

## Improvement properties of protective coatings on zirconium alloys and austenitic stainless steels by pre-treatment with high-intense pulsed ion beams

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**Abstract.** The report discusses the influence of pre-treatment of metal substrates with a high-intense pulsed ion beam on functional properties of subsequently deposited protective coatings. Austenitic stainless steel and the Zr-1%Nb alloy have been studied, which are used in the nuclear industry as structural materials. The following irradiation parameters have been applied: the accelerating voltage of 200 kV, pulse duration of 90 ns, and the energy density per pulse of 1.5 J/cm<sup>2</sup>. After irradiation, coatings of both Fe-Cr-Al and Al-Si-N systems have been deposited by magnetron sputtering. Then, both normal and accidental losses of coolant conditions for water-cooled nuclear reactors are simulated. Radiation damage was modeled using 400 keV protons with a current density of 0.667  $\mu\text{A}/\text{cm}^2$  and a fluence of  $2.25 \cdot 10^{16}$  proton/cm<sup>2</sup>. The second modeling method was the hydrogenation of samples – 360 °C, pressure of 2 atm for 2 hours. After irradiating the coatings with protons or saturating them with hydrogen, high-temperature oxidation of the samples was carried out in air and steam at a temperature of 1000 °C for 180 seconds. Finally, the oxidized samples have been studied by scratch tests and subsequent investigations using scanning electron microscopy in order to understand the effect of the pre-treatment procedure.

**Keywords:** high-intense pulsed ion beam, reactive magnetron sputtering, surface modification, thin films, E110, stainless steel.

### 1. Introduction

The deposition of protective coatings on structural materials significantly increases the resistance of their surface when they are used in aggressive environments and severe operating conditions. At the same time, the key condition for the successful improvement of the performance and functional properties of the modified materials is the high adhesion of the deposited coatings. One of the effective ways to increase the adhesion is the pre-treatment of metal substrates with high-intense pulsed ion beams (HIPIB), which clean the surface, form a specific microrelief, and change the microstructure, phase composition, distribution of internal stresses, and chemical activity of the surface [1, 2]. The aim of this work was to research the influence of HIPIB pre-treatment of austenitic stainless steel and zirconium alloy substrates on mechanical and oxidation resistance properties of deposited Fe-Cr-Al and Al-Si-N thin films.

### 2. Materials and methods

Polished plates 20×20×0.5 mm<sup>3</sup> in size made of the E110 (99% Zr, 1% Nb) alloy and 321 austenitic stainless steel (1.2% C, 18% Cr, 10% Ni, 1% Ti) were irradiated with the ‘TEMP-4M’ HIPIB accelerator [3]. The following parameters were used: an accelerating voltage of 200 kV, a pulse width at half maximum of 100 ns, and energy density of 1.5 J/cm<sup>2</sup>. Number of pulses was 3. The HIPIB consisted of about 85% carbon ions and 15% protons.

Protective coatings were deposited by magnetron sputtering technique. Before deposition of the coatings, the samples were additionally cleaned with an ion source for 10 min. Fe-Cr-Al films were deposited from two magnetrons. AISI430 stainless steel target was installed on one of the magnetrons, aluminum target (99.995% purity) was installed on the second one. The temperature during sputtering was 300 °C for stainless steel specimens and 180–200 °C for E110 specimens. A bias voltage of 100 V was applied to the substrates. According to the results of X-ray fluorescence

analysis, the content of the coating components was 76 wt.% Fe, 15 wt.% Cr, 10 wt.% Al. Al-Si-N films were deposited by reactive magnetron sputtering from two targets (Al/Si – 25%/75% and aluminum target with 99.995% purity) in Ar/N atmosphere. The thickness of the resulting coating was measured using a Linnik interferometer on witness samples and was about 5  $\mu\text{m}$ .

Images of the surface and cross-sections were obtained on a Carl Zeiss EVO 50 electron microscope. To research the adhesion and crack resistance of the deposited coatings, as well as the wear resistance, the scratch test method with fixation of the acoustic emission signal was used with the Micro-Scratch Tester MST-S-AX-0000 device.

