# Influence of High Temperature Pulsed Plasma Flows Treatment on the Corrosion Resistance of Steels

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**Abstract – The results on investigations of the influence of a treatment by high temperature pulsed gas plasma flows (HTPPF) on the corrosion of steels and zirconium alloys in various aggressive environments are presented. The corrosion resistance of low-alloy and corrosion-resistant steels, which are applied in nuclear power, exposed to intergranular corrosion tests using the AM method, in a liquid lead flow, under interaction with the simulators of fission products (cesium, tellurium and iodine), as well as the corrosion resistance of zirconium alloys in a water-steam environment were investigated.**

**The preliminary treatment by HTPPF has been found to result in increasing the corrosion resis-tance of all the investigated steels. At that, a change of the corrosion character from intergranular to frontal is observed. As to the zirconium alloys, the influence of plasma treatment on their corrosion is insignificant.**

## 1. Introduction

One of the main problems of the modern materials science is increasing the corrosion resistance of structural and functional materials of various destinations. Taking that into consideration, investigations of the influence of pulsed plasma treatment on the corrosion of a number of steels and alloys in various aggressive environments were carried out.

The HTPPF preliminary treatment was performed on a Z-pinch type DESNA-M installation [1]. The main variable parameters of the treatment were the charging voltage of a capacitor bank (U=10–18.5 kV) determining the energy density of an inci-dent plasma flow, the number of irradiation pulses $N$=3–21, and the kind of plasma-forming gases (helium, nitrogen, and oxygen). The pulse duration was ~15 $\mu$s for all the experiments.

## 2. Intergranular corrosion tests

Intergranular corrosion tests were carried out by the AM method according to GOST (State Standard) 6032-89V; the samples were held for $\tau$= 24 h in a boiling aqueous water solution containing 130 g/dm$^3$ $CuSO_4$ and 120 cm$^3$/dm$^3$ $H_2SO_4$. The character and the extent of the corrosion interaction were determined by metallography using transverse sections.

The following structural steels were studied: 25Kh1MF, 35Kh, 38Kh2MYuA, St.20, 14Kh17N2, and 08Kh18N10T. The samples for corrosion tests were produced from plates 4 mm thick and had a cross section of 15×25 mm$^2$, as well as from rods in the form of disks 12 mm in diameter and 4.5 mm thick. Before the irradiation, these samples were preliminarily annealed at 600 °C for 2 h to remove residual stresses arising under preparation of the samples.

The influence of the kind of a plasma-forming gas (helium, nitrogen, argon, and air) on the corrosion of carbon and low-alloy steels, at a constant charging voltage of a capacitor bank $U$=18 kV and a constant number of irradiation pulses $N$=3 was investigated at the first stage. Results of the corrosion tests show that the low-alloy steels in the initial state undergo intense corrosion [2]. In case of a preliminary treatment by plasma flows, the total (two-sided) thinning of the 38Kh2MYuA steel samples decreased from ~1.0 to 0.35 mm, depending on the composition of plasma. Since only one side of the samples was irradiated by HTPPF, the corrosion rate V of the treated steels is:

$$V=(L-L_0/2)/t,$$

where: $L$ and $L_0$ are the total thinning of the treated and initial sample, respectively.

The average corrosion rate (for $\tau$=24 h) of the modified steels was estimated to decrease from ~21.0 to 3.3 and 6.7 $\mu$m/h during the treatment by the argon and air plasma, respectively. In this case, the total (two-sided) thinning of the samples treated by the nitrogen and helium plasma was ~0.35 and 0.45 mm, respectively, which indicates virtually total inhibition of corrosion from the modified surface. The influence of the plasma type on the extent of increasing the corrosion resistance of steels is apparently due to a different change of the phase composition of modified steels. The X-ray phase analysis showed that after the treatment of the low-alloy steels by HTPPF of various compositions, two phases – quenched martensite ($\alpha'$–Fe) of the tetragonal lattice and retained austenite of the face-centered cubic lattice were observed in each sample. At that, the content of the retained austenite, that underwent higher intergranular corrosion, increases for the following sequence of plasma-forming gases: nitrogen, helium, argon, and air. It is in a full agreement with the obtained results on increasing the corrosion resistance of the low-alloy steels modified by plasma flows. The best results were obtained when flows of nitrogen and helium plasma were used.

Metallographic investigations of the surface and the transverse sections of samples made from 14Kh17N2 and 08Kh18N10T corrosion-resistant steels after the corrosion tests showed (Fig. 1) that in contrast to the low-alloy steels they didn't undergo a significant braking.

