 1. Results of EDS analysis for corroded and non-corroded wires. The coating has also low level (~1%) of impurities.

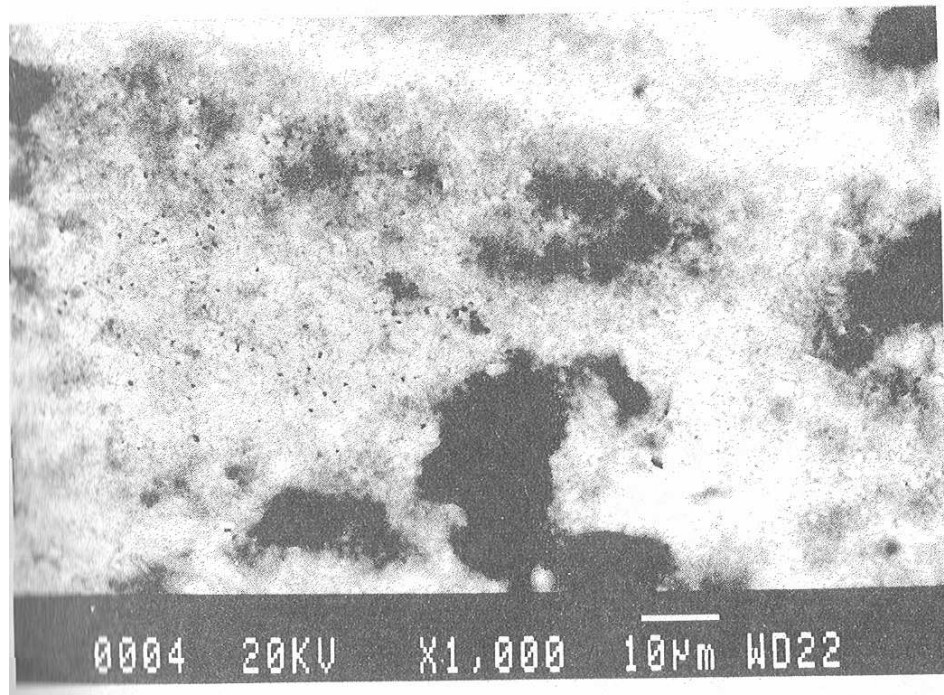| Elements		Middle of coating		Surface of wire	
		Non corroded	corroded	Non corroded	corroded
Fe	mol %	4.39	5.37	3.95	3.56
Zn	mol %	94.73	93.71	96.05	75.72
S	mol %	~0	~0	~0	1.52
O	mol %	~0	~0	~0	18.36

Fig. 1. A SEM image of the corroded wire.

From the XRD patterns (Fig. 2, 3), the presence of Fe and Zn is obvious. Some of these peaks 1 and 2 correspond to the ζ- FeZn$_{15}$ and Fe$_{11}$Zn$_{40}$ phases. The chloride phases of Fe or Zn, which have a negative effect on the existence of Zn on the coating, are also present. It is most probable that this component inhibit Fe-Zn phase growth. This is documented from the comparison between the two XRD patterns. In the same patterns one or two peaks belonging to ZnCl$_2$ phase have appeared. In the case that such a peak was not revealed (or was weak), the growth of Fe-Zn phases appeared. During the precipitation of the Fe-Zn phases at the iron-zinc interface and their subsequent growth by a diffusion controlled mechanism, the iron chloride layer which was probably formed in a previous stage act as barrier layer at the interface and slow the diffusion rate of additional atoms [1]. Zinc sulfides and other sulfur-zinc compounds such as ZnSO$_4$ which are supposed to be formed in the surface of coating, due to the heavy industrially polluted environment, are rather impossible to be detected by X-ray diffraction as their mass is only a small fraction of the total weight of the sample.
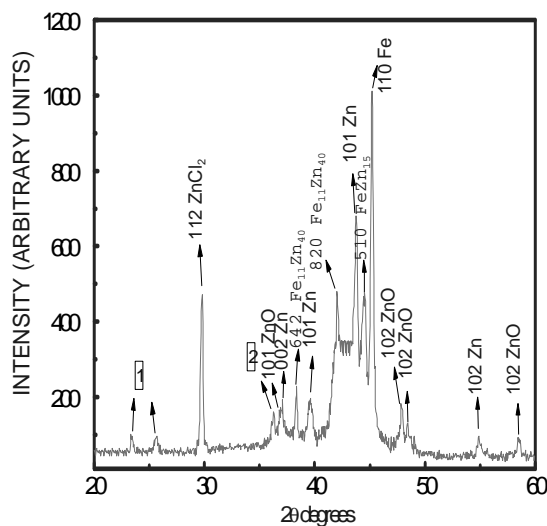

