Combined thermochemical treatment of steel construction parts to increase their corrosion resistance

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Abstract. Electrochemical corrosion of construction parts made of structural steels appears due to different electrochemical potentials (ECP) of contacting materials. The values of ECP of carbon steels may be more or less compensated by forming of alloyed layers or coatings by methods of thermochemical treatment (TCT). The following combinations of TCT were examined for surface modification of steels: (a) application of zinc coatings by a method of cold zinc-plating with subsequent classical gas nitriding in ammonia; (b) joint diffusion saturation by zinc and nitrogen; (c) joint diffusion saturation with chromium and nickel. Metallographic and microhardness methods were used for the study of modified layers and coatings. Strengthened layers with a thickness up to 140…150 microns were formed in low-carbon steels after nitriding of zinc coatings at 540°C for 24 hours, and after combined TCT with multicomponent saturation by Cr+Ni at 1000°C for 7 hours. Both methods of TCT increase the corrosion resistance of low-carbon steels and low-alloyed steels. Corrosion products examination in 5% NaCl salt fog shows that the dissolution of nitrided Zn coating and formation of corrosion products slow down with the increase of zinc concentration in the coating.

1. Introduction
Elements of metal constructions such as steel bridges carcass, parts of movement joints, fixings (clinchers, bolts or bolt-rivets) work in the corrosive environment of atmosphere, precipitations, humidity, and condensed moisture that leads to the development of corrosion processes. Corrosion of bridgework parts is the main reason for their lifetime decrease: it reduces mechanical properties of steels, causes cracks in concrete, and its exfoliation from a metal carcass.

In many cases, the main reason for steel parts corrosion consists in the difference of electrochemical potentials of contacting metals in a couple “bolt – girder”. This effect is a consequence of steels’ different chemical composition. As a rule, fixing elements are made of low-carbon steels (0.1…0.2% С), whereas constructive elements of bridges are made of alloyed steels containing chromium, silicon, nickel, and copper [1].

Two ways are applicable for corrosion resistance increase of carbon steels working in contact with alloyed steels: deposition of protective coatings or forming of alloyed layers with electrochemical potentials close to ECP of contacting steel.

Zinc-plating is one of the most popular techniques for fixing elements protection against corrosion [2, 3]. Zinc coatings provide two mechanisms of corrosion protection: cathodic (electrochemical)
mechanism and barrier mechanism similar to the protection mechanism of painted films [4, 5]. The application of protective coatings leads to the formation of a sharp boundary with a steel substrate. Low adhesion of coatings decreases the resistance of bolt-rivets to mechanical stresses during its mounting. Usage of such coatings for fixing elements may cause their exfoliation during gripping or press-fitting.

Techniques of thermochemical treatment (TCT) using the principles of diffusion saturation form modified layers in steels with gradual structural changes give smooth microhardness depth profiles [6]. To a certain extent, the microhardness gradient represents the residual stress differential through the layer. Therefore, the smooth microhardness profile of a layer is a factor of its good adhesion. It was shown [7] that using TCT for steels with coatings gives the opportunity of their adhesion strength increase due to the transition diffusion layer forming at the interface of a coating with steel substrate.

Diffusion methods of surface alloying by metals are alternative to the coatings’ application. TCT techniques allow providing joint saturation of steels by several metals or by metals in combination with non-metal elements, such as nitrogen [8].

The objective of this paper consists in the study of processes of thermochemical treatment for forming the strengthened corrosion-resistant coatings and layers in steels traditional for bridge metal constructions.

2. Experimental Methods

For the experimental study, specimens from three types of steel were prepared (table 1): 10x10x1 mm plates for metallographic examinations, 20x40x5 mm plates for electrochemical tests, and cylinders with the diameter of 4 mm for corrosion tests in a salt fog. All specimens were annealed at 850°C, mechanically grinded, and the surface was degreased.

| Ref. No. | %C    | %Mn | %Si | %Cr | %Ni | %Cu | S_max | P_max |
|----------|-------|-----|-----|-----|-----|-----|-------|-------|
| A        | 0.14– 0.22 | 0.4– 0.65 | 0.15– 0.3 | <0.3 | <0.3 | <0.3 | <0.05 | <0.4  |
| B        | 0.07– 0.14 | 0.35– 0.65 | 0.17– 0.37 | <0.15 | <0.25 | <0.25 | <0.04 | <0.035 |
| C        | 0.12– 0.18 | 0.40– 0.70 | 0.40– 0.70 | 0.60– 0.90 | 0.30– 0.60 | 0.20– 0.40 | <0.035 | <0.035 |

Three experimental TCT processes were studied:

Nitriding of zinc coatings. Zinc coatings were applied to the steel substrate by painting with a primer containing finely dispersed Zn-powder and film-forming substance: organic binder (modified polyurethane), or silicate binder (potassium water glass with the density 1.2 g/sm³). Zinc concentration varied up to 85% in organic-based primer and up to 75% in silicate-based primer. The coatings were dried for 48 hours. Nitriding of specimens with Zn coatings was carried out in ammonia atmosphere at a temperature of 540°C for 24 hours.