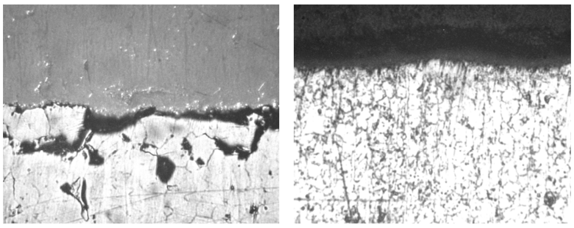

Fig. 1. Microstructure (×500) of the transverse sections of the 08Kh18N10T steel samples after corrosion tests: (a) initial state; (b) preliminary treatment by HTPPF ($U$=16 kV, $N$=3)

As a whole, the 14Kh17N2 ferritic-martensitic steel had a higher corrosion resistance in comparison with that of the 08Kh18N10T austenitic steel, which is in a good agreement with the literature data. The HTPPF preliminary treatment resulted in a significant (by 5–8 times) increase of the corrosion resistance of the steels; the maximum depth of the corrosion interaction zone decreased from 63 to 8 $\mu$m and from 31 to 6 $\mu$m for the 08Kh18N10T and 14Kh17N2 steels, respectively. The corrosion character was found to change from intergranular to frontal (Fig. 1). In this case, the composition of plasma does not practically influence the extent of decreasing the corrosion of the corrosion-resistant steels.

## 3. Increasing the corrosion resistance of EP823 steel tubes in liquid lead

In connection with the works on creation of a safe fast-breeder power reactor, in particular, the BREST reactor, the problem of physicochemical interaction of liquid lead with the cladding materials of fuel elements, as well as the development of methods to increase the corrosion resistance of these materials are an urgent question for the modern reactor materials science [3].

The EP823 (16Kh12SMVFBR) high-alloy chromium ferritic-martensitic steel, which is a prospective cladding material for the fuel elements of fast-breeder reactors, was selected as the material for investigations. The samples were made from standard fuel cladding tubes 6.9 and 10.5 mm in diameter and 50 mm in length and treated by nitrogen and helium plasma flows. Besides, the influence of a surface liquid-phase alloying by aluminum and chromium with the use of HTPPF on the corrosion resistance of the steel was studied. The corrosion tests were carried out on the TsU-1 lead circulation test stand at an increased ($(5–8)\cdot 10^{-5}$ wt.%) controlled oxygen content, at the temperature of 650 °C during 1000 and 1680 h for samples modified by HTPPF and surface-alloyed samples, respectively [3]. The velocity of a lead flow was 1.0±0.1 m/s.

The typical pictures of the transverse microstructures of samples after the corrosion tests are shown in Fig. 2.

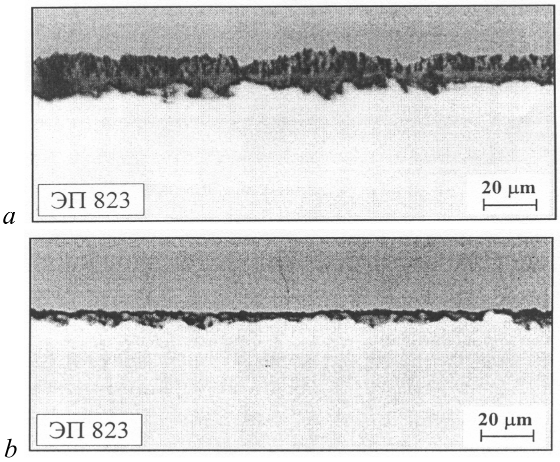

Fig. 2. Oxide films of the EP823 steel samples after endurance in a liquid lead flow at 650 °C for 1000 h: (a) initial sample; (b) after post-radiation anneal of samples preliminarily irradiated by HTPPF

The figure shows that the forming oxide film has a significant non-uniformity along its depth, both on the initial tubes and the tubes which were preliminarily modified by pulsed plasma flows. In this case, the oxide film thickness of the initial samples can change in the 7–19 $\mu$m range.

An analysis of the metallographic results obtained showed that the averaged thickness of the oxide film on the tubes treated by plasma flows decreased, on the whole, twice in comparison with that of the initial samples. The post-radiation anneal of the samples modified by helium plasma before their corrosion tests results in an additional decrease of the oxide film thickness; their corrosion resistance increases by more than 3 times, and the mean corrosion rate of the modified samples decreases up to 4.5 nm/h in comparison with ~14 nm/h for the standard fuel tubes. This is due, as shown by the results of X-ray investigations (Fig. 3), to decreasing the stresses arising under the plasma treatment.

The surface liquid-phase alloying of tubes by aluminum, a silumin-based alloy, and chromium with the use of HTPPF results in a significant (by 3–10 times) decrease of the corrosion extent and, in some cases, its total suppression (Table 1).

