Protection of steel constructions against wear and corrosion in difficult climatic conditions by new techniques of zinc metallization

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Abstract. In the paper modernized techniques of zinc metallization of steel in combination with nitriding are considered. Two methods of combined surface modification of low-carbon steel are studied: application of zinc coatings by painting technique and subsequent gas nitriding; simultaneous thermo-diffusion saturation by zinc and nitrogen. Microstructure and microhardness of steel samples were examined; forming of a transition zone was determined under visually observed surface layer/coating with increased concentrations of Zn and N. Combined saturation by zinc and nitrogen forms diffusion layers with increased wear resistance and reduced friction coefficients together with improved corrosion resistance in salt fog. Nitriding of Zn coatings protects the steel both in salt and acid mediums.

1. Introduction

Corrosion and wear of steel components of bridge constructions are the main damages limiting their lifetime in difficult climatic conditions. Both phenomena are the consequences of metal interaction with external factors; their appearances depend on composition and structure of the metal’s surface. Techniques of coatings application and surface modification are widely used for protection against wear and against corrosion. The problem is that, as a rule, the structure of the surface layer increasing wear resistance simultaneously decreases corrosion resistance and vice versa. Can we receive coatings or layers which influence positively both wear and corrosion resistance? Some previous results suggest promising solutions on forming of multi-component layers in steels by combined techniques of metallization and nitriding [1, 2].

It is known that zinc-based coatings application provides effective corrosion protection of steel parts and constructions working in a corrosive environment of atmosphere, precipitations, humidity, condensed moisture, etc. There are several methods of Zn-based coatings and layers application which can be categorized into two main groups according to the factors of existence or absence of diffusion processes.

The first group includes processes of thermodiffusion metallization by zinc with forming of diffusion layers of gradual structure [3, 4]. Corrosion resistance of such layers is the consequence of the protective properties of different Fe-Zn phases. We have supposed that the combination of diffusion saturation by zinc and nitrogen may influence the structure and phase composition of the steel surface layer and may amend wear-corrosion relation.

Processes of application of so-called zinc-rich coatings belong to the group of “diffusion-free”
processes [5, 6]. Such coatings are applied by painting techniques, for example, by cold zinc-plating, and provide two possible mechanisms of corrosion protection: electrochemical (cathode) mechanism and barrier mechanism of painted films. Protective Zn coatings have a distinct boundary with a steel substrate without enough adhesion. The origin of low adhesion lays in the sharp change of residual stresses at the interface of a coating with a metal substrate. To a certain extent, the residual stress profile corresponds to the microhardness gradient along the transition zone. Therefore, the control of microhardness gradient across the surface layer may be a tool for the prevention of coatings exfoliation. Gradual microhardness profiles are attributes of diffusion layers receiving by thermochemical treatment (TCT). Thus, nitriding is one of the basic TCT processes for wear resistance increase for different steel components and tools. The nitriding process is based on the principles of diffusion saturation; and it forms diffusion layers with gradual structural changes [7, 8].

The purpose of the study consists in the investigation of the nitriding effect on corrosion and wear resistance of Zn coatings and in the examination of properties of modified layers received by combined processes of zinc diffusion metallization with nitriding.

2. Methods of Study

Low-carbon steel 09Mn2Si was used for experimental study (Table 1).

| Table 1 | Chemical composition of 09Mn2Si steel according to the GOST RF 19281-89 |
|---------|--------------------------------------------------|
| Steel grade | ASTM analog | C | Mn | Si | Cr | Ni | Cu | Fe |
| 09Mn2Si | A515-55 | <0.12 | 1.30-1.70 | 0.50-0.80 | <0.30 | <0.30 | <0.30 | Bal. |

Two techniques were applied for surface modification of steels:

A. Diffusion metallization by zinc and nitriding. Slip suspension is the source of diffusion saturation of steel by zinc. It contains zinc powder (25%), quartz sand (70%) as a filler, ammonium chloride \( \text{NH}_4\text{Cl} \) (5%) as a transportation agent, and PVA-glue as a binder. Diffusion saturation of covered specimens occurred in the ammonia atmosphere at 600°C for 4 hours.

