Influence of the pulsed plasma treatment on the corrosion resistance of the low-alloy steel plated by Ni-based alloy

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Abstract. This paper presents investigation results of the influence of high temperature pulsed plasma flows (HTPPF) treatment on the corrosion resistance of low-alloy steel 0.2C-Cr-Mn-Ni-Mo cladded by the rapidly quenched nickel-based alloy. A technique that allows obtaining a defect-free clad layer with a good adhesion to the substrate was developed. It is shown that the preliminary treatment of steel samples by nitrogen plasma flows significantly increases their corrosion resistance in the conditions of intergranular corrosion test in a water solution of sulfuric acid. A change of the corrosion mechanism of the clad layer from intergranular to uniform corrosion was observed as a result of sub-microcrystalline structure formation and homogeneous distribution of alloying elements in the plasma treated surface layer thus leading to the significant increase of the corrosion resistance.

1. Introduction
Reliability, durability and performance of parts and components of various mechanisms are largely determined by their surface properties. In particular, modification of only the surface layers of products by pulsed laser, electron, ion or plasma sources is often sufficient and cost-effective for improving their corrosion and wear resistance [1-5]. Therefore, an important task is to develop new methods of obtaining the targeted microstructure and properties of the surface layers of materials.

Carbon and low-alloy steels are widely used as a structural material. However, they tend to intensive corrosion damage due to various corrosive environments, which makes the use of these steels in parts and components of systems economically unprofitable. Therefore, at this time, an urgent task is to improve the corrosion resistance of these materials for use in various branches of industry. A technique of improving the corrosion resistance of the low-alloy steels by their pre-cladding with high quenched solder alloys and subsequent treatment by high-temperature pulsed plasma flows (HTPPF) is presented in this work.

2. Experimental procedure
Low-alloy steel 0.2C-Cr-Mn-Ni-Mo was used as the substrate material for cladding. Samples were made in the form of disks with a diameter of 20 mm and a thickness of 5 mm. The surface of the disk samples was mechanically polished to a roughness Ra=0.4. Thin tapes of a thickness about 35-50 μm were used for cladding of the samples. To obtain the sub-microcrystalline structure tapes were produced by rapid quenching from the melt of the nickel-based alloy (Ni (base) - 18% Cr - 10% Si).

The chosen method of cladding was the following. A thin foil of the fine-crystalline nickel-based alloy was welded to the disk substrates by spot welding along the disk periphery (figure 1). On a next
step, samples with a welded tape were heated to a temperature of 1150 °C in a vacuum furnace at a residual pressure not higher than 6.5 \times 10^{-3} \text{ Pa} and subsequently cooled at the different regimes: 1 - "sawtooth" cycle (heating to 1150 °C → Cooling); 2 - heating with the exposure (Δt) for 1-5 min at the maximum heating temperature of 1150 °C followed by cooling.

![Image](image.png)

**Figure 1.** Method of nickel based alloy cladding of steel.

Samples were treated by means of the Z-pinch type plasma installation "Desna-M" [6] by high-temperature pulsed nitrogen plasma flows in various regimes. The energy density (Q) of plasma flows ranged from 22 to 31 J/cm² and their power density from 1.1 \times 10^6 to 1.5 \times 10^6 W/cm². The number of pulses was \( N = 2 \) for each cycle of irradiation. The pulse duration was 20 μs.

Intergranular corrosion tests were performed using the method based on a Russian state standard GOST 6032-2003. The samples were exposed for 8 h in a boiling aqueous solution containing 120 g/dm³ of CuSO₄ and 120 cm³/dm³ of H₂SO₄. The tests were carried out in a flask with a reflux condenser. Copper shavings were located at the bottom of the flask to create a redox potential of +0.1 V. The samples were placed into the flask so as to avoid any contact with each other.

The nature and level of corrosion interaction were determined by ZEISS EVO 50 XVP (Zeiss, Germany) scanning electron microscope (SEM) using cross-section samples and by mass loss of the sample.

### 3. Results and discussion

Microstructure studies of plated samples showed (figure 2, a) that the surface microstructure was fairly homogeneous. Regardless of the cladding regimes, three distinct zones with different phase contrast were observed in all the samples: equiaxed grains with a mean size of about 20 μm (1), an intergranular layer along the grain boundaries (2) and faceted inclusions (3) of various shapes with sizes varied from 2 to 10 μm. SEM study of the microstructure of plated samples cross-sections (figure 2, b) showed the formation of a clad layer with relatively uniform thickness (~ 35-40 microns) on the entire surface of the sample. During the cladding process diffusion bonding of cladding alloy with the substrate occurs thus leading to the good adhesion of the clad layer to the substrate without the formation of microcracks and pores.

