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The influence of N on the D retention within W coatings for fusion applications

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Plasma facing components (PFC) within a fusion device are subjected to a harsh operating environment involving high heat fluxes and exposure to high flux of hydrogen isotopes. This exposure can lead to a high fuel retention that can raise serious concern from safety point of view. One of the reason for the use of W as a material for construction of the first wall is aimed to reduce the fuel retention compared to carbon wall.

Nitrogen seeding, used in the operation of fusion equipment, represents a method to cool the divertor plasma and to reduce the W source in the divertor during inter ELMs. The effects of light impurity seeding have been analyzed so far mainly with focus on plasma heat transport and energy confinement and less on the plasma-wall interaction. However an exposure of the PFC to a combination of hydrogen isotopes and nitrogen can lead to changes in properties of exposed surfaces or to unexpected material behavior.

In the present work the influence of nitrogen on deuterium retention into the W coatings produced by high power impulse magnetron sputtering (HIPIMS) in a D+N atmosphere has been investigated.

Keywords: Deuterium containing coatings, HiPIMS, Tungsten nitride, Nitrogen seeding

1. Introduction

The transition from carbon wall to a metallic wall structure of fusion devices was mainly dictated by high erosion rates of carbon, induced by chemical sputtering, and a high co-deposition rate of hydrogen isotopes. This high co-deposition can produces high tritium retention with direct impact on operation safety. A long term reduction of fuel retention with a factor of 10-20, a significant reduction of erosion and, consequently a reduction of material migration from the main chamber to the divertor and from divertor to remote regions, are few advantages of JET-ILW compared with JET-C [1,2] from PFC point of view.

Concerning the operation of a fusion device with a metallic wall, the reduction of power loads on divertor, required in some operating scenario, or the mitigation of the W source in the divertor during inter ELMs[1] ask the seeding the plasma with nitrogen or noble gases (Ar or Ne). The seeding of impurities into the fusion plasma has been used in many experiments performed in TEXTOR, ASDEX Upgrade [3] and JET [4]. Improvement of general plasma performance was revealed during the nitrogen seeding experiments at JET ITER-ILW and ASDEX Upgrade. Thus nitrogen lead to increased radiative power and improved plasma energy confinement in the high-shape ELMy H-mode [5–6] in JET experiments and demonstrate .favorable properties in cooling the edge plasma and increasing the plasma confinement in ASDEX Upgrade [7].

The injection of nitrogen in the “scrape-off” layer of the fusion plasma can generate energetic N ions that can be further implanted in PFC materials (W and Be) leading to the formation of nitrides [8]. Moreover the combined exposure of surface of PFC to hydrogen isotopes and energetic nitrogen ions and consequently a possible formation of N compounds in the surface regions can lead to significant changes of exposed surfaces properties (melting point, sputtering yield, gas retention capabilities and so on). Recently laboratory studies have been performed on the formation of Be [8] or W [9-11] nitrides,studies focused on D implantation into metallic nitrides or subsequent exposure of such nitride films to D plasma.

In the present work, W-D+N films sputter-deposited from W target in a D+N atmosphere were applied as a model for re-deposited W layers in fusion devices after discharges with nitrogen seeding. The final objective of this paper was to assess the nitrogen influence on the deuterium retention in W coatings.

2. Experimental

W-D coatings with different N content have been deposited by HiPIMS (High Power Impulse Magnetron Sputtering) deposition method. The coatings were deposited on Mo substrates of 12x15x1mm and on FGG (Fine Grain Graphite) substrates of 8x18x1.5mm. The deposition were performed in an Ar+D atmosphere in a partial pressures ratio Ar:D of 6.3:1 The total deposition pressure were p= 3 10^{-3} torr. The Ar and D flow rates were kept constant during all experiments and just N flow rates were varied. Three types of coatings were obtained at different N flow rates between 0.5 sccm and 3.0 sccm. A reference W+D coating, used for

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comparison purpose, has been obtained in similar deposition conditions (general discharge parameters and D flow rate) with W-N+D coatings. A W adhesion layer was deposited on all samples before the admission of reactive gases (D and N) in the deposition chamber. The coatings main characteristics are summarized in the next table.

Table 1. Summary of the characteristics of the obtained coatings.

