Structure of Zinc Coating on Steels Formed by Diffusion Saturation in Nitrogen-Containing Atmosphere

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Abstract. Diffusion technique of metallization is applied for receiving of zinc coatings on low-carbon steel with transitional zone. Structure of diffusion zinc layers after saturation of 09Mn2Si steel in ammonia at different temperatures is examined. Effects on saturation temperature on thickness of diffusion layers are discovered. Process at 600°C forms diffusion layers with high strengthening level and with smooth microhardness profiles. Elements (Fe, Zn, N) spectrums are analyzed, and phase composition of zinc coating and of transitional zone is determined.

1 Introduction

Zinc coatings are widely used for corrosion protection of steel components and constructions working in hard climatic conditions. Corrosion damage is the main factor of reduced service life of bridge constructions elements made of low-carbon steels. For increase of such parts reliability, protective coatings are applied. In particularly zinc coatings are effective for steel corrosion protection [1-3].

There is a number of techniques for zinc coatings deposition. Diffusion metallization methods are most in demand as they allow receiving gradient structure of the layer providing good adhesion of a coating with steel substrate [4-5]. As it was examined before, nitriding of zinc coatings not only improves their adhesion but also enforces strengthening and increases wear resistance [6]. Thus zinc diffusion metallization in nitrogen-containing atmosphere may be the way to enhance the properties of steel surface providing protective layers resistant against wear and corrosion.

The purpose of this paper consists in study of structure and phase composition of zinc diffusion layers obtained in low-carbon steels in active ammonia atmosphere.

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2 Methods of experimental study

Diffusion metallization with zinc was conducted for 09Mn2Si steel by thermo-chemical treatment of specimens covered by zinc-containing suspension. In addition to zinc powder (20%) the suspension contained quartz sand (75%) as a filler, NH_4Cl as an agent, and a binder. Specimens were saturated in ammonia atmosphere at temperatures 600...1000°C during 1...4 hours.

Metallographic examinations were made in AXIOVERT 25CA optical microscope; microhardness of the layers was measured by PMT-3 tester. Methods of scanning electron microscopy (JEOL JSM-6610LV) and Auger electron spectroscopy (PHI-680) were used to study of structure and composition of diffusion layers.

3 Results and discussion

Thickness of obtained diffusion coatings and their structure depends on the process time and temperature. Diffusion saturation during 1 hour at 800°C forms metallographically observed layer of 30 μm thickness (Fig. 1 a). Prolongation of the process duration up to 4 hours increases the thickness of the layer until 70 μm (Fig.1 b). Saturation at temperature 1000 °C forms in 1 hour a layer of 50 μm thickness (Fig. 1 c). A coating of the same thickness grows up during 4-hours saturation at 600°C (Fig. 1 d). After the saturation at this temperature, a sublayer (transitional zone) is observed under the zinc coating: the total thickness of the layer increases up to 110...120 μm .

Fig. 1. Micrographs of zinc diffusion coatings received at different process regimes: a) 800°C, 1 hour, b) 800°C, 4 hours, c) 1000°C, 1 hour, d) 600°C, 4 hours

Due to the formation of the transitional zone, microhardness profile becomes smooth between coating and steel base (curve 1 at Fig. 2). At well as processes at higher temperatures forming coatings without transitional zone have sharp microhardness gradient and less level

of strengthening (curve 2 at Fig. 2).

SEM examination shows that the surface of a zinc coating is not uniform (Fig. 3). Fragments identified as ZnO oxide (point Spectrum 1 with the proportion 49.7 at.% Zn+50.3 at.% O) alternate spots containing Zn₃N₂ nitride (point Spectrum 2 with 29.4% at. N).

Fig. 2. Microhardness profiles of 09Mn2Si steel specimens after zinc diffusion metallization at 600°C, 4 hours (1) and at 1000°C, 1 hour (2)

Fig. 3. SEM images of zinc coating surface and elements spectrums at points 1 and 2

For study of elements concentration changes along the diffusion layer, spectrums were quantitatively analyzed at different points remoted from a starting point (12...15 μm below the surface). Using Fe-Zn phase diagram, possible phases (intermetallic compounds and

solid solutions) were determined in these points based on the Fe/Zn concentrations ratio (Table 1).

