Materials surface damage and modification under high power plasma exposures

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Abstract. Influence of powerful plasma impacts on several materials used for the construction of energy systems, i.e. different grades of steels as well as tungsten coatings, has been discussed. Irradiations of these materials with hydrogen and helium plasma streams have been performed in several high-current-pulse and quasi-stationary plasma accelerators which provided the variation of a power load upon the exposed surface as well as changes of the particle flux in wide ranges: the energy flux density in the range of 1-25 MJ/m², particle flux - up to 10^{26}-10^{29} ion/m²s, the plasma stream velocity - up to about 500 km/s, and the pulse duration in the range of 1-250 µs.

A response of the investigated materials to extreme plasma loads, which are relevant to transient events in fusion reactors, is briefly discussed. It is demonstrated that a broad combination of mechanisms of powerful plasma interactions with various materials includes not only a surface damage caused by different erosion mechanisms, but under certain conditions it may also result in a significant improvement of material properties in the near-surface surface layer of several tens of µm in thickness. Some improvement of the structure and substructure of such a layer may be caused by the high-speed quenching, the shock wave formation and material alloying with plasma- and coating-species. The creation of unique surface structures and a considerable improvement of physical and mechanical properties of different materials can be achieved by the pulsed plasma alloying, i.e. pre-deposited coating modifications and mixing caused by the impacting plasma streams.

1. Introduction

Some low-activation steels are considered as constructional materials for nuclear and fusion devices due to their high swelling resistance and low irradiation creep-rates (i.e. slow changes in dimensions of materials exposed to prolonged stresses, caused by X-rays, γ-rays and neutron irradiation, etc.). In particular, such steels might be a possible option at the choice of plasma-facing materials for the first wall surfaces in DEMO [1-3].

The main drawback of such steels at their application as the plasma facing materials is their high sputtering rate under influence of energetic ions (particularly hydrogen isotopes). It is directly related with the generation of impurities as well as with a lifetime of the plasma facing components [3-4]. One of the prospective ways towards an improvement of the steel properties is the alloying of their surface layers with some refractory elements [3]. Plasma ions can of course be considered as a source of the alloying elements which should be introduced into a modified layer structure [5]. Another possibility of the alloying during the pulsed plasma processing is the mixing of previously deposited thin ($h_{coat} < h_{material}$) coatings of a different pre-determined composition with the chosen substrate in the course of its melting driven by powerful plasma impacts [6-7].

The alloying of a surface layer in result of the coating-substrate mixing allows achieve a desirable chemical composition of the processed surface layers [5-9]. Nevertheless, the modification processes
in plasma facing materials, which can be induced by repetitive plasma impacts and synergetic effects (caused by different factors) are still not understood satisfactorily to make reasonable predictions for steels behavior during the fusion-reactor operation. All the mentioned issues require comprehensive studies of prospective steel materials with different powerful plasma devices (simulators) and coordinated activities, which should address relevant issues - associated with the impact of intense heat and particle loads on the investigated plasma facing materials.

Analyses and comparisons of experimental results of research on materials behaviour under their irradiation with steady-state and high-power pulsed plasma-streams, which can be generated in different plasma devices with various specific heat loads and different particle fluxes, are necessary. They can give the unique possibility to understand the important common features of surface damages at extreme conditions, to investigate the peculiarities of the surface modification of low-activation steels and possible erosion mechanisms in dependence on the plasma parameters and the impact load.

This paper presents experimental studies of the alloying and modification of the chosen commercial grades of steels, and particularly the (Cr18Ni10Ti) austenitic steel and ferritic/martensitic Eurofer alloy (Cr - 9.7%, Mn - 0.7%, Fe - 89.6%) with some tungsten admixture introduced by the plasma-induced mixing. There are also discussed studies of the sputtering of the surfaces covered by tungsten and exposed to powerful plasma streams.

