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Morphology and composition of Fe-W model alloys after deuterium plasma exposure

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Abstract. A model system representing the RAFM steel EUROFER-97 is produced by magnetron sputter deposition of iron and 1.5 at.% tungsten and investigated in order to study the consequences of plasma exposures. . The alloy is deposited as coatings with a thickness of 400 nm on polycrystalline, high purity iron substrates. To understand the erosion mechanisms and morphology changes the coatings were exposed to a linear plasma device with an ion flux of $3*10^{21}$ D^+ $m^{-2}s^{-1}$ and an electron temperature of 13 eV. Samples were exposed at sample temperatures of about 420 K and 770 K at incident ion energy of 30 eV (floating potential), 70 eV and 190 eV. Additionally, the effect of ion fluence was investigated. The coatings before and after plasma exposure were investigated by electron microscopy and glow discharge optical emission spectroscopy (GD-OES). Microstructure observation revealed a complex morphology with distinct sharp spikes formed under the plasma exposure at incident ion energies of 70 and 190 eV. The tungsten enrichment by a factor of 3 in the spikes was visualised by backscatter electron observation and confirmed by both energy-dispersive X-ray spectroscopy and GD-OES. No visible erosion and by that tungsten enrichment was observed after the plasma exposure at an incident ion energy of 30 eV.

1. Introduction

The main candidates for plasma-facing materials in fusion devoices are currently tungsten and beryllium [1]. For DEMO and future power plants, however, reduced activation ferritic martensitic (RAFM) steels such as EUROFER-97 are also considered mainly due to their availability and much lower cost [2]. Such steels are already foreseen as a structural material in future fusion devices [3]; however the possibility to employ them as a plasma-facing material requires additional research. To assess the compatibility, EUROFER-97 steel needs to be

comprehensively studied mainly in respect to its behaviour under plasma/ion irradiation. Special attention must be placed on the erosion behaviour of such steels since it would play a major role in component lifetime assessment, in particular when considering potential effects of selective (preferential) sputtering of the various elements in the steel. At low energy D bombardment one can expect initially reduced sputtering of the high-Z components such as tungsten (up to 0.5 at.%), compared to pronounced Fe sputtering which may lead to a W enrichment at the surface. Such an enriched surface layer should have an influence on lowering the overall sputtering yield for the steel. To better understand the mechanisms of such a preferential sputtering and possible W enrichment, a binary Fe-W model system was produced and exposed to plasma in the linear device PSI-2 within the framework of EUROfusion activity WPPFC. Recent results [5] of exposure to D ions in the high current source "HSQ" set-up at IPP Garching confirm the presence of actual W surface enrichment in such model systems. However, its morphology after plasma exposure and W enrichment is still not examined. The main objective of this work is to determine the composition and morphology change of such a model system under low energy deuterium bombardment. The influence of exposure time, temperature and incident ion energy is investigated.

2. Experimental

A set of binary Fe-W mixed layers were produced by magnetron sputtering [Leybold, UNIVEX 450B] with two independent cathodes – Fe and W – with Ar as source gas. The W concentration was controlled by adjusting the input power for the cathodes and set to meet 1.5at.%. The W fraction is about 3 times higher than in typical EUROFER-97 steel. The coatings with thicknesses of about 380-400 nm were deposited on polycrystalline, iron substrates [5].

Mirror polished samples with the size of 12 x 12 mm^2 were exposed in the linear plasma device PSI-2 to a D^+ plasma with an electron temperature of 13 eV, an ion flux of $3*10^{21}$ D^+ $m^{-2}s^{-1}$ and a fluence range between $8.5*10^{24}$ and $5.4*10^{25}$ D^+ m^{-2}. Samples were exposed at a temperature of 420 K and an incident ion energies of 30 eV (floating potential), 70 eV and 190 eV (at 460 K). Furthermore, the model alloy was exposed at 770 K with an incident ion energy of 70 eV and a fluence of $8.5*10^{24}$ D^+ m^{-2}. Additionally, a Fe-W model system was annealed at 800 K for 1 h in order to investigate the influence of the high temperature on the stability of the alloy film structure.

The surface morphology of the alloy before and after plasma exposure was analysed using a field emission scanning electron microscope (FE-SEM) [Zeiss Crossbeam 540]. A dual beam scanning electron microscope/focused ion beam (SEM/FIB) device, equipped with an energy dispersive X-ray analyser (EDX) was used for both surface imaging, cross section preparation, cross section imaging and elemental composition analysis. EDX microprobe and backscattered electron images (BSE) were employed for determining the W surface concentration. All observations were carried out at electron energies up to 5 keV and a sample tilt 54° with respect to the surface normal. The sample tilt was employed to better visualize the surface topography. EDX mapping was performed on the thin lamella, with an electron energy of 20 keV and a beam current 5 nA. BSE images were taken at electron energy of 10 keV.