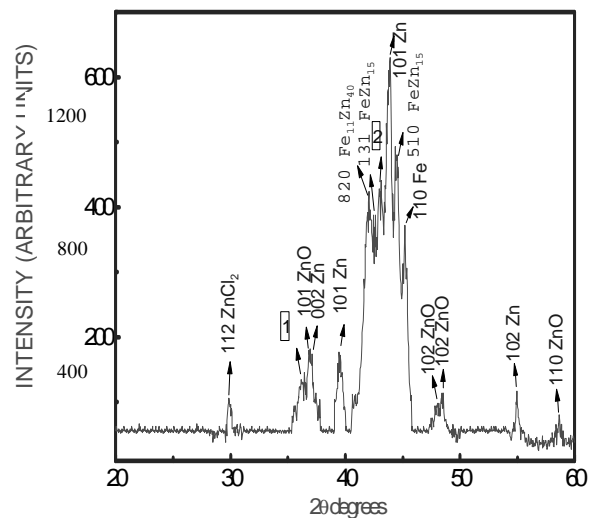Fig. 2. X-Ray diffraction pattern of the sp the specimen with diameter 1960 μm.

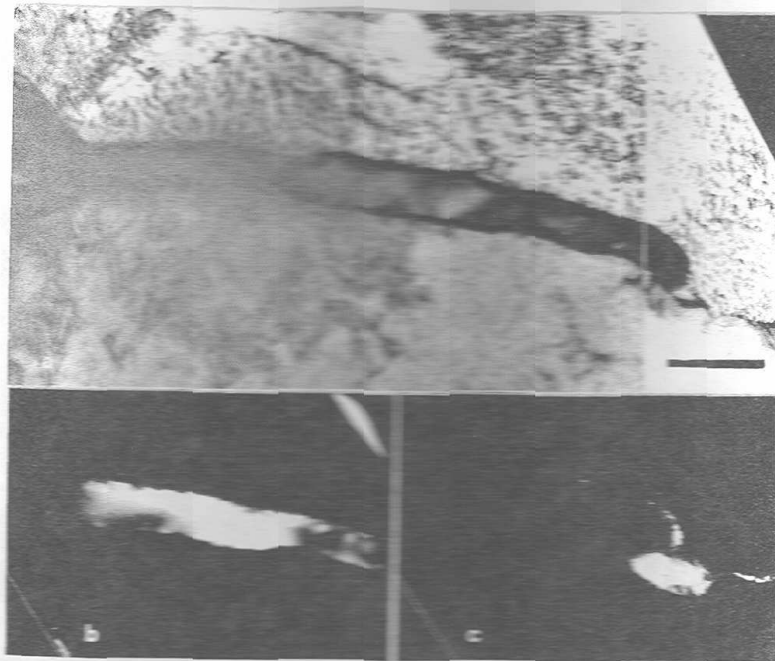Fig. 3. X-Ray diffraction pattern of the spe specimen with diameter 2050 μm.