The maximum load was 20 N. The wear resistance of the samples was determined by the maximum scratch depth  $D_s$  (the depth of scratch at an indenter load of 20 N), as well as by the magnitude of the applied load required to create a scratch with a depth of 5  $\mu\text{m}$  ( $F_{15}$ ). The profiles of the obtained scratches were studied using an optical microscope and a non-contact profilometer Micro Measure 3D Station. Determination of the mechanical characteristics (hardness and elastic modulus) of coatings and substrates was carried out by nanoindentation on an Agilent Nano Indenter G200 in accordance with ISO 14577-1:2002. The maximum load was 50 mN for all tested materials.

To simulate radiation damage, the samples were irradiated on an ESG-2.5 accelerator with a proton beam with an energy of 400 keV and a current density  $j = 0.667 \mu\text{A}/\text{cm}^2$  to achieve a fluence  $\Phi = 2.25 \cdot 10^{16}$  proton/ $\text{cm}^2$ . To simulate the process of hydrogen accumulation in the coating, hydrogen saturation was carried out on an automated complex Gas reaction controller in the SOAK mode [4], in which the samples are kept at a 2 atm pressure and at 360 °C temperature for 80 min. This mode provides the hydrogen concentration in the E110 alloy, close to the hydrogen concentration during the operation of the fuel element (5 years) (200–300 ppm) in water cooled reactors.

High-temperature oxidation was carried out at a temperature of 1000 °C in water steam for 180 seconds. Weight changes were determined by weighing the samples using the ‘RADWAG MXA-21’ scales with a maximum error of  $\pm 0.01$  mg

### 3. Results

#### 3.1. Mechanical properties

As a result of nanoindentation, the values of hardness  $H$  and elastic modulus  $E$  of the researched substrates and films were determined. It has been found that HIPIB treatment slightly increases the hardness of the substrates: by 6% (up to 4.8 GPa) for stainless steel and by 16% (up to  $6.1 \pm 0.1$  GPa) for the E110 alloy. The hardness of Fe-Cr-Al coatings was  $8.3 \pm 0.2$  GPa and  $12.4 \pm 1.1$  GPa when deposited on stainless steel substrates and E110 alloy, respectively. The HIPIB treatment of the substrates reduced the hardness of the Fe-Cr-Al coating deposited on the stainless steel substrate by 17% and increased the hardness of the coating deposited on the E110 alloy substrate by 13%. The hardness of the Al-Si-N coatings was  $52.2 \pm 1.6$  GPa (on a stainless steel substrate) and  $43.4 \pm 1.2$  GPa (on an E110 alloy substrate). Irradiation of the substrates by HIPIB reduced the hardness of deposited Al-Si-N films by 4.6% (on a stainless steel substrate) and 13.6% (on an E110 alloy substrate). The change in the value of the elastic modulus  $E$  correlated with the change in the hardness values for the studied samples. The modulus of elasticity of the Fe-Cr-Al films deposited on a stainless steel substrate was  $250 \pm 30$  GPa and decreased to  $217 \pm 68$  GPa in the case of modification of the substrate by HIPIB. When using E110 alloy substrates, the modulus of elasticity was  $271 \pm 9$  GPa (for untreated substrates) and  $278 \pm 5$  GPa (for HIPIB processing substrates). The modulus of elasticity of Al-Si-N coatings on a stainless steel substrate was  $648 \pm 8$  GPa (untreated substrate) and  $527 \pm 7$  GPa (HIPIB treated substrate), and  $376 \pm 5$  GPa

(untreated substrate) and  $323 \pm 4$  GPa (HIPIB treated substrate) for films deposited on E110 alloy substrates.

Thus, the effect of the pre-treatment of substrates by HIPIB slightly increases the hardness of substrates made of stainless steel and E110, as well as the hardness of the Fe-Cr-Al coatings deposited on them. The hardness and modulus of elasticity of Al-Si-N coatings, on the contrary, decrease for substrates processed by HIPIB.