Glow discharge optical emission spectroscopy (GD-OES) was utilized to obtain depth profiles with more detailed W distribution along the coating. During the measurement the sample was sputtered using glow discharge Ar plasma. Source conditions to obtain static sputtering were set to 1000 V, 15 mA and Ar pressure of 3.5 mbar. Sputtering was conducted for 10 s to reach about 1 μm in depth.

Coatings were also analysed for their elemental composition by Rutherford Backscattering spectrometry RBS using 1.4 MeV $^4He^+$. The backscattered particles were analysed using a 100 μm thick Si detector with a resolution of 15 keV FWHM. The spectra were analysed using SimNRA 6.06 [6] and Rutherford cross-sections.

Sputtering yields were obtained assuming D^+ to be the dominant species and the ion flux determined by a Langmuir probe upstream.

3. Results and discussion

Figure 1 presents the SEM BSE image of the Fe-W coating (marked with red lines) on Fe substrate in as received state (a) and after annealing for 1 h at 800 K (b). In the initial state no visible elemental segregation appears. It can be stated (up to resolved nanometer resolution) that the coating is homogeneous. It's impossible to say anything about the sub-nanometer, atomic W distribution. Annealing at 800 K for 1 h leads to visible W segregation as illustrated in Fig. 1 b). W rich islands with a size of 10 – 20 nm are relatively homogeneously distributed at the surface of the coating. No trace of contiguous W enrichment close to the surface was found.

The surface morphology of a reference sample and a sample exposed to D^+ plasma are shown in Fig. 2. The initial state is characterized by typical surface morphology for samples produced by magnetron sputtering. Slightly different deposition conditions depending on different substrate grain orientation results in visible coating surface inhomogeneity, corresponding to the underlying Fe grain. Figure 2 b) and c) illustrate the SEM image of surface morphology of samples exposed at 420 K at incident ion energy of 30 eV for 100 and 300 min, which corresponds to fluences of 1.8 10^{25} D m^{-2} and 5.4 10^{25} D m^{-2}, respectively. No distinguishable difference can be noticed when compared to initial sample. Some surface smoothening can be observed but it's not significant.

When the incident ion energy increases to 70 eV, already at lower fluence the surface morphology is visibly modified (Fig. 2 d)). The modification becomes more significant when ion energy increase to 190 eV (Fig. 2 e)). The surface of the sample exposed to 70 eV D bombardment at 770 K is characterized by areas with and without W. At these conditions the initial coating was nearly or fully eroded, depending on substrate grain orientation. Prepared FIB cross sections confirm presence of W spikes on part of the coating and eroded substrate on other parts. It appears that the coating grown on different substrate grains has slightly different properties with respect to erosion resistivity. In some parts a bit of W leftover was still present, whereas on the others the Fe-W layer was completely eroded.

More information about the surface modification under low energy deuterium particles bombardment can be learnt from Fig. 3 presenting the SEM images of FIB prepared cross sections of the coating.

The coating thickness in the initial state has about 380 nm, and does not change significantly after exposure to plasma with ion energy of 30 eV. The measured difference in thickness of 10 nm is within the error range and can be a result of slight coatings thickness inhomogeneity. Effective sputtering yield, at a fluence of 1.8 10^{25} D^+ m^{-2} is 1.11 10^{-06} and 1.16 10^{-04} for Fe and W, respectively.

Thickness of the coating exposed to 70 eV and 190 eV D bombardment decreases to 300 and 170 nm respectively. The effective sputtering yield at 70 eV is 4.37 10^{-06} and 1.71 10^{-03} for Fe and W, respectively and at 190 eV 2.68 10^{-05} and 2.67 10^{-03} for Fe and W, respectively. Moreover on the top of the eroded coating sharp spike like structures are present. The height of the spikes is 50 and 100 nm respectively, and the brighter contrast on a SEM image can indicate a different composition than in the underlying coating.

Figure 4 presents the GD-OES profiles of the samples in initial state (a) and after plasma exposure with incident ion energies of 30 eV (b) and 70 eV (c). The black curve represents atomic concentration of Fe, green of W and red of Mo which is the impurity from the sample holder. The measured W concentration in the coating, on GD-OES profiles, is at the level of 1.3 at.%.