Table 1. Chemical and phase compositions of zinc diffusion layer in control points by depth from surface

Depth from starting point, μm	Elements concentration, weight %				Phases
	Zn	Fe	Si	Mn	
0	92.46	4.94	1,0	1.60	$\delta\text{-FeZn}_7$
4.0	89.62	8.90	-	1.48	$\delta\text{-FeZn}_7$
5.8	79.24	19.08	-	1.68	$\Gamma\text{-Fe}_3\text{Zn}_{10}$
8.90	40.50	57.88	1.29	1.62	$\text{Fe}_\alpha(\text{Zn}) + \Gamma$
13.12	28.33	69.52	0.78	1.36	$\text{Fe}_\alpha(\text{Zn}) + \Gamma$
16.91	26.98	71.74	-	-	$\text{Fe}_\alpha(\text{Zn}) + \Gamma$
20.02	20.46	77.13	1.32	1.09	$\text{Fe}_\alpha(\text{Zn}) + \Gamma$
25.81	21.50	76.87	0.71	0.92	$\text{Fe}_\alpha(\text{Zn}) + \Gamma$
28.92	18.56	79.50	0.84	1.10	$\text{Fe}_\alpha(\text{Zn})$
35.60	18.75	78.90	1.15	1,2	$\text{Fe}_\alpha(\text{Zn})$
39.60	15.11	82.01	0.95	1.93	$\text{Fe}_\alpha(\text{Zn})$
43.61	3.43	94.28	0.89	1.40	$\text{Fe}_\alpha(\text{Zn})$
48,50	1.12	96.61	0.87	1.40	$\text{Fe}_\alpha(\text{Zn})$
53.40	0.00	97.67	0.85	1.48	Base - Fe_α
59.80	0.00	97.49	0.82	1.69	Base - Fe_α

Analysis shows that directly below the surface hexagonal δ -phase FeZn_7 (88.5...93 weight % Zn) is formed with a thin layer of BCC Γ (gamma)-phase $\text{Fe}_3\text{Zn}_{10}$ (72...79 weight % Zn) under it. At a greater depth a thick double-phase area of $\text{Fe}_\alpha(\text{Zn}) + \Gamma$ is supposed with smooth zinc concentration decrease. A fragment of the layer with zinc concentration less than 20% Zn corresponds to single-phase area of zinc solid solution in ferrite $\text{Fe}_\alpha(\text{Zn})$. This layer of 20 μm thickness was determined as a part of transitional zone formed as the result of zinc diffusion penetration into iron. In deeper points, elements concentrations corresponds to the chemical composition of the basic steel.

Examination of coatings by Auger-spectroscopy discovered increased nitrogen concentration (up to 10.8 at.% N) directly at the interface between the coating and the transitional zone. Nitrogen concentration gradually decreases in the transitional zone; concentration profiles shows that nitrogen excess concentration remains at higher depth than zinc concentration (Fig. 4). Thus the structure of the transitional zone may be described consisting of two sequential plots of solid solutions: $\text{Fe}_\alpha(\text{Zn}, \text{N})$ and $\text{Fe}_\alpha(\text{N})$.

Fig. 4. Auger-profiles of elements in transitional zone under zinc coating

4 Conclusion

Saturation of low-carbon steel samples covered by zinc-containing suspension in ammonia allows forming a multiphase diffusion layer that composed of zinc coating and of transitional zone. Zinc coating has ZnO oxide and Zn_3N_2 nitrides at the surface and consequently precipitated intermetallic compounds ($\delta\text{-FeZn}_7$ and $\Gamma\text{-Fe}_3\text{Zn}_{10}$). The thickness of coatings and achieved microhardness depends on the process temperature. After saturation at 600°C , parallel nitriding occurs, and strengthened transitional zone is formed with smoothly decreased microhardness by the depth. The transitional zone has the structure of solid solution $\text{Fe}_\alpha(\text{Zn}, \text{N}) \rightarrow \text{Fe}_\alpha(\text{N})$. Elevated microhardness of the transitional zone comparing to microhardness of steel base is the consequence of solid solution strengthening of ferrite by dissolved nitrogen.

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