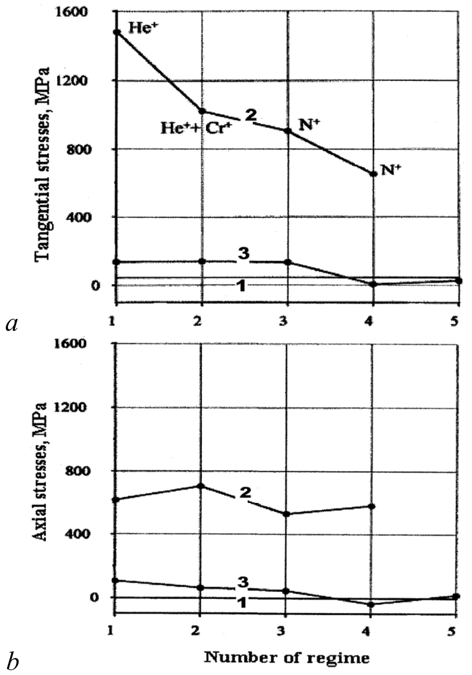

Fig. 3. Influence of the pulsed plasma treatment regimes on the tangential (a) and axial (b) macrostresses in the tube: (1) initial sample; (2) after the treatment by HTPPF; (3) after the post-radiation anneal of the samples treated by plasma

Table 1. Corrosion of the surface alloyed fuel cladding tubes in a lead flow ($T$=650 °C, $\tau$=1680 h)

| Coating | | Condition of plasma treatment | | Oxide film thickness, μm | | |
|---|---|---|---|---|---|---|
| Material | Thickness, μm | $q_\Sigma$, J/cm² | $N$ | $d_{min}$ | $d_{max}$ | $<d>$ |
| EP823 initial | | – | | 9 | 18 | 12 |
| EP823 initial | | purification | | 6 | 10 | 8 |
| EP823 initial | | 423 | 7 | 3 | 8 | 5 |
| Cr | 0.6 | 292 | 4 | 3 | 6 | 5 |
| | 0.6 | 246 | 5 | 2 | 6 | 3 |
| | 0.3 | 330 | 6 | 3 | 6 | 5 |
| | 0.9 | 475 | 7 | 5 | 8 | 6 |
| | 0.4 | 397 | 6 | 0 | 0 | 0 |
| Al | 1.5 | – | | 6 | 13 | 8 |
| | 0.2+0.7 | 675 | 12 | 0 | 0 | 0 |
| | 0.4 | 240 | 5 | 0 | 1 | 1 |
| | 0.5 | 449 | 8 | 1 | 5 | 3 |
| Al–Si | 1.3 | 1368 | 21 | 0 | 5 | 2 |
| | 1.1 | 1473 | 21 | 3 | 9 | 5 |
| | 0.4 | 449 | 8 | 1 | 8 | 4 |

Metallographic and X-ray investigations showed that the found influence of a preliminary plasma treatment on the corrosion of the steel in liquid lead was due to the formation of a modified layer with a microcrystalline structure and a changed structural-phase state being a barrier for the penetration of oxygen into the depth of the material.

In case of a surface alloying, in particular by aluminum and a silumin-based alloy, a thin and dense oxide film of $Al_2O_3$ forms on the surface of a material that also hinders the penetration of oxygen. It is found that for practically total suppression of the oxidation of tubes in a lead flow with an increased oxygen content, at the temperature of 650 °C, the aluminum concentration in the surface layers must be more than 13–14 wt. %, and the concentration of chromium, more than 16.5 wt. %.

## 4. Corrosion of structural steels under interaction with simulators of fission products (SFP)

The plasma treatment influence on the corrosion of fuel tubes made of a ChS-68 (06Kh16N15M2G2TFR) austenitic corrosion-resistant steel and 08Kh18N10T, 09G2SA, and 25G2S structural steels, used for production of the internal units of containers for transportation and storage of spent fuel assemblies, under their interaction with vapors of SFP such as cesium, tellurium, and iodine is studied [4].

The ChS-68 steel tubes were irradiated using three main regimes, which were selected on the basis of the previous experimental results on modifying the structural-phase state of steels by HTPPF: I – weak action (without the surface melting); II – hard action (remelting of the surface layers followed by high-speed cooling); III – combined irradiation (hard action followed by moderate irradiation). In doing so, helium and oxygen plasma was used for all the regimes. Plates of the 08Kh18N10T austenitic steel and 09G2SA and 25G2S carbon steels were treated by flows of the helium and nitrogen plasma with the power density of a flow $Q=6\cdot10^6$ and $1.5\cdot10^6$ W/cm², respectively, at the number of irradiation pulses $N$=3.

