## TECHNICAL INFORMATION

## EFFECT OF ALUMINUM IN ZINC BATHS ON THE FORMATION OF THE DIFFUSION COATING IN HOT-DIP GALVANIZING OF STEEL

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Small aluminum additions (0.1-0.3%) in the zinc bath have a substantial effect on the formation of the diffusion coating in hot-dip galvanizing. The interaction of low-carbon steel with molten zinc containing aluminum is characterized by an incubation period [1, 2]. During this period the aluminum inhibits growth of the diffusion layer but causes tight adherence of the coating to the base metal. However, the mechanism by which aluminum affects the process has not been investigated in detail because of methodological difficulties in investigating the structure and phase composition of thin diffusion coatings (less than  $1-2\mu$ ).

The use of a light microscope and x-ray analysis for investigations of thin intermediate layers are equally ineffective, and no studies have been made with an electron microscope and electron diffraction analysis.

We investigated the effect of aluminum on the structure and phase composition of the diffusion coating by means of electron microscopy and electron diffraction analysis of laboratory and production samples.

The laboratory samples were obtained by hot-dip galvanizing of steel 08kp at 450 °C for 20 sec in molten zinc with as much as 0.3% Al. Production samples were prepared from strip galvanized by the Sendzimir method in the MMK apparatus.

Electron microscopic studies were made of sloping sections of the zinc coating. To reveal the structure we developed a method of etching in two successive electrolytes at a potential of 1-2 V: a) 0.5% ferric chloride; b) a mixture of 8 ml acetic acid, 1 ml perchloric acid, and 1 ml water. The section etched was limited by the clamps. The phase composition of the diffusion coating was determined by means of electron diffraction analysis. The zinc coating on the samples was removed by means of a special reagent [3]. This same reagent was used for slow etching of the coating to different depths.

For the microdiffraction studies the iron-aluminum compounds in the diffusion coating were extracted in carbon replicas by the electrochemical method in 0.5% ferric chloride at a potential of 1-2 V.

The thickness of the diffusion coatings was determined by the standard method on microsections in a light microscope.

d, Å	Intensity of reflection	d, Å	Intensity of reflection
4.90	Weak	2.12	Strong
3.83	Weak	2.06	Strong
3.22	Moderate	1.88	Weak
2,38	Weak	1.75	Weak
		1.68	Weak

Electron microscopic examination was used in some cases to determine the approximate thickness of thin layers.

TABLE 1

Central Scientific-Research Institute of Ferrous Metallurgy. Translated from Metallovedenie i Termicheskaya Obrabotka Metallov, No. 4, pp. 60-62, April, 1973.

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Fig. 1. Microstructure of diffusion coatings on hot-dipped galvanized steel (2500  $\times$ ). a) Zinc bath without Al; b) with 0.05% Al; c) 0.3% Al.

Figure 1 shows electron micrographs of the sloping section of the coatings.

The diffusion coating formed in pure zinc (Fig. 1a) consists of  $\zeta$ ,  $\delta_1$ , and  $\Gamma$  phases, which are intermetallic compounds FeZn<sub>13</sub>, FeZn<sub>7</sub>, and Fe<sub>3</sub>Zn<sub>10</sub> respectively, and  $\eta$  and  $\alpha$  solid solutions [4]. The layer of  $\zeta$  phase has a coarse crystalline structure and consists of crystals in the form of prisms elongated in the direction of heat withdrawal. The crystals of  $\delta_1$  phase are equiaxed and rounded. The structure of  $\Gamma$ phase was impossible to determine, but blurred lines on the diffraction patterns indicate that is has a fine crystal structure. The layer of  $\eta$  and  $\alpha$  solid solutions differs from the steel and pure zinc in its intracrystalline structure (substructure), which can be seen from the relief after etching.

Figure 1b shows the electron micrographs of the coating from the bath with 0.05% Al, where  $\text{Fe}_2\text{Al}_5$  is observed along with  $\Gamma$ ,  $\delta_1$ , and  $\zeta$  phases, forming a thin layer between the  $\Gamma$  and  $\alpha$  phases. The crystals of Fe-Zn intermetallic compounds have more distinct faceting.



Fig. 2. Microstructure (a) and diffraction pattern (b) of  $\text{Fe}_2\text{Al}_5$ . 2500 ×.

The diffusion coatings from the bath with 0.1% Al contain  $\zeta$  and  $\delta_1$  phases in addition to Fe<sub>2</sub>Al<sub>5</sub>, while coatings obtained from the bath with 0.2-0.3% Al contain only  $\delta_1$  phase. In the diffusion coating from the bath with 0.2% Al the  $\delta_1$  phase forms a continuous layer above Fe<sub>2</sub>Al<sub>5</sub>. Coatings from the bath with 0.3% Al have separate crystals of  $\delta_1$  phase embedded in the layer of Fe<sub>2</sub>Al<sub>5</sub> (Fig. 1c). With increasing concentrations of aluminum in the zinc bath the density and thickness of the Fe<sub>2</sub>Al<sub>5</sub> layer increase. A change in the aluminum concentration from 0.05 to 0.3% causes an increase in the thickness of Fe<sub>2</sub>-Al<sub>5</sub> from hundredths to tenths of a micron.

In structure and phase composition the production diffusion coatings are quite similar to those obtained with 0.3% Al and differ only in the smaller thickness of the  $\text{Fe}_2\text{Al}_5$  layer. The  $\alpha$  and  $\eta$  solid solutions were found in all coatings from baths with aluminum.

Thus, the diffusion coatings obtained from baths with aluminum contain a new phase –  $Fe_2Al_5$ . Figure 2 shows the structure and diffraction pattern of this compound extracted by the electrochemical method. The interplanar distances of  $Fe_2Al_5$  are given in Table 1 (ASTM data).

With increasing aluminum concentrations in the zinc bath (0, 0.05, 0.1, 0.2, 0.3% Al) the thickness of the diffusion coating decreases, amounting to 20, 14, 6, 1 and less than  $1 \mu$  respectively.

In galvanizing of steel in baths with aluminum a layer of  $\text{Fe}_2\text{Al}_5$  is formed immediately due to the higher affinity of aluminum for iron than for zinc, which acts as a barrier during the incubation period, restraining the growth of the diffusion coating. With increasing thickness and density of the  $\text{Fe}_2\text{Al}_5$  layer the Fe  $\pm$  Zn diffusion rate decreases and the incubation period increases.

## LITERATURE CITED

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