B. Zinc coatings application and nitriding. We used a painting technique for the zinc-coatings application. Paint mixtures contained fine-dispersed Zn powder and film-forming substances: organic binder (modified polyurethane) or silicate binder (sodium liquid glass with a density 1.2 g/sm³). Zinc concentration was up to 85 weight % in organic-based mixtures and up to 75 weight % in silicate-based mixtures. Nitriding of painted specimens occurred in the ammonia atmosphere at 540°C for 24 hours.

We used the following methods and tests: metallographic examinations and Auger-spectroscopy for the study of the structure of coatings and diffusion layers, microhardness tests, two methods of corrosion tests: standard salt fog tests in 5%-solution of sodium chloride (NaCl with pH=6.5) and electrochemical corrosion tests in 0.5M solution of sulfuric acid \( \text{H}_2\text{SO}_4 \), and standard wear tests with friction coefficients measurement and detection of volume wear parameter.

3. Results and Discussion

3.1. Microstructure of diffusion layers and nitrided zinc coatings

The combined process of diffusion saturation of steel by zinc and nitrogen forms modified layers with the thickness up to 100 microns. The diffusion layer contains an external surface case enriched by zinc (up to 80–92%Zn directly at the surface) and a transition zone (Fig. 1). The thickness of the surface zone is about 30 microns, and it consists of intermetallic compounds \( \delta-\text{FeZn}_7 \) and \( \Gamma-\text{Fe}_2\text{Zn}_{10} \) in \( \text{Fe}_n(\text{Zn}, \text{N}) \). Specific of the combined metallization-nitriding technique consists in the consumption of previously applied suspension during the saturation process that leads to the diffusion of zinc atoms (from suspension) into the steel substrate, their solution in ferrite, and forming of Fe-Zn intermetallic compounds. Parallel diffusion of nitrogen from the gas atmosphere results in forming of a nitrogen-
enriched solid solution. Since the diffusivity of nitrogen (interstitial element) in metals is significantly higher than the diffusion ability of zinc (substitution element) then nitrogen deeper penetration to the steel substrate is evident. The data in the Table 2 confirms the decreasing concentrations of zinc and nitrogen in different areas of the layer. Thus, we suggest considering the nitrogen-enriched $\text{Fe}_x(N)$ sub-layer as the transition zone; the thickness of this zone is 30…40 microns.

![Figure 1. SEM-image of diffusion layer after combined diffusion saturation by zinc and nitrogen.](image)

| Shooting point | Concentration of elements, [at.%] |
|---------------|----------------------------------|
|               | $N$   | $Zn$   |
| Area 4        | 10.8  | 4.5    |
| Area 3        | 7.1   | 0      |
| Area 5        | 3.3   | 0      |

The diffusion layer has increased microhardness compared to the steel core; this is the result of the formation of intermetallic compounds in the surface zone and of solid solution strengthening in the transition zone. Due to the gradual changes of structure and saturating elements' concentration in the diffusion layer the microhardness depth profile is quite smooth (Fig. 2).

![Figure 2. Microhardness profiles of Zn-N diffusion layer (1) and of nitrided zinc coating (2).](image)

We considered the technique of Zn-coated steel nitriding as an alternation to the combined diffusion metallization-nitriding. The expectation was to receive a similar transition zone under zinc coating due to the diffusion processes activation. The possibility of nitrogen diffusion through Zn
coating was never studied before; moreover, zinc was used as a protective covering against nitriding. After gas nitriding of previously applied zinc coating, the film of about 50 microns thickness is formed at the surface having a visible boundary with steel substrate. Auger-spectroscopy detects both zinc and nitrogen under Zn coating after nitriding (Fig. 3). This confirms that nitriding activates zinc diffusion from the coating and nitrogen diffusion through the coating to the steel substrate.

Figure 3. Auger-profiles of zinc and nitrogen concentrations in nitrided zinc coating and in diffusion zone.