Sample id	N flow rate (sccm)	D (at.%)	N (at.%)	Thickness (μm)
WN0	0	25	0	3.2
WN05	0.5	48	22.7	6.4
WN2	2.0	51.2	24.9	6.3
WN3	3.0	54.5	22.3	5.3

The pulse duration and repetition frequency of the HiPIMS discharge were set to 5 μs and 7.1 kHz, respectively. A peak current of about 23 A was reached during the voltage pulse. The corresponding peak power density on the target surface was about 0.5 kW/cm^2.

Thermal Desorption Spectroscopy (TDS) has been used as an instrument in evaluate the gas content released from the coatings in general, and to comparatively asses the deuterium content within the coatings, in particular. The experiments were performed at 900^0 C. The heating rate was ~1.4 ^{0}C/s.

A Spectruma GDA 750 equipment has been used for Glow Discharge Optical Emission Spectrometry (GDOES) analysis. The equipment is provided with a monochromator with a Czerny-Turner design and with a focal length of 480 mm. The monochromator operates in the spectral range 190-800 nm and is provided with 3 gratings (1200, 2400 and 3600 l/mm). The spatial resolution of the monochromator is 0.025 nm. The analysis of the spectral data showed that for quantification of D content within the coatings, the D emission line at 656.078 nm is suitable.

X-ray diffraction (XRD) analysis was performed by using a Bruker D2 Phaser diffractometer operating in theta-theta geometry and using a Cu Kα radiation (λ=1.5405 nm). The scanning range was from 20 to 100° with a scanning step of 0.1°.

X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Escalab Xi spectrometer with an Al Kα radiation (1486.6 eV). An in situ Ar ion etching cycle (accelerating voltage 2kV for 180s) was performed in order to remove the surface contaminants. The XPS survey scans were acquired using the following parameters: pass energy=100 eV, energy step size=0.5 eV. The survey spectra were taken over a binding energy (BE) range from 4 to 1000 eV. High-resolution spectra for W 4f, O 1s, C 1s, and N 1s core level shave been obtained by performing five scans at pass energy of 50 eV. Advantage software was used for the analysis of all XPS spectra. High-resolution XPS spectra have been used in evaluating the chemical states of nitrogen.

3. Results and discussion

The use of HiPIMS for synthesis of W-D+N coatings take advantage of the all benefits of this deposition method in terms of crystallinity, roughness and compactness of the deposited films. The morphology of the coatings has been investigated by Scanning Electron Microscopy investigations (SEM). The investigations have been performed on cross section of the coatings deposited on FGG substrates.In Fig. 1 a SEM image of a WN3 sample is illustrated. The aspect of the fracture indicates a compact morphology with a columnar structure at the interface region (where the adhesion layer is situated). However the fracture doesn't have a smooth cleavage aspect and this might be an indication concerning the brittleness of the coating.

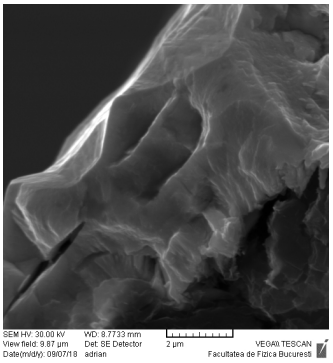
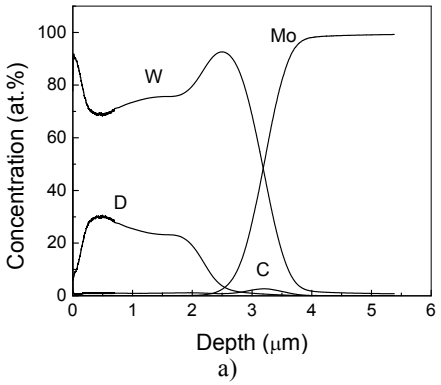


Fig. 1.SEM image of a cross section on WN3 sample

The elemental depth profiles of the coatings were performed by GDOES investigations. The GDOES depth profiles for two coatings are presented in Fig. 2. In Fig. 2a) the W+D reference coating (WN0) depth profile is presented whereas in Fig. 2b) a GDOES depth profile for a W-N+D coating (WN05) is shown.