2. Samples, experimental devices and diagnostics

In the reported experiments there were applied planar samples (of dimensions of 20×20×1 mm³), made of the well-known austenitic steel of the Russian trademark (Cr18Ni10Ti), which has the following composition (18 wt% of Cr, 10 wt% of Ni, 1 wt% of Ti, and the rest - Fe). Such a steel is an analog of the stainless steel marked as AISI 321. The samples made of the Eurofer alloy (Cr-9.7%, Mn-0.7%, Fe-89.6%) were prepared and delivered by the SCK•CEN laboratory (Belgium). All the samples had the size of 10×10×0.5 mm³. These samples were covered by tungsten coatings of about 3 μm in thickness, which were deposited with a PVD technique [7] within a Bulat-type facility. Earlier such coatings were applied for estimations of their performance as plasma-facing surfaces (in a comparison with monolithic tungsten targets). They enabled also an analysis of the adhesion properties of the PVD coatings, and an investigation of the plasma-facing components prospective for the reactor first wall construction [10].

Surface modifications by powerful pulsed plasma streams were carried out with the use of a QSPA Kh-50 quasi-stationary plasma accelerator and a MPC magneto-plasma compressor [10-12]. The main parameters of the QSPA hydrogen plasma streams were as follows: ion impact energy was about (0.4…0.6) keV, the maximum plasma pressure reached up to 0.32 MPa, and the plasma stream diameter was about 18 cm. The surface energy loads, as measured with a calorimeter, amounted to 0.6 MJ/m² (i.e. near the tungsten melting threshold). The load pulse shape was approximately triangular, and the pulse duration was 0.25 ms [10-12]. The MPC facility generated compressed plasma streams of the density amounting to about 10¹⁸ cm⁻³, and a plasma energy density was varied in the range of 0.05–0.5 MJ/m². The amplitude of the discharge current in the accelerating channel amounted to about 500 kA, and the discharge half-period was equal to about 10 μs. The experiments were carried out using pure helium at the initial pressure equal to 266.64 Pa. The surface energy loads, as measured with calorimeters, amounted to 0.4 MJ/m². During the reported experiments, the target surface before each plasma pulse was maintained at the room temperature.

The sputtering procedures were performed within the DSM-2 stand described in an earlier paper [13]. An ion source was the system based on a microwave discharge in argon within a mirror magnetic trap, which was operated at the electron cyclotron resonance (ECR) frequency of 2.37 GHz. The plasma density n_e in this system was about 10¹⁶ cm⁻³, and the electron temperature T_e reached about 5 eV. According to measurements, performed with an Omegatron-type gas analyzer, the main impurity was water, but the total impurity amount was negligibly in a comparison with the argon content. The plasma ions were accelerated by a negative potential (~600 V) applied to the water-cooled holder. The density of the ion current upon the mirror surface was equal to 1.6 mA/cm².
The energy density in free plasma and the surface heat loads were measured by means of the local calorimeters. Observations of plasma interactions with the exposed surfaces were performed with a high-speed 10-bit CMOS pco.1200s digital camera of the PCO AG type (in the spectral range from 290 nm to 1100 nm, with an exposure time ranging from 1 μs to 1 s) [10-12]. The surface analysis of the exposed samples was carried out with a MMR-4 optical microscope, equipped with a CCD camera. There were also performed measurements of weight losses, as well as precise measurements of the surface roughness with a Hommelwerke T500 tester. To study a micro-structural evolution and contents of elements and phases in the exposed targets, the x-ray diffraction technique (XRD) was applied [14-17].

3. Experimental results

3.1. Initial state of sample surfaces

The values of the initial micro-hardness and roughness of the Cr18Ni10Ti samples amounted to 350 kg/mm² and $R_a < 0.1 \mu m$ ($R_{max} \approx 0.1 \mu m$), respectively. Upon the virgin surfaces only some lines corresponding to the $\gamma$-Fe phase were observed [17]. It should be mentioned that a face-centred cubic lattice was attributed to that phase.

For the Eurofer samples the initial micro-hardness and roughness were 190 kg/mm² and $R_a < 0.1 \mu m$ ($R_{max} \approx 0.1 \mu m$), respectively. Surface profiles of these samples are shown in Figure 1.

![Surface profiles of the Eurofer samples](image)

Figure 1. Surface profiles of the Eurofer samples: (a) for a virgin sample, (b) for that exposed to 5 QSPA-plasma pulses, and (c) for that covered by a W-layer and exposed to QSPA plasma. In those cases the heat load was $Q = 0.6 \text{ MJ/m}^2$.

The composition the Eurofer samples in the initial (virgin) state and after their processing is shown in Table 1.