For the sample exposed to lowest ion energy slight W enrichment of +0.2 at.% on the surface was measured but not exceeding first 20 nm. This phenomenon was however not observed by electron microscopy observation. The possible explanation could be that the FIB cross-sectioning is very local (10 – 20 μm), whereas the GD-OES signal collects space averaged information from an area of 5 mm^2. That would mean that there are some areas with slightly higher W concentration but not covering the whole sample surface. In the case of sample exposed at 70 eV D^+ W enrichment in the spikes area is more distinct. Relative W concentration in the spikes region was around 5 at. %. One needs to notice at this point that during the GD-OES analysis the measured surface was not flat. At the same time top of the spikes and the surface area in-between, was sputtered and measured. For that reason the real concentration of W in the spikes must be higher. This supposition was partially confirmed by EDX mapping performed on the thin lamellas (to increase the lateral resolution of the analysis).

The clear W enrichment inside the spikes is visible in Fig 5 showing an SEM image of a FIB prepared cross-section of sample after plasma exposure with an incident ion energy of 190 eV and a fluence of $8.5*10^{24}$ D m^{-2} together with EDX mapping. What is even more interesting the Fe signal measured in the spikes region was very low, what would indicate that the spikes formed under plasma exposure consist almost only of W.

Since the energy threshold for D^+ sputtering of Fe is about 45 eV and of W about 200 eV [7] no predominant erosion was expected in case of 30 eV D^+ bombardment, and was confirmed by performed investigation. Exposure at incident ion energy of 70 eV and 190 eV (above the threshold for Fe but below the threshold for W) caused expected Fe erosion, but also low W erosion, which is unexpected below the threshold. The explanation proposed by Roth [8] suggest the energy transfer via intermediate Fe collision, which would reduce the energy threshold down to around 80 eV and by that allow the observed W erosion. Another explanation could be a presence of small amount of O and N impurities in the plasma, which could cause the sputtering at lower ion energies.

Further investigation including lower fluence exposition at ion energy of 70 eV at 420 K to better understand the beginning of the spike formation process is required. Additionally surface composition analysis with better resolution is essential to confirm potential W enrichment at 30 eV D^+ bombardments is ongoing.

4. Conclusions

Fe-W binary coatings were exposed to low energy D plasma at 420 and 770 K. Different surface morphology depending on the exposure conditions was observed. No erosion and by that very limited surface change was observed in case of lowest incident ion energy. Sharp spikes at the samples exposed to 70 eV and 190 eV with high W enrichment was noticed. The origin of spike formation is up to now not clear and further investigation is requires. Below the spikes the composition of the coating seems to be unchanged. Tungsten enrichment after plasma exposure does not cover continuously the exposed coating – the iron containing film has always contact with the plasma. Similar results should be expected in the case of EUROFER-97 steel. On the other hand one cannot forget about much more structural complicity of EUROFER-97 steel which would require dedicated studies, to confirm these findings observed on the model system. Such studies are currently ongoing.

Acknowledgement

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References

[1] R.A. Pitts et al. J. Nucl. Mater., 415 (2011) 957–964

[2] R.L. Klueh et al. J. Nucl. Mater., 371 (2007) 37–52

[3] N. Baluc et al. Nucl. Fusion 44 (2004) 56–61

[4] R. A. Causey et al. Physica Scripta T94 (2001)

[5] K. Sugiyama et al. Journal of Nuclear Materials (2014)

[6] M. Mayer American Institute of Physics Conference Proceedings 475 (1999) p. 541

[7] W. Eckstein et al. IPP report 9/82 (1993)

[8] J. Roth et al. Journal of Nuclear Materials 454 (2014) 1–6

Figures

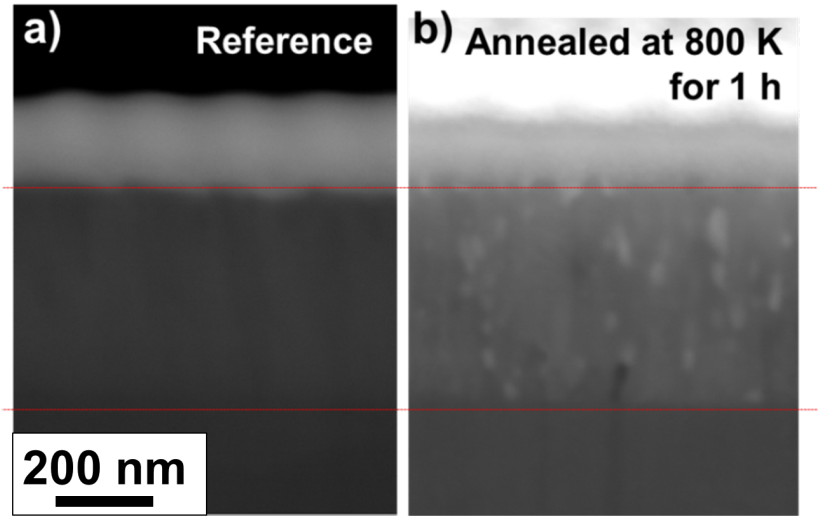

Figure 1 SEM BSE images of a FIB cross-section of samples in initial state (a) and after annealing at 800 K for 1 h (b). The coating is marked in red.