The interaction between SFP-vapors and the ChS-68 steel samples was investigated under isothermal conditions at 600 and 725 °C ($\tau$=150 h); the samples of 08Kh18N10T, 09G2SA, and 25G2S structural steels were studied at 300, 500, and 700 °C (for the endurance time up to 720 h).

The experimental results obtained have shown that the ChS-68 steel has a higher corrosion resistance in comparison with the other investigated austenitic steels. In this case, the depth of the corrosion interaction zone practically corresponds to the corrosion depth of a ferritic-martensitic steel. But the corrosion of the ChS-68 steel tubes is intergranular as opposed to frontal for the ferritic-martensitic steel. The treatment by helium plasma flows results in changing the character of the ChS-68 steel corrosion damage from intergranular to frontal and decreasing the depth of the corrosion interaction zone. At that, as found by gravimetric investigations, a significantly less (more than by order of magnitude) specific overweight is observed for the modified steel samples after the tests in the environment of cesium and oxygen than for the standard samples: 0.4±0.1 and 5.3±0.1 mg/cm², respectively.

The results of investigation of 08Kh18N10T, 09G2SA, and 25G2S structural steels have not shown any corrosion damages of all the materials at the temperature of 300 °C and the endurance time up to 720 h. The corrosion damage extent at temperatures of 500 and 700 °C significantly depended on the composition and the treatment of the investigated materials, as well as the endurance time in the environment of gaseous SFP.

A preliminary treatment of the 09G2SA steel by pulsed nitrogen plasma flows at the test temperature of 500 °C for 500 and 720 h results in a change of the corrosion character from intergranular to frontal. Besides, a small decrease of the interaction zone depth is observed. It is in an agreement with the results obtained for the ChS-68 austenitic steel samples. At a higher test temperature ($T$=700 °C), the corrosion character practically didn't change, but the interaction intensity decreased. An X-ray phase analysis shows that the main phase in the interaction layer is magnetite $FeO \cdot Fe_2O_3$.

The corrosion interaction zone of the 25G2S steel samples with a higher content of carbon is not strongly pronounced, as opposed to what is typical for intergranular corrosion. However, a preliminary modification of the given steel also decreases the interaction zone depth at the endurance for 500 and 720 h and at the temperature of 500 °C; for the nitrogen plasma at $T$=700 °C.

At high temperatures, corrosion of the 08Kh18N10T steel has a mixed character. It changes to frontal one at decreasing the temperature. Modifying this steel by pulsed nitrogen plasma flows results in some decrease of the corrosion zone at the interaction temperature of 500 °C and the endurance time of 720 h.

## 5. Influence of plasma treatment on the corrosion of zirconium alloys

Investigations were carried out with the purpose to find the possibilities of increasing the corrosion resistance of fuel cladding tubes of E110 and E635 zirconium alloys in water by the HTPPF-treatment [5]. Samples in the form of cuts made of standard tubes of E110 and E635, 50 and 100 mm in length and the external diameter of 9.13 mm, were treated by flows of pulsed helium, nitrogen, and oxygen plasma under various regimes: the power density of a plasma flow $q$=7–78 J/cm$^2$; the number of pulses $N$=2–8.

The samples were exposed to corrosion tests in autoclaves with water at $T$=350 and 400 °C and the endurance time up to 720 h.

It is found by transmission electron microscopy that opposed to the steels and the nickel alloys, formation of a microcrystalline (cellular) structure doesn't take place in the irradiated zirconium alloys. Nevertheless, the microstructure of modified layers significantly differs from the initial one; for both the alloys, the HTPPF-action results in formation of a "needle-shaped" structure, which is typical for the zirconium alloys quenched from the temperature that is higher than the temperature of allotropic transformation from $\alpha$- to $\beta$-zirconium. That is also confirmed by the results of X-ray investigations.

The experimental results obtained have shown that the structural-phase transformations taking place in materials, the formation of a developed surface relief, and the generation of residual tensile stresses don't promote a noticeable increase of the corrosion resistance of fuel cladding tubes in a water-steam environment, and in some cases they lead to an increase of their overweight in comparison with the standard treatment of these tubes.

Therefore, the experimental results obtained make it possible to conclude that the preliminary treatment by pulsed plasma flows results in increasing the corrosion resistance of both low-alloy and corrosionresistant steels under their exposure to intergranular corrosion tests in a liquid lead flow and during their interaction with the simulators of nuclear fuel fission products.

It has been found for the first time that as a result of a pulsed plasma treatment, independently of the composition of an aggressive environment, modifying the structural-phase state of the steel surface layers changes the character of the corrosion interaction from intergranular to frontal.

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