The results of the X-ray microanalysis (Table 1) showed that the equiaxed grains and the intergranular layer are nickel based solid solution containing different amount of chromium, iron and silicon. The atomic concentration of silicon in the intergranular layer is higher and chromium concentration is lower than in the grains. The fine-dispersed inclusions are carbosilicides of chromium and nickel Cr₃Ni₂SiC. It should be noted that the formation of precipitates is observed both in the bulk of grains and along their boundaries. The quantity of such precipitates increased more than twice with the increase of duration of cladding process (the exposure time at the maximum temperature varied from 1 to 5 min). At that, carbosilicide precipitates were predominantly located along the grain boundaries. Quantitative analysis of the SEM micrographs showed that the most homogeneous structure with a relatively low density of formed precipitates and equiaxed grains of similar sizes were observed at the exposure time during cladding of 1 and 3 min.
Figure 2. The surface (a) and cross-section (b) microstructure of steel cladded by nickel-based alloy ($\Delta t = 1$ min).

**Table 1** – Elemental composition of steel 0.2C-Cr-Mn-Ni-Mo samples cladded by STEMET1305.

| Area of the element analysis (according to Fig. 2, b) | C   | Si    | Cr   | Fe   | Ni   |
|---------------------------------------------------|-----|-------|------|------|------|
| Initial STEMET 1305 tape                          | -   | 10    | 18   | -    | Bal. |
| 1 – grain                                         | < 0.5 | 6.67  | 16.23| 9.73 | Bal. |
| 2 – intergranular layer                           | < 0.5 | 15.23 | 3.43 | 3.30 | Bal. |
| 3 – precipitates                                  | 5.28 | 8.64  | 47.63| 1.33 | Bal. |

The treatment of cladded samples by nitrogen plasma results in melting of their surface layer and significantly smoothers the surface relief. At that, traces of the original microstructure of clad samples are practically not observed (figure 3, a). At higher magnification a submicrocrystalline ordered cellular structure with a typical cell size about of 100-200 nm (figure 3, b) is observed in the clad samples for all the regimes of cladding. However, intensive cracking of the surface of samples cladded at the maximum temperature for $\Delta t = 5$ min took place (figure 4, a). The cracking is due to the temperature gradient, different coefficients of thermal expansion of various phases formed during the cladding and subsequent radiation heating and rapid heating and subsequent cooling of the surface layer during plasma treatment.

Figure 3. The surface microstructure of clad ($\Delta t = 1$ min) steel samples after the treatment by nitrogen pulsed plasma flows ($Q = 22$ J/cm$^2$).
SEM investigations of finely polished treated samples have shown (Figure 4, b) that the origin and the development of cracks occur mainly in the grain boundary interlayer (2), i.e. in areas in which in the initial (untreated by HTPPF) state there is an increased content of silicon, as well as along the brittle precipitates of chromium and nickel carbosilicides (3), while the equiaxed grains themselves (1) are not subjected to cracking. The surface cracking at $\Delta t = 1$ and 3 min is not observed because of decreased number of brittle phases.

![Figure 4](image)

**Figure 4.** The surface microstructure of clad ($\Delta t = 5$ min) steel samples after the treatment by nitrogen pulsed plasma flows ($Q = 22$ J/cm$^2$).

Microstructure analysis of the clad samples treated by HTPPF showed that the degree of decreasing the surface relief increased with decreasing the holding time of samples at the maximum temperature. The most smooth relief is observed for samples cladded using the regime of $\Delta t = 1$ min. The energy density of plasma flows and the total energy release also influence the smoothing of the initial surface relief and the uniform mixing of elements after plasma treatment. Studies of clad samples ($\Delta t = 1$ min) treated by plasma flows using the regime of 2 pulses in a cycle with a sequential increase of the flow energy density ($Q_1 = 22 + Q_2 = 25 + Q_3 = 28 + Q_4 = 31$ J/cm$^2$) showed that the most homogeneous and practically defect-free surface layers are formed after sequential treatment by 6 pulses ($Q_1 + Q_2 + Q_3$, $N = 2$). Whereas after 4 irradiation cycles ($Q_1 + Q_2 + Q_3 + Q_4$, $N = 2$), there is a formation of local cracks and micro pores in the surface of samples which can significantly decrease the corrosion resistance.