Fig. 4. A bright field TEM image (a) together with two dark field images (b, c) corresponding to the same particle. The dark field images were taken from two independent spots both belonging to the $ZnCl_2$ phase. This means that the whole particle consists of few crystallites belonging to the same phase. Bar = 0.2 μm.
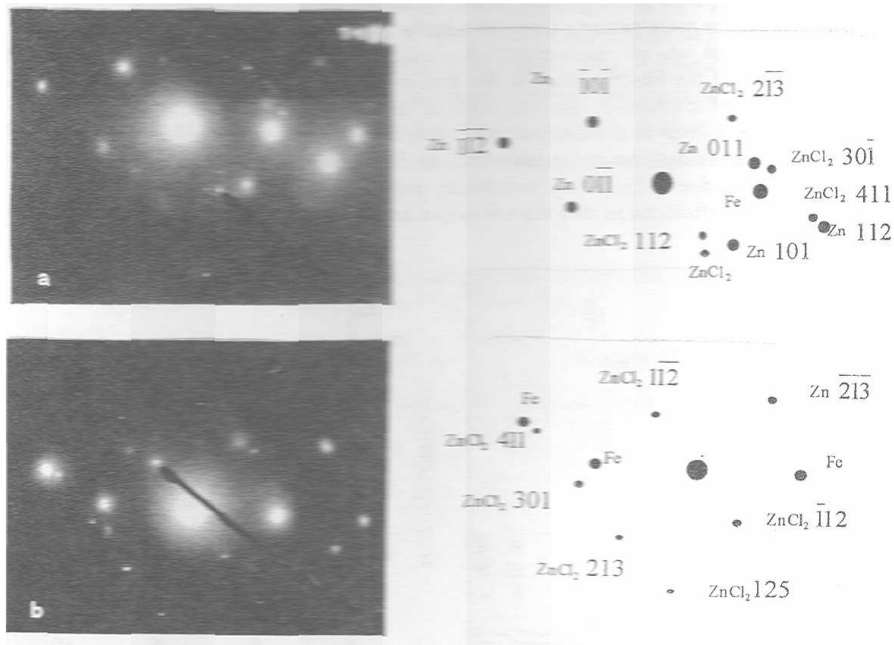

Fig. 5. Electron diffraction patterns (a,b) with arrows indicating the specific spots used for the dark field images of Fig. 4. Each pattern was accomplished by the drawing of all spots, where the different phases as well as the hkl indices of all detected phases are noticed.

The TEM study has been performed on cross-sectional specimens in the vicinity of the surface of the coatings and in the coating width. This is in order to detect the different phases developed on the surface after the exposure to the environment. Nearby the interface between the iron wire and the Zn coating, the $ZnCl_2$ phase was detected. Fig. 4 shows a narrow and lengthy particle belonging to this phase, together with two dark field images taken from two different spots of two different diffraction patterns from the same area.

As it is explained in Fig. 5 both spots belong to the $ZnCl_2$ phase. Additionally in both diffraction patterns the Fe and Zn spots are also detected. The existence of this phase can be possibly explained. The treatment with $ZnCl_2$ during the coating procedure leaves limited quantities of this compound on the iron wire surface, covered in the procedure of galvanizing by the Zn. This means that this compound remains inside the Zn coating in the final product. On the surface of the Zn coating, the ZnO phase was also detected. Fig. 6 shows a dark field image taken from spots belonging to this phase. The image presents the crystalline size as well as their distribution on the coating surface.
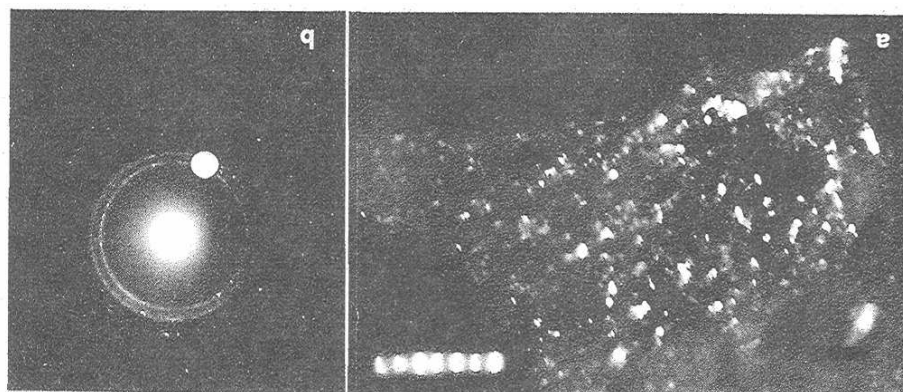

Fig. 6. TEM dark field micrograph (a) taken from spots belonging to the ZnO phase. Diffraction pattern where apart from the distinguished spots, a polycrystalline ring pattern was detected corresponding to the ZnO phase. Bar=0.1 μm.

4. Conclusions

Zinc coatings are stable in ambient temperature. This is because the zinc oxide acts as a protective film. However in a polluted area environment the existing SO_2 and CO_2 in the atmosphere react under ambient conditions with the zinc coating producing zinc salts which finally terminate the formation of the $ZnSO_4$ and $ZnCO_3$ phases. The exact places where the zinc sulfate and zinc carbonate are formed, are possible due to the existence of free zinc ions in these specific points of the coating. Additionally $ZnSO_4$ is very soluble into the water and so little by little the procedure leads to the destruction of the coating.

References

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