### *3.2 Adhesion and crack resistance of films*

#### *3.2.1 Stainless steel substrates with Fe-Cr-Al films*

The treatment of the substrates by HIPIB before deposition of the Fe-Cr-Al films reduces the hardness and wear resistance of the coating-substrate system. The  $D_s$  value increased by 80% compared to untreated substrates. The adhesion of the films, as follows from the acoustic emission signal, increased after treatment of the substrate by HIPIB. The crack resistance of the coating also increased significantly – the integral value of the acoustic emission signal over the entire value of the load applied during the scratch test decreased by 20 times. The obtained results can be explained by tempering the modified layer during coating deposition. The effect of HIPIB treatment on the increase in the adhesive strength of the coating due to the modification of the relief and the increase in the free energy of the surface was retained. After induction of radiation damage by a proton beam and hydrogenation of the samples, their wear resistance did not undergo significant changes, which indicates a decrease in the mobility of dislocations in the modified layer due to induced radiation defects and hydrogenation and, as a result, the restoration of its mechanical strength. The crack resistance of coatings deposited on HIPIB treated substrates after hydrogenation and proton beam irradiation was also higher.

The integral value of the acoustic emission signal after hydrogenation for samples treated with HIPIB was 6 times lower, and after irradiation with protons, it was 3 times lower. The magnitude of the load leading to the onset of active cracking also increased.

#### *3.2.2 E110 alloy substrates with Fe-Cr-Al films*

The pre-treatment of the substrate by HIPIB from the E110 alloy improves the resistance to deformation by the indenter at a low load. The  $F_{15}$  value for the sample with HIPIB treatment is 2 times higher compared to the sample without HIPIB treatment of the substrate, but when a certain load value is exceeded, a sharp plastic deformation of the sample occurs and, as result, an increase in the value of  $D_s$ . In this case, the acoustic emission signal has bursts over the entire range of the applied load  $F_i$ , the amplitude of which is an order of magnitude higher than the magnitude of the acoustic emission signal from the substrate. The absence of a pronounced threshold value  $F_i$  leading to active cracking indicates the cohesive nature of the coating wear. Thus, it can be concluded that the HIPIB-hardened substrate has a high effect on the wear resistance of the sample. Irradiation of samples with a proton beam increases the wear resistance of samples by 30–35%, most likely, as in the case of stainless steel substrates, due to induced radiation defects.

#### *3.2.3 Stainless steel and E110 alloy substrates with Al-Si-N films*

Despite the high hardness values of Al-Si-N films, the deposition of coatings on stainless steel substrates did not increase the wear resistance of the samples. The presence of a high level of the acoustic emission signal even at minimal  $F_i$  (from 1–2 N) indicates peeling of the coating material due to poor adhesion. HIPIB treatment did not have a positive effect on Al-Si-N adhesion. In the case of deposition of Al-Si-N on E110 alloy substrates, the adhesion have been increased, due to which an increase in the resistance of the sample to punching by 25% was achieved.

### 3.3 High-temperature oxidation

#### 3.3.1 Stainless steel substrates with Fe-Cr-Al films

Fe-Cr-Al coatings deposited on a stainless steel substrate showed good resistance to high-temperature oxidation in steam. In this case, neither chipping nor local swelling of the coating was observed. Only local changes in the color of the coating were found in the form of lighter spots with a characteristic size of about 100  $\mu\text{m}$ , and this was more pronounced on samples that were not subjected to HIPIB treatment before coating deposition.

As expected, films irradiated with a high-energy proton beam or hydrogenation before oxidation had a lower resistance to high-temperature oxidation.

After saturation of the samples with hydrogen and oxidation in steam, the coating acquired noticeable porosity. In this case, in the coating deposited on the HIPIB treated substrate, the pore sizes were approximately two times smaller (1 and 2  $\mu\text{m}$ , respectively).