**Table 2** – Elemental composition of samples of steel 0.2C-Cr-Mn-Ni-Mo cladded by STEMET1305 after HTPPF treatment.

| HTPPF treatment regime | Main elements, wt. % |
|------------------------|----------------------|
| $Q_1=22$ J/cm$^2$      | C: $<0.5$ Si: $8.8 \pm 1.7$ Cr: $13.4 \pm 3.3$ Fe: $8.8 \pm 1.6$ Ni: Bal. |
| $Q_1=22$ J/cm$^2 + Q_2=25$ J/cm$^2+ Q_3=28$ J/cm$^2$ | C: $<0.5$ Si: $8.2 \pm 0.3$ Cr: $13.6 \pm 0.5$ Fe: $10.3 \pm 0.40$ Ni: Bal. |

Microstructure studies of the samples after corrosion tests have shown that the initial samples of steel are exposed to significant corrosion damage that is quite uniform over the sample surface. Treatment of the sample surface by HTPPF flows decreases the corrosion rate of samples by up to 3-10 times depending on the treatment conditions. However, corrosion interaction with the initial material matrix begins to intensively occur after destruction of a thin (~10 $\mu$m) modified layer. More detailed results of the effect of plasma treatment on the corrosion resistance of steels were reported earlier.
Corrosion tests were carried out for two types of clad samples (without any treatment): those obtained using the "sawtooth" regime and samples held at the maximum heating temperature for 1-3 min. In all cases there was a significant corrosion damage of the surface layer (figure 5, a), the corrosion of the cladded layer occurred predominantly along the intergranular layer (figure 5, b and c). In addition, delamination of the clad layer and formation of long cracks in it (figure 5, c) took place due to penetration of an aggressive medium to the substrate through the clad layer.

![Figure 5](image)

**Figure 5.** Microstructures of surface (a, b and e) and cross-sections (c, d and f) of clad samples after corrosion tests: without (a-c) and after the HTPPF treatment (d-f).

Studies of samples cladded and treated by plasma flows with $Q_1 = 22 + Q_2 = 25 + Q_3 = 28$ J/cm$^2$ after corrosion tests showed that, in general, only edge areas of the samples were exposed to damage, i.e. the interface between the clad layer and the substrate. At that, the modified layer preserves undamaged on the surface of samples (figure 5, d) and only local areas of corrosion damage (figure 5, e) were observed. The estimated difference in levels between the modified clad surface and the corroded area of the initial steel at the sample edge is ~ 200 $\mu$m (figure 5, f) which corresponds to 25 $\mu$m/h corrosion rate for initial steel and therefore clearly shows the significant corrosion protection effect of the plasma treated clad layer.

These results allow us to make the following assumptions about the mechanism of the corrosion resistance increase of the plated and treated by HTPPF samples. Corrosion of the cladded samples occurs mainly as a result of damage of the clad layer due to selective dissolution of intergranular layer. Penetration of the aggressive medium to the substrate leads to the destruction and exfoliation of the cladding layer. Corrosion of plasma modified cladding layer occurs by a mechanism different from the corrosion destruction of untreated samples. As shown above, plasma treatment leads to the formation of a homogeneous nanostructured layer with uniform distribution of the elements and this layer contains ~ 13.5 wt. % Cr (table 2). Creating such a layer prevents intergranular corrosion. Also, as is known, alloying nickel alloys with chromium (typically 10-25%) provides high corrosion resistance due to the formation of the protective oxide film, and thus prevents destruction of the material in contact with a corrosive medium.
4. Conclusions
A technique of cladding of the samples of low-alloy steel 0.2C-Cr-Mn-Ni-Mo by rapidly quenched tape of STEMET 1305 nickel-based alloy has been developed. It allows obtaining of a 35-40 μm thick clad layer which is sufficiently uniform in microstructure and the elemental composition and has a good adhesion to the substrate.

It was found that the treatment of the cladded samples by pulsed plasma flows leads to the smoothing of the surface relief and to the formation of sub-microcrystalline cellular structure with a mean size of cell about 150-200 nm and uniform distribution of alloying elements.

It was found that the cladding of low-alloy steel samples by nickel-based alloy STEMET 1305 followed by pulsed plasma flows treatment significantly reduces the corrosion rate compared to untreated samples. The optimal mode of cladding and plasma treatment for improving the corrosion resistance of low-alloy steel was chosen. At the same time there is a change of corrosion mechanism from intergranular to uniform corrosion that caused by microstructure and phase composition changes in the surface layers after plasma processing.

Acknowledgements
This work was performed within the framework of the Center of Nuclear Systems and Materials supported by MEPhI Academic Excellence Project (contract № 02.a03.21.0005, 27.08.2013).

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