Examination by microspectral X-ray analyses proves that during heating in ammonia Zn penetrates into the steel substrate under the coating (Fig. 4a); besides the analysis detects iron directly in Zn-coating (Fig. 4b) that is the consequence of Fe atoms counter diffusion from the substrate.

Phase composition in areas of the coating and of the diffusion layer was estimated on the basis of detected elements’ concentrations (Table 3). Near the surface the composition of the coating is quite close to ZnO oxide (Spectrum points 1 and 2). The diffusion layer contains Zn in Feα-solid solution (Spectrum points 4 and 5). The diffusion transition layer consists of the “Zn+N solid solution zone” Feα(Zn,N) and of epy “nitrogen solid solution zone” Feα(N). This diffusion layer softens the microhardness profile (see curve 2 in Fig. 2) that promotes better adhesion of the coating. Increased microhardness of the internal part of the layer is the consequence of the solid solution hardening by nitrogen.

Figure 4. SEM-image of nitrided Zn coating (spectrum points 1-3) and the diffusion layer below
(spectrum points 4-7) (a); spectrum example at “Spectrum 3” point (b).

Table 3. Microspectral X-ray analysis in spectrum points according to the Fig. 4

| Spectrum point | Localization | Elements concentration, weight % | Estimated phases |
|----------------|--------------|-----------------------------------|------------------|
| 1              | Coating      | Fe 80.15 Zn - Si - Mn 19.85       | ZnO              |
| 2              | Coating      | 0.89 Fe 82.31 Zn - Si - Mn 16.80  | ZnO              |
| 3              | Coating      | 33.76 Fe 54.57 Zn - Si - Mn 11.67 | ZnO+Feα(Zn)      |
| 4              | Diffusion layer | 93.82 Fe 3.75 Zn 1.56 Mn 0.87    | Feα(Zn)          |
| 5              | Diffusion layer | 95.67 Fe 1.85 Zn 1.31 Mn 1.16    | Feα(Zn)          |
| 6              | Steel substrate | 97.88 Fe 0.99 Zn 1.14             | Feα              |
| 7              | Steel substrate | 97.98 Fe 0.90 Zn 1.12             | Feα              |

3.2. Corrosion tests results

Electrochemical corrosion tests by measuring of potentiodynamic curves (PD) and passivation curves detect parameters of local corrosion: stationary corrosion potential \( E_c \) (the potential of anodic dissolution), and anodic current density of corrosion \( i_{\text{MAX}} \). The lower is corrosion current the better is the protection. Both methods of surface treatment of Zn metallization and nitriding increase the corrosion resistance of steel in a diluted saltwater solution: the decrease of \( i_{\text{MAX}} \) value indicates this (Table 4).

Table 4. Electrochemical corrosion parameters of 09Mn2Si steel in 16.5 g/l NaCl water solution

| Treatment                  | \( E_c \), mV | \( i_{\text{MAX}} \), \( \mu \text{A}/\text{sm}^2 \) |
|----------------------------|---------------|-----------------------------------------------|
| As-received                | -412          | 12.37                                         |
| Nitrided Zn coating        | -460          | 0.58                                          |
| Diffusion saturation Zn+N  | -403          | 3.7                                           |

Salt fog chamber tests have shown that combined diffusion saturation of the steel by zinc and nitrogen increase its resistance against corrosion in salty atmospheres: the protection time parameter \( \tau \) is higher, and the damage area parameter \( S \) is less compared to the parameters of untreated samples (Fig. 5).

Figure 5. Results of salt fog chamber 36-hour tests for as-received steel specimens and for specimens after Zn+N diffusion saturation.

The corrosion resistance of steel in acid solution after diffusion saturation by zinc and nitrogen is less than the resistance of as-received Zn coating: current density \( i_{\text{MAX}} \) value is about 3 times higher.
(Table 5). At the same time, the passivation interval $E_{p}^* - E_{p}^s$ remains about the same as for the steel with Zn coating (Fig. 6). Passivation parameters of Zn+N saturated steel are much better comparing to the parameters of the steel nitrided in the same process mode (Table 5).