The W adhesion layer applied at the start of the deposition can be clearly identified in GDOES depth profiles. It can be observed for WN05 coating a thickness of ~6.4 μm with a relatively uniform profile of the W, D and N.



a)

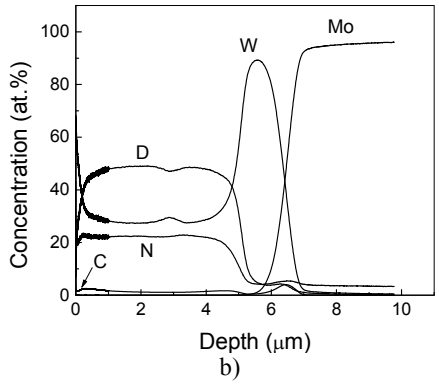


Fig. 2.GDOES depth profile for the WN0 sample (a) and WN05 (b)

Concerning theWN0 coating, obtained without N inclusions, the D content as measured by GDOES is significantly lower. An average D content of 25 at% has been measured for WN0 coating compared with a D content of ~ 50 at.% observed within the W coatings containing N (WN05). The D and N concentrations for the others coatings can be found in Table 1.

TDS measurements were performed on coatings deposited on Mo substrate. As this analysis doesn't give any indication of the D and N distribution within the coatings, the experiments have more an indicative character. D, N and Ar content released from W coating have been recorded simultaneously. In Fig. 3 a TDS spectrum of the WN2 coated sample in illustrated. As it can be observed a single major peak of the D released from the coatings occurs at ~380^0 C. This release temperature for deuterium is close to the release temperature observed by other authors [12]. At the same temperature similar peaks of the Ar and N have been observed, but theirs amplitude are significantly lower. However for the N, the major release peak occurs at higher temperature (700^0 C) indicating additional trapping sites of the N within the coatings. This quite high release temperature indicated that the N is trapped in W in high binding energy sites.

As the first peak of N release occurs at lower temperature (380^0C) this represents an indication of release of N atoms weak bonded, from the similar trapped sites with D and Ar, whereas the second release peak (~700^0C) seems to be the result of tungsten nitride decomposition [11].

Similar desorption spectra were obtained for the other samples coated with W-N+D coatings (WN05 and WN3). The differences between them were related to the amplitudes of desorption peaks.

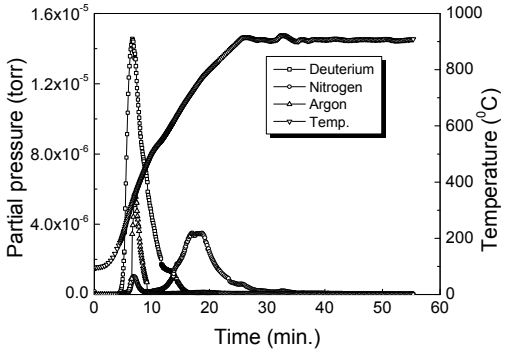


Fig. 3.TDS spectra of D, N and Arreleased from sample WN2

In order to evaluate the N bonding state within the coatings, XPS measurements were performed. XPS is a surface analysis technique with a probing depth of few nanometers that can supply important details about the chemical composition and chemical states of the investigated elements. XPS can be used in analysis of all elements except H and He [13].The analysis of the N1s spectral zone indicates after peak decomvolution, the occurrence of two components N1 and N2 (Fig. 4).

The N1 component at 400.3 eV is attributed to nitrogen N1s state [11] whereas the second component N2 at ~ 397.8 eV are attributed to metallic nitrides [14].The XPS analysis showed that the N fraction bonded in nitride phase decrease with the increase rate of the nitrogen flow used in the deposition process. In this way this percent drops from 96.09 % for WN05 coated samples, at 89.02 % for WN2 and finally to 87.88 % for WN3 sample.

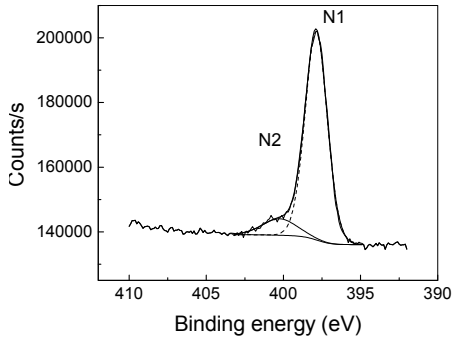


Fig. 4. N1s detailed spectrum for a WN3 coating

The diffraction pattern ofthe WN0 coating shows a polycrystalline tungsten cubic structure which exhibits a preferential growth on W (110) orientation (positioned at 2θ~40^0). When nitrogen is introduced into the deposition atmosphere a mixture of phases consisting of cubic W, and cubic NW phase starts to be formed. The NW phase shows important reflections after the (111) orientations at 37.69^0 and (220) direction situated at 63.67^0. This crystallographic phase is clearly identified and prevails over the W phase for WN2 and WN3 samples.