Joint diffusion saturation by zinc and nitrogen. Specimens were covered by slip suspension containing metal zinc powder (25%), quartz sand (70%) as a filler, ammonium chloride NH₄Cl (5%) as a transportation agent, and PVA-glue as a binder. Diffusion saturation was carried out in ammonia at temperatures of 600…1000°C during 1…4 hours.

Multicomponent diffusion surface alloying. Specimens were covered by slip suspension containing 50% of alloying metal powder (chromium, nickel, or their mixtures), 50% of ammonium chloride NH₄Cl, and zapon-varnish as a binder. Diffusion saturation was carried out in the induction furnace blown by CO₂ protective gas at temperatures of 900°C and 1000°C during 1…7 hours.

Metallographic examinations of coatings and diffusion layers were made in the AXIOVERT 25CA microscope. Microhardness tests were carried out by the PMT-3 measurer.

Corrosion tests of specimens were conducted in a salt fog chamber Ascott S120iP; the 5%-solution of sodium chloride (NaCl with pH=6.5) was sprayed inside the chamber by compressed air. The testing temperature was 35°C, and humidity was 95…100%. Specimens were placed in the chamber below the spraying level that excluded the direct action of salt solution. The salt fog was condensed at
specimens’ surface with the constant rate; testing time was from 24 to 240 hours. The results of the tests were estimated visually by examination of corrosion products.

Electrochemical corrosion tests were made consisting of tracing the anodic and potentiodynamic (PD) curves in the direct passage and the reverse passage. The solution of sulfuric acid (0.5M H₂SO₄) was used as a testing environment. The following parameters of the corrosion process were determined: electrochemical potentials of the start and the end of passivation (Eₚₛ and Eₚₑ), and the passivating interval (Eₚₑ - Eₚₛ). Parameters for evaluation of local corrosion protection properties of coatings were measured: the stationary potential of free corrosion Eᵋ, i.e. the potential of the beginning of the anodic dissolution of metal and maximum value of anodic current density iₘₐₓ. The higher the negative value of Eᵋ is and the lower the value of iₘₐₓ is, the better the corrosion resistance of a tested metal is.

3. Results and discussion

3.1. Consequent Process: Nitriding of Zinc Coatings

Visible coating 50 microns thick with maximum microhardness is formed in low-carbon steel after nitriding of previously applied zinc coating (figure 1). Gas nitriding of specimens of both carbon steel and low-alloyed steel with zinc coatings forms modified layers with gradually decreasing microhardness profile. The diffusion sub-layer of about 100 microns thickness was identified as the internal nitriding zone containing elevated concentrations of zinc and nitrogen in ferrite. Increased microhardness of this zone compared to the substrate’s microhardness is the consequence of solid solution strengthening.

![Figure 1. Micrograph: x500 (a) and microhardness profile (b) of nitrided steel “A” with Zn coating.](image)

Both alloyed steel and carbon steel with nitrided zinc coatings have increased corrosion resistance in the low-salt environment. It was experimentally shown that the corrosion velocity of nitrided steel “A” with a zinc coating (>80%Zn in the primer) in the 5%-NaCl solution is about 0.25 mm per year that is several times less compared to the annual corrosion rate of untreated steel.

The corrosion resistance of nitrided zinc coatings depends on the initial thickness of a coating, on zinc concentration in the primer, and the type of a binder. Nitrided coatings with different zinc concentrations demonstrate different progress of the corrosion process during the tests in the salt fog chamber. Dissolving the coating with 45%Zn was observed after about 100 hours of tests. After 240 hours of tests, the square of dissolved coating reached 10% of the surface: centers of “red corrosion” of iron appeared (figure 2). The coating with 65%Zn remained intact after 240 hours of tests; in this case, the products of the so-called “white corrosion” of Zn plays as the additional protector.
Nitriding increases the resistance of zinc coatings against electrochemical corrosion in 0.5M H₂SO₄ solution (figure 3). Increase of the $E_c$ negative value and decrease of the $i_{max}$ value are observed compared to the parameters for un-nitrided organic-based coating. Minimum values of $i_{max}$ are measured for nitrided double-layer zinc coating. For nitrided silicate-based zinc coating the value of $i_{max}$ decreases 4 times, whereas some reduction of $E_c$ parameter is observed. Corrosion parameters of low-alloyed steel “C” after combined treatment have similar values for both types of film-former. After the most effective combination of cold zinc-plating with nitriding, the 25-time decrease of the $i_{max}$ parameter is achieved compared to the value for the as-received specimen without treatment. The optimum process provides the decrease of the current density value $i_{max}$ more than 6 times compared to this parameter for the steel after hot zinc-plating.