**Table 5.** Electrochemical corrosion parameters of 09Mn2Si steel in 0.5M solution of sulfuric acid $H_2SO_4$.

| Treatment                              | $E_{p}^* - E_{p}^s$, mV | $i_{max}$, $\mu A/cm^2$ |
|----------------------------------------|-------------------------|--------------------------|
| Zn coating                             | 1106                    | 55                       |
| Diffusion saturation Zn+N at 600°C/NH$_3$, 4 h | 1089                    | 157                      |
| Nitriding at 600°C/NH$_3$, 4 h         | 54                      | 26                       |

**Figure 6.** Passivation curves of 09Mn2Si steel with Zn coating (a), and after Zn+N diffusion saturation (b).

In contrast to the method of Zn+N diffusion saturation, the technique of nitriding of Zn coatings protects the steel both in salt and acid mediums. Table 4 shows that nitriding moves anodic dissolution potentials of Zn coatings $E_c$ toward the higher negative values, and significantly decreases the anodic current density.

The corrosion resistance of nitrided zinc coatings depends on the parameters of the coatings: thickness, initial zinc concentration, and type of a binder. For example, Zn coating on the basis of silicate binder is more resistant than on the basis of organic binder; and double-layered coatings are more resistant than single-layered. Nitriding shades down these contradictions (Table 6).
Table 6. Electrochemical corrosion parameters of Zn coatings on 09Mn2Si steel in 0.5M solution of sulfuric acid H$_2$SO$_4$

| Zn-coating parameters       | $E_c$, mV | $i_{\text{max}}$, $\mu$A/sm$^2$ | As-received | Nitrided | As-received | Nitrided |
|-----------------------------|-----------|---------------------------------|-------------|----------|-------------|----------|
| Silicate binder, 1-layered  | -486      | -627                            | 11.32       | 2.89     |              |          |
| Organic binder, 1-layered   | -452      | -690                            | 26.23       | 3.14     |              |          |
| Organic binder, 2-layered   | -452      | -630                            | 16.21       | 2.48     |              |          |

3.3. Wear tests results
Wear tests have shown that combined processes of nitriding with Zn metallization increase wear resistance of steel. Both studied processes provide quite similar volumetric wear indicators $W$, which are about 5 times less compared to the wear rate of Zn coating without nitriding (Table 7). The process of Zn+N diffusion saturation improves the time profile of friction coefficient $\eta$ and decreases $\eta_{\text{min}}$ and $\eta_{\text{max}}$ values (Fig. 7).

Table 7. Wear indicators of steel samples after different treatment modes

| Treatment                     | $\eta_{\text{min}}$, $V$, mm$^3$ | $\eta_{\text{max}}$, W, mm$^3$/h |
|-------------------------------|----------------------------------|----------------------------------|
| Zn-filled coating             | 0.006 0.330                      | 0.650 1.50                       |
| Nitriding of Zn coating       | 0.113 0.056                      | 0.895 0.26                       |
| Zn-N diffusion saturation     | 0.004 0.066                      | 0.320 0.30                       |

Figure 7. Time profiles of friction coefficient for steel samples: 1 – with Zn coating; 2 – with nitrided Zn coating; 3 – after Zn+N diffusion saturation.

4. Conclusions
Combined diffusion saturation of steel by zinc and nitrogen may be a good alternative to zinc-filled coatings for usage in conditions of corrosion and wear. Diffusion layers have a proper structure with transition zone/internal nitriding zone of significant thickness. This zone has increased zinc and
nitrogen concentration due to the diffusion of the elements under the surface layer. The diffusion layer with transition zone has a gradual microhardness profile that decreases residual stress at the boundary with the substrate steel and promotes adhesion improvement. Zn+N diffusion layers in low-carbon steel have increased wear resistance and reduced friction coefficients comparing to the parameters of Zn coatings either nitrided or not. Steel with such layers shows significant corrosion resistance increase in salt fog in comparison with untreated steel. On the other hand, for reasons of maximum improvement of electrochemical corrosion parameters Zn coatings remain more effective.

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