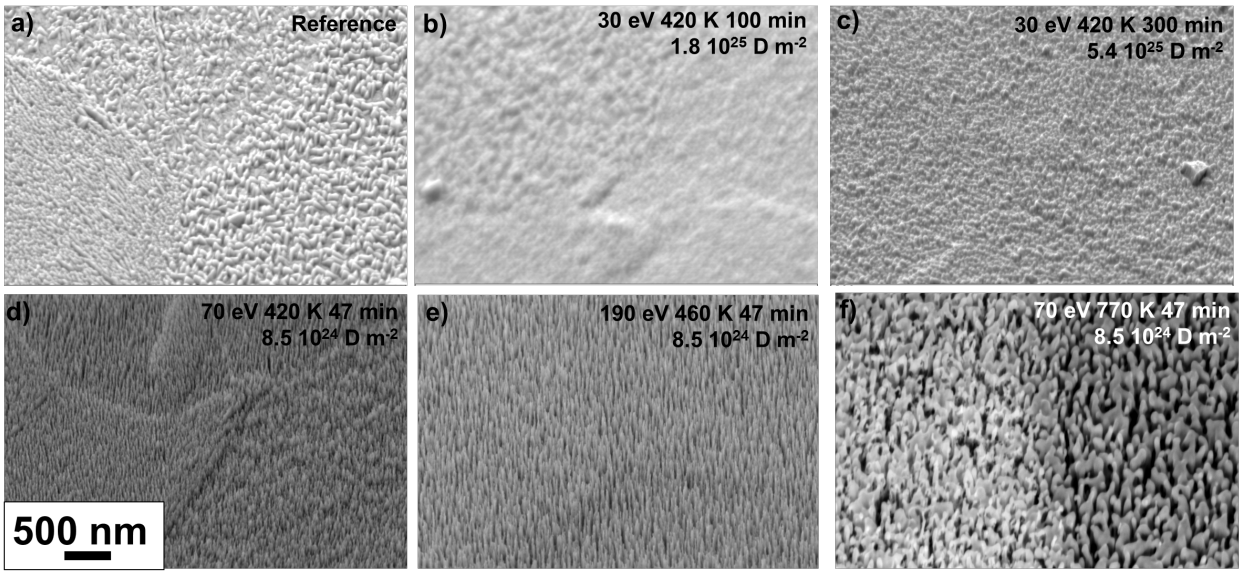

Figure 2 SEM image of the surface morphology of sample in initial state (a) and after plasma exposure (b-f)

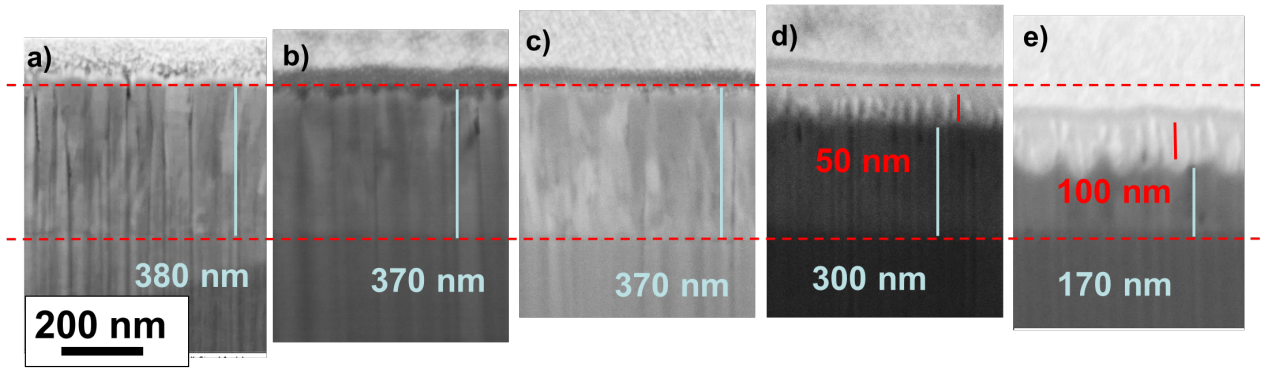

Figure 3 SEM image of a FIB cross-section of sample in initial state (a) and after plasma exposure – 30 eV 420 K 1.8*10^{25} D m^{-2} (b), 30 eV 420 K 5.4*10^{25} D m^{-2} (c), 70 eV 420 K 8.5*10^{24} D m^{-2} (d), 190 eV 460 K 8.5*10^{24} D m^{-2} (e). In blue the thickness of Fe-W layer is marked, in red the thickness of W enriched layer is indicated.