During structural studies of the samples surfaces there were observed lines corresponding to the $\alpha$-Fe phase only. It should be noted that to that phase there was attributed the body-centred cubic crystal structure. The results the diffraction measurements are presented in Figure 2.
Figure 2. Diffraction patterns (Fe-K α1 radiation) of the Eurofer samples: (a) measured in the initial state, (b) measured for the sample coated with a W-layer and exposed to QSPA-plasma pulses, and (c) measured for the sample coated with a W layer, modified by QSPA-plasma pulses and irradiated by the Ar-ion’s beam.

Table 1. Element content of the investigated Eurofer samples

| Sample                              | Cr (wt %) | Mn (wt %) | Fe (wt %) | W (wt %) |
|-------------------------------------|-----------|-----------|-----------|----------|
| Initial                             | 9.7       | 0.4       | 89.9      | -----    |
| Coated with W and exposed to QSPA-plasma | 1.3       | ----      | 12.95     | 85.8     |
| Coated with W, exposed to QSPA-plasma and sputtered by the Ar-ion beam | 8.9       | 0.36      | 89.64     | 1.1      |
| Coated with W and exposed to MPC-plasma | 9.7       | 0.4       | 88.8      | 1.1      |
| Coated with W and sputtered by the Ar-ion beam | 9.6       | 0.4       | 88.9      | 1.1      |

3.2. Surface modification by powerful plasma

Irradiations of the Cr18Ni10Ti-steel and Eurofer-alloy samples by plasma streams within the QSPA and MPC facilities led to the surface melting and resulted in the development of re-solidified surface layers, which are presented in Figures 3 and 4.
Figure 3. Optical microscope images of the Cr18Ni10Ti-steel surface exposed to 5 plasma pulses within the MPC (left) and QSPA (right) facilities. The lower parts of both images show the same modified surfaces after their sputtering by the Ar⁺ beam. The black marker-stripe length is 100 μm.

Figure 4. Optical microscope images of the Eurofer-alloy surface exposed to 5 plasma pulses within the MPC (a) and QSPA (b) facilities. The black marker-stripe shows the scale.

The surface morphology was changed mainly due to the formation of the plasma-melted layers. The roughness of the exposed surfaces was increased up to $R_{max} \approx 0.3 \, \mu m$ (see Figure 1b). The $\alpha$-Fe phase was identified together with lines corresponding to the $\gamma$-Fe phase upon the treated surfaces of the Cr18Ni10Ti samples. In contrary the content of phases upon the Eurofer surface was not changed.

It should be noted that the micro-hardness of the modified surface of the Cr18Ni10Ti sample as well as that of the Eurofer sample was increased up to 400 kg/mm² and 260 kg/mm², respectively, due to the stresses and quenching induced by the plasma treatment [18].

3.3. Modification of tungsten coatings deposited on steel substrates

The process of the steel-surface alloying consisted of two stages. During the first stage the tungsten coating was deposited upon the sample surface by means of the PVD method. After the deposition of the tungsten coatings on the treated Cr18Ni10Ti and Eurofer surfaces their roughness was slightly increased. During the second stage the W-coated samples were exposed to 5 plasma pulses in the QSPA or MPC device.

After the irradiation of the Cr18Ni10Ti sample by plasma within the MPC or QSPA device the surface morphology was changed due to the formation of macro- and micro-cracks as well as some pores, as shown in Figures 5 and 6.
Figure 5. Optical microscope images of the Cr18Ni10Ti-steel surface coated by a W-layer and exposed to 5 plasma pulses in the MPC (left) and QSPA (right) facilities. The lower parts of both images show the same modified surfaces after their sputtering by the Ar⁺ beam. The length of the black marker-stripe is 100 μm.

The roughness of the exposed surfaces increased up to $R_a \approx 0.3 \, \mu m$, $R_{\text{max}} \approx 3.4 \, \mu m$ (see Figure 1c), and the intensity of tungsten lines was considerably higher than that of the substrate lines (see Figure 2b). For the Cr18Ni10Ti samples the delamination of the deposited coatings was not observed (see Figure 4). An increase in the tungsten concentration (up to several wt %) was observed upon the modified surfaces.

The delamination of the coatings upon the Eurofer surfaces was not observed during their irradiation by plasma streams within the QSPA facility. The concentration of tungsten in the surface layer of 4 μm in depth achieved 85.8 wt% (see Table 1). In contrary, the Eurofer surfaces coated by W-layers and irradiated by plasma in the MPC device showed some delamination of these coatings, as shown in Figure 6.