3.2. Joint Diffusion Saturation with Zinc and Nitrogen

The processes of joint saturation of steels with zinc and nitrogen form modified layers with diffusion zones. Thus, after saturation during 4 hours at 600°C, a modified layer was received in low-alloyed steel “C” with a thickness of about 140 microns. The layer consists of the external zone (40 μm) enriched by zinc at the surface up to 86%Zn, of the intermediate zone of nitrides (30...40 μm), and of the internal nitriding zone – solid solution of Zn and N in ferrite with nitrides precipitations (figure 4). Such structural changes in the modified layer provide the flowing microhardness depth profile with a slight maximum corresponding to the nitrides interlayer. Achieving strengthening is higher than the hardening of nitrided zinc coatings (figure 1).
The increase of the diffusion process’ temperature leads to some significant changes in the structure of modified layers. After the treatment at 1000°C the surface layer of 50 microns is formed without any transition zone (figure 5). The absence of the transition zone explains sharp microhardness decline under the layer. The increased volume fraction of pearlite is observed at the boundary with the layer; this may be caused by carbon migration out of the layer into the steel core. High temperatures of saturation activate zinc diffusion; this decreases the diffusion ability of nitrogen and reduces the depth of its penetration.

Electrochemical tests show that steel “C” after high temperature diffusion saturation by zinc and nitrogen is not passivized in the H₂SO₄ solution (figure 6).

3.3. Multicomponent Diffusion Surface Alloving
For the forming of coatings on carbon steels with protective properties comparable to the corrosion resistance of alloyed steels, the processes of diffusion saturation by chromium and nickel were applied. Taking into account the presence of a nitrogen-containing component (ammonium chloride) in slip suspensions, we can suppose the parallel nitrogen diffusion into the ferrous matrix at high
temperatures of such processes.

The temperature of 900ºC was determined as the lowest temperature for effective diffusion metallization. It was experimentally found the possibility of suitable diffusion layers forming at the temperature 1000ºC and the process duration up to 7 hours. Under these conditions, after joint diffusion saturation by chromium and nickel of steel “B”, the modified layer has a thickness of 150 microns. Two zones are observed in the layer (figure 7): surface compound zone (70…80 μm) with maximum strengthening due to the high volume fraction of uniaxial nitride particles and the internal sub-layer of austenite containing lamellar precipitations typical of ferrous nitrides (γ'-phase). Microhardness increase is the consequence of joint strengthening mechanisms: solid solution hardening and dispersion strengthening by nitrides. Microhardness falls gradually corresponding to the reduction of saturating elements concentrations with the depth.

Figure 6. PD-curve of steel “C” after Zn+N diffusion saturation in ammonia (900ºC/4 h) tested in 0.5M solution of H2SO4.

Figure 7. Micrograph: x500 (a), and microhardness profile (b) of steel “B” after Cr+Ni diffusion saturation (1000ºC, 7h).

Diffusion metallization by chromium and nickel expands the passivating interval of low-carbon steel “B” to the level of this parameter for the alloyed steel “C” (table 2). A comparison of electrochemical parameters shows that corrosion resistance of the carbon steel after diffusion Cr+Ni saturation is higher than corrosion resistance of the alloyed steel as after nitriding and after combined saturation by zinc and nitrogen.
Table 2. Electrochemical parameters of investigated steels in 0.5M solution of H$_2$SO$_4$

| No. | Treatment | $E_{p^s}$, mV | $E_{p^e}$, mV | $E_{p^e}$ - $E_{p^s}$, mV |
|-----|-----------|---------------|---------------|-------------------------|
| C-1 | as-received| 529           | 1635          | 1106                    |
| C-2 | Nitriding: 540ºC/24 h, NH$_3$ | 432           | 486           | 54                      |
| C-9 | Zn+N-saturation: 900ºC/4 h, NH$_3$ | 774           | 963           | 189                     |
| B-1 | Cr+Ni-saturation: 900ºC/6 h, NH$_4$Cl | 491           | 1571          | 1080                    |

4. Conclusion

Forming the strengthened modified layers in low-carbon steels and low-alloyed steels is experimentally determined as the result of combined TCT processes: nitriding of steels with zinc coatings, joint diffusion saturation by zinc and nitrogen, and joint diffusion saturation by chromium and nickel.

An alloyed Cr+Ni layer in carbon steel shows better corrosion resistance in the 0.5M H$_2$SO$_4$ solution compared to the corrosion resistance of steel after classical nitriding and joint diffusion saturation by zinc and nitrogen. Electrochemical parameters of surface alloyed carbon steel are close to the parameters for low-alloyed steel.

The corrosion resistance of nitrided zinc coatings increases in a salt solution (NaCl), in salt fog, and slightly acidic environment due to the synergy of cathodic and waterproofing protection mechanisms. Full-scale tests of fixing parts in metal construction of the overpass have shown that nitrided bolts keep coatings integrity longer than the components with standard hot-plated coatings.

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