On cross-section images, local delaminations of the coating were found, and the sizes of these areas differed significantly. For the untreated samples, the absence of contact between the coating and the substrate reached a few millimeters, while for HIPIB irradiated samples, the delamination areas did not exceed 100  $\mu\text{m}$  in size.

An analysis of the distribution of elements in the coating after oxidation showed that aluminum was displaced at the boundaries of the coating. In addition, the oxygen content at the inner and outer boundaries of the coating increased. Moreover, for the sample not treated with HIPIB, most of the aluminum migrated to the surface of the coating, while it mainly accumulated at the interface with the substrate in samples treated with HIPIB. Apparently, the increased chemical activity of the surface of the substrate treated with HIPIB plays a role here, as shown by previous studies [1].

For the coatings, the oxidation of which was carried out after hydrogenation, no preferred direction of aluminum migration was found. However, aluminum in all cases migrated to the inner and outer boundaries of the coating.

Significantly different patterns of migration of coating components were observed during high-temperature oxidation of samples with coatings irradiated with accelerated protons. Coarse-crystalline precipitations of a rounded shape with a diameter of up to 1 mm were found on their surface. X-ray fluorescence microanalysis of cross-section showed that the surface of such formations was formed by iron oxide up to 50  $\mu\text{m}$  thick, under which there was a layer of aluminum oxide about 5  $\mu\text{m}$  thick and then a loose layer about 50  $\mu\text{m}$  thick with a chromium content increased by 2 times relative to the initial level. Elemental analysis of the surface between loose round formations showed a result similar to the oxidation of the untreated coating, i.e., an increased content of aluminum and oxygen at both of its boundaries, and the thickness of such a layer at the interface with the substrate reached 3  $\mu\text{m}$ , while the initial thickness of the Fe-Cr-Al coating was 5  $\mu\text{m}$ .

The results of weighing the samples before and after high-temperature oxidation showed that samples with a surface treated by HIPIB had a smaller weight gain. This was true both for samples without Fe-Cr-Al coatings and for samples with coatings that were subjected to additional treatment before oxidation (irradiation with a proton beam or saturation with hydrogen).

#### 3.3.2 Stainless steel substrates with Al-Si-N films

After high-temperature oxidation of all samples of stainless steel coated with Al-Si-N films, the coating was completely destroyed, only individual fragments remained on the metal surface, covering less than 10% of the sample area. The remaining fragments of the coating had clearly defined sharp edges, which indicates that it first cracked over the entire area and to the full depth, followed by delamination and shedding from the surface of the sample. However, significant differences were observed in the surface of the stainless steel oxidized after peeling off the coating.

The surface treated with HIPIB before coating deposition had a grid pattern repeating cracks in the coating and a large number of small areas with a diameter of 30–50  $\mu\text{m}$  with the formation of iron oxide (similar areas of the oxidized surface were observed on uncoated steel samples). On samples without HIPIB pre-treatment, no “imprints” of the coating were found on the surface, as well as surface areas with the formation of iron oxide. Such differences can be explained by the greater adhesion of the coating to the HIPIB-treated substrate, as a result of which the formed cracks in the coating had time to propagate deep into the base metal before the coating peeled off and created local damage to the surface, which became centers of accelerated corrosion.

### 3.3.3 E110 alloy substrates with Fe-Cr-Al and Al-Si-N films

All samples with coatings showed unsatisfactory resistance to high-temperature oxidation. The coatings were destroyed or peeled off, regardless of the HIPIB pre-treatment, hydrogenation, or proton beam irradiation. Thus, HIPIB pre-treatment did not have a positive effect on the resistance to high-temperature oxidation of coated E110 samples. The most likely reason was the formation of zirconium intermetallic compounds with coating components, including eutectics, which contributed to this result [5]. Thus, it has been shown that the HIPIB pre-treatment was insufficient to significantly improve the adhesion of the Fe-Cr-Al and Al-Si-N coatings on the E110 substrates, and additional studies are required on the compatibility of various types of coatings with zirconium alloys [6]. The best results in the oxidation of the E110 alloy in all cases were obtained for samples with HIPIB-treated substrates. They had the least weight gain, their surfaces were without visible erosion centers and cracks, and also had the smaller thickness of the oxide layer. Because of it, we can conclude that further research on the use of HIPIB processing and optimization of its modes is promising in order to improve the energy characteristics of a modified surface layer with a smooth relief and a chemical composition corresponding to the original alloy.

## 4. Conclusion

As a result of the research, the following conclusion points can be drawn:

1. The effect of pre-treatment of substrates by HIPIB slightly increases the hardness of substrates made of stainless steel and E110 alloy, as well as the hardness of the Fe-Cr-Al coatings deposited on them. The hardness and modulus of elasticity of Al-Si-N coatings, on the contrary, decrease for samples with HIPIB-treated substrates.
2. HIPIB treatment of the E110 alloy and deposition of protective Fe-Cr-Al films on stainless steel are effective methods for increasing the wear resistance of these structural materials, including under conditions of radiation exposure to accelerated ions and long-term operation in water cooled nuclear reactors.
3. HIPIB treatment of stainless steel substrates has a positive effect on the anti-corrosion properties of the Fe-Cr-Al films during oxidation in a steam environment heated to 1000 °C. This is expressed in a smaller weight gain of the samples, a decrease in the area of delamination of the coating from the substrate, and the formation of smaller pores after preliminary hydrogenation.
4. During oxidation in steam heated to 1000 °C, the components of Fe-Cr-Al films migrate with the formation of layers with a high content of aluminum and oxygen at the inner and outer boundaries.
5. The effect of irradiation by 400 keV protons with  $2.25 \cdot 10^{16} \text{ cm}^{-2}$  fluence on the coating reduces the anti-oxidation properties of coatings much more than their hydrogenation to a level comparable with that after 5 years of operation in water cooled reactors.
6. All samples with films deposited on the E110 alloy substrates showed unsatisfactory resistance when tested in high-temperature steam. The coatings were destroyed or peeled off, regardless of the HIPIB pre-treatment, hydrogenation, or proton beam irradiation.

7. The HIPIB pre-treatment of the stainless steel substrates has a positive effect on the anti-oxidation properties of the deposited Fe-Cr-Al films during oxidation in a steam environment heated to 1000°C. This is expressed in a smaller weight gain of the samples, a decrease in the fraction of the delaminated coating from the substrate, and the formation of smaller pores during hydrogenation.

8. Fe-Cr-Al coatings improve the resistance of austenitic stainless steel to high temperature oxidation. In this case, the HIPIB pre-treatment of substrates improves the adhesion of coatings even under conditions of their previous saturation with hydrogen or radiation damage formed by the proton beam.

9. The studied types of coatings (Fe-Cr-Al and Al-Si-N) deposited on E110 zirconium alloy peeled off during high-temperature oxidation in steam at a temperature of 1000 °C for 180 seconds and did not significantly affect the resistance to high-temperature oxidation. The most likely reason was the formation of zirconium intermetallic compounds with coating components, including eutectics, which contributed to this result.

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### 5. References

- [1] Tarbokov V., Pavlov S., Smolyanskiy E., Uglov V., Slobodyan M., Remnev G., *Coatings*, **11**, 1169, 2021; doi: 10.3390/coatings11101169
- [2] Remnev G.E., Tarbokov V.A., *IEEEJ Trans. Fundam. Mater.*, **124**, 487, 2004; doi: 10.1541/ieejfms.124.487
- [3] Remnev G.E., et al., *Surf. Coat. Tech.*, **114**, 206, 1999; doi: 10.1016/S0257-8972(99)00058-4
- [4] Kudiiarov V., Sakvin, I., Syrطانov M., Slesarenko I., Lider A., *Metals*, **10**, 247, 2020; doi: 10.3390/met10020247
- [5] Grabke H.J., Schutze M., *Oxidation of Intermetallics*. (New York: WILEY-VCH, 1998).
- [6] Slobodyan M., *Nucl. Eng. Des.*, **382**, 111364, 2021; doi: 10.1016/j.nucengdes.2021.111364