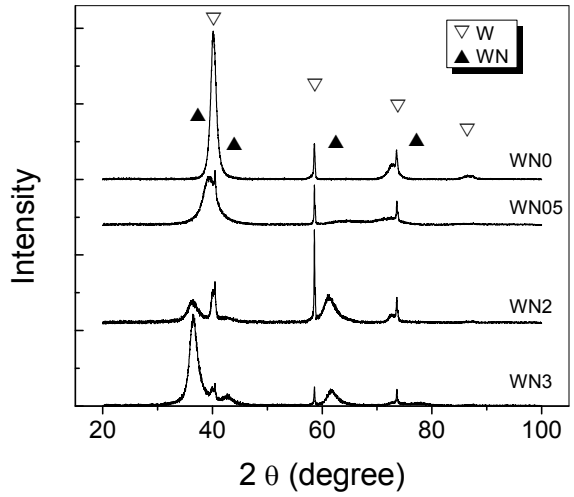


Fig. 5.XRD patterns for deposited coatings

4. Conclusions

The experiments concerning the deposition of W coatings in D+N atmosphere showed a higher D content trapped within the coatings compared with W coatings deposited in D atmosphere for the same deposition parameters. It has been noticed that the D content increase with the N flow rates used during the deposition process. The N is bonded mainly in metallic nitrides and the largest nitrogen fraction bonded in nitrides was observed for coating obtained at lowest N flow rate. A significant release of nitrogen at ~700^{0}C has been observed during the TDS experiments indicating a possible decomposition of metallic nitride phase.

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References

[1] G.F. Matthews, JET EFDA Contributors, the ASDEX-Upgrade team, Plasma operation with an all metal first-wall: Comparison of an ITER-like wall with a carbon wall in JET, Journal of Nuclear Materials 438 (2013) S2–S10

[2] S. Brezinsek, JET-EFDA contributors, Plasma-surface interaction in the Be/W environment: Conclusions, drawn from the JET-ILW for ITER, Journal of Nuclear Materials 463 (2015) 11–21

[3] J. Schweinzer et al., Confinement of 'improved H-modes' in the all-tungsten ASDEX Upgrade with nitrogen seeding, Nuclear Fusion, 51, 11, (2011)

[4] M. Oberkofler et al, First nitrogen-seeding experiments in JET with the ITER-like Wall, Journal of Nuclear Materials 438 (2013) S258–S261

[5] J. Rapp et al, Highly radiating type-III ELMy H-mode with low plasma core pollution J. of Nucl. Mat. 390–391 (2009) 238–241.

[6] J. Rapp et al., Integrated scenario with type-III ELMy H-mode edge: extrapolation to ITER, Nucl. Fusion 49 (2009) 095012.

[7] A. Kallenbach et al., Non-boronized compared with boronized operation of ASDEX Upgrade with full-tungsten plasma facing components, Nucl. Fusion 49 (2009) 045007

[8] M. Oberkofler et al, Plasma–wall interactions with nitrogen seeding in all-metal fusiondevices: Formation of nitrides and ammonia, Fusion Engineering and Design 98–99 (2015) 1371–1374

[9] L. Gao, W. Jacob, T. Schwarz-Selinger, A. Manhard, Deuterium implantation into tungsten nitride: Negligible diffusionat 300 K, Journal of Nuclear Materials 451 (2014) 352–355

[10] L Gao1, W Jacob, P Wang, U von Toussaint, A Manhard, Influence of nitrogen pre-implantationon deuterium retention in tungsten, Phys. Scr. T159 (2014) 014023

[11] K. Schmid, A. Manhard, C. Linsmeier, A. Wiltner, T. Schwarz-Selinger, W. Jacob, and S. Mändl, Nucl. Fusion, 50, (2010),025006

[12] V. Tiron et al, Tungsten nitride coatings obtained by HiPIMS as plasma facing materials for fusion applications, Applied Surface Science 416 (2017) 878–884

[13] R. E. Galindo, R. Gago, D.Duday, C. Palacio, Towards nanometric resolution in multilayer depth profiling: a comparative study of RBS, SIMS, XPS and GDOES, Anal Bioanal Chem (2010) 396:2725–2740

[14] J. F. Moulder, W. F. Stickle, P. E.'Sobol, K. D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Published by Perkin-Elmer Corporation, 1992