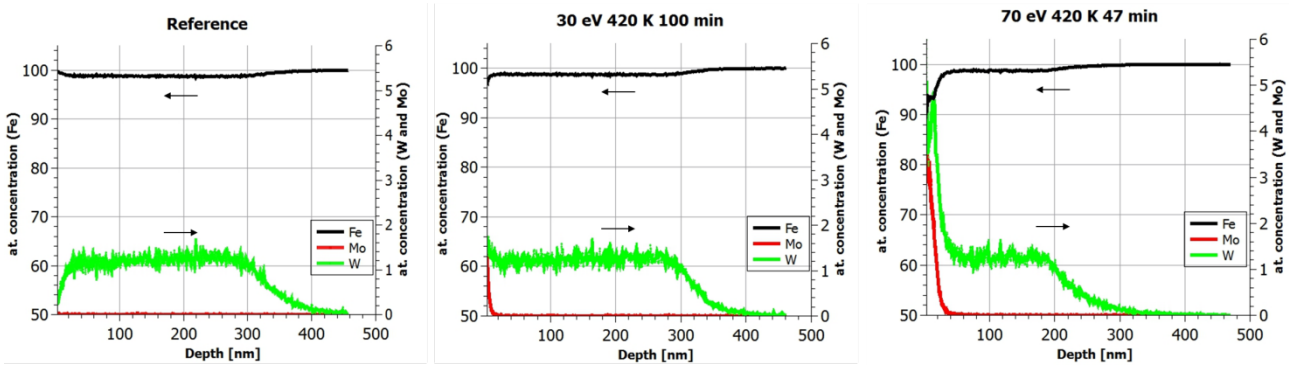

Figure 4 GD-OES profiles of sample in the initial state (a) and after plasma exposure with incident ion energy of 30 eV (b) and 70 eV (c). The black curve represents atomic concentration of Fe, green of W and red of Mo – impurity from the sample holder.

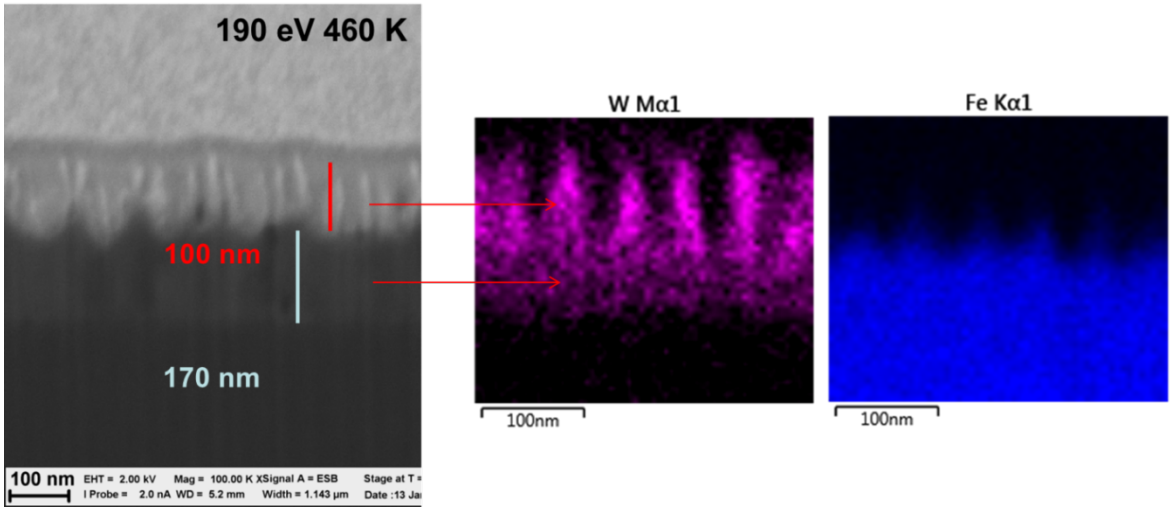

Figure 5 SEM image of FIB prepared cross-section of sample after plasma exposure with an incident ion energy of 190 eV and a fluence of $8.5*10^{24}$ D m^{-2} together with EDX mapping showing Fe and W distribution along the coating.