NANO-POREOUS COATINGS FOR GAS RETENTION STUDIES


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Abstract. One way to produce coatings with high gas retaining capability is to manipulate their structure towards a nano-porous one. Combined Magnetron Sputtering and Ion Implantation (CMSII) technique was used to produce pores of 1–10 nm in tungsten layers of about 1 μm in thickness. STEM, EDX, RBS, TDS and GDOES techniques were used for analyses of these layers. By heating the layer at 950°C the pores size increased up to 30 nm. The total amount of Ar retained in these layers was 3.9 · 10^20 atoms/m^2 while in compact W coating of the same thickness only 2.7 · 10^19 atoms/m^2 it was found.

Key words: nano-porous coatings, tungsten, argon.

1. INTRODUCTION

Nano-porous materials were intensively studied in the last decade, due to their prospective applications in biology, medicine, sensors and advanced energy technologies. The term refers to materials containing a structure of pores with diameters ranging from few nanometers to hundreds of nanometers. Particularly, nano-porous metallic materials have peculiar, structure related, electrical, magnetic, optical and catalytic properties which recommend them for the above mentioned applications.

Anodization was proved to result in formation of a spongelike porous Au film with a uniform pore size of approximately 20 nm [1]. Laser etching combined with phase selective electrolysis was used to fabricate nano-porous Ni membranes, with pores of 100–200 nm diameters, with improved catalytic properties [2]. Sol-gel methods have led to fabrication of 3D interpenetrating porous structures with pore diameters in 50 nm – few hundreds nm range [3], with applications ranging from high-power density batteries, antimicrobial scaffolds to hydrogen storage [4].
The plasma-wall interaction during the operation of a nuclear fusion device leads to a migration of materials associated with erosion and re-deposition phenomena [5]. Together with the re-deposited material certain amounts of gases from the discharge chamber are captured into the surface layer.

The investigation of the mechanism of gas retention in fusion materials, and in particular in W has a major importance as it can supply valuable information for assessment of tritium retention in future fusion devices. Tritium inventory represents a critical issue from safety point of view [6] in fusion devices and its amount must be limited. That is why a large scientific effort was devoted to the assessment of gas content and retention mechanism within materials used in fusion devices [7–10].

Ex-situ investigation of the fusion materials such as W and Be containing D, T, He, N, O and Ar is an important subject for fusion research. Another requirement for gas containing materials is manufacturing of reference samples for calibration of LIBS and GDOES equipment with D and He lines. The development of analytical methods for D and He quantification will allow a better estimation of the trapped gas inclusion in fusion materials. At the moment there are no such samples available on the market. The paper addresses to this new application of nano-porous coatings.

2. MANUFACTURING OF THE NANO-POREUS COATINGS

One way to produce coatings with high gas retaining capability is to manipulate their structure towards a nano-porous one. In this paper Combined Magnetron Sputtering and Ion Implantation (CMSII) technique was used to produce nano-porous coatings. This technique was initially developed for production of compact W coatings with a thickness in the range of 10–25 µm and high thermo-mechanical performances [11]. The CMSII method consists of a magnetron deposition method assisted by a high voltage pulsed discharge and it was applied at the industrial scale for W-coating of more than 4000 carbon fiber composite (CFC) and fine grain graphite (FGG) tiles for JET, ASDEX Upgrade and WEST tokamaks. JET (Joint European Torus) is at the moment the biggest operational tokamak in the world. Details about the applied technology are given in ref. [12, 13] however typical parameters for the high voltage pulse discharge are: \( U = 30–50 \text{kV}, \tau = 20 \mu \text{s}, f = 25 \text{Hz} \). The deposition technology involves a Mo interlayer with a thickness of 2–3 µm deposited between the substrate and the W coating for accommodation of the thermal expansion coefficients of W and carbon based material. In this way the adhesion between the W layer and the substrate was improved. When the limits of these W coatings were investigated at a large number of pulses (3000), with a surface temperature of 1400–1500°C, it was observed that degradation of the coating