Figure 6. Optical microscope images of the Eurofer-alloy surface coated by a W-layer and exposed to 5 plasma pulses within the MPC (left) and QSPA (right) facilities.

In the considered case the concentration of tungsten in the modified layer was below 1.1 wt % (see Table 1). It should be mentioned that changes of the micro-hardness of the modified coatings upon the Cr18Ni10Ti and Eurofer samples were not very different from those observed during the modification of pure steel surfaces.
3.4. Sputtering tests of steels
The sputtering tests of the Cr18Ni10Ti and Eurofer samples were carried out for the virgin (initial) surfaces, as well as for those coated by a W-layer and those modified by plasma streams of different pulse length. The roughness of the initial surfaces was noticeably increased due to the sputtering of boundaries of the grains, as shown in Figures 3 and 7.

*Figure 7.* Optical microscope images of the Eurofer (left) and Cr18Ni10Ti steel (right) surfaces, as obtained for the initial virgin state (top parts of the pictures) and for the same surfaces after their sputtering by the Ar⁺ beam (the lower parts of the pictures).

The roughness of the surfaces of the both grades of steel, which were coated by a W-layer and modified by the pulsed plasma streams, was decreased due to the sputtering of non-uniform melted and re-solidified layers and delamination of the coatings, as shown in Figures 5 and 8.

It should be noted that practically identical mass losses were measured for the steel surfaces coated by a W-layer, and for those covered with a W-layer and subsequently modified by plasma streams.

*Figure 8.* Optical microscope images of the Eurofer surfaces coated by a W-layer, exposed to 5 plasma pulses in the MPC (left) and QSPA (right) facilities, and finally sputtered by the Ar⁺ beam.

4. Discussion and conclusions
The most important results of these studies can be summarized as follows: Experimental research on surface modifications of different stainless-steel (SS) grades was performed. These SS-grades are a possible options as plasma-facing materials of the DEMO-reactor first wall. The samples of the Cr18Ni10Ti austenite- and Eurofer (Cr-9.7%, Mn-%0.4, Fe-89.6%) ferritic/martensitic-steels covered by tungsten coatings were treated within the QSPA Kh-50 quasi-stationary plasma accelerator and the MPC magneto-plasma compressor. The heat load upon the sample surface was near the melting threshold (i.e. about 0.6 MJ/m², with pulse duration \( \tau = 0.25 \) ms in the QSPA Kh-50, and about 0.4
MJ/m², with pulse duration τ = 20 µs in the MPC). The preliminary tungsten coatings were deposited by a PVD method. The sputtering tests of the modified surfaces were also performed.

Possibility of the alloying of SS-surfaces with tungsten coatings was demonstrated. An increase in the tungsten concentration was observed. The tungsten phase was identified together with some lines of the Fe phase upon the treated surfaces. The presence of the α-Fe phase created good conditions for the tungsten penetration into the affected layer. The tungsten concentration achieved several wt% in the surface layer of thickness up to 4 µm. The maximum tungsten content of about 85 wt% was observed in the surface layers of the Eurofer samples modified by plasma streams in the QSPA. Nevertheless, symmetrical tensile stresses up to 270 MPa were recorded in the near surface layer. As a result of the stresses development, some delamination of the coatings during the pulsed plasma irradiation was observed. The surface morphology was changed mostly by the melting and re-solidification of a surface layer. Macro- and micro-cracks appeared also on the modified surfaces.

The sputtering yield for the SS-samples modified by plasma streams was not very different from that observed for the virgin samples. An explanation of such a surface behaviour might be the accumulation of elastic energy in the stressed surface-layer, and not very good adhesion of the modified tungsten coatings to the steel substrates. As a result of those effects some delamination of the coatings could develop. A possible way to improve the coatings resistance might be the application of several cycles of the plasma treatment [6]. During the first stage of such a cycle the tungsten coating of 1-2 µm in thickness should be deposited on the sample surface by the PVD method. During the second stage the coated samples should be processed with pulsed plasma streams. The reduction of the coating thickness together with an increase in the number of plasma treatment cycles might create conditions for the better penetration of an alloying element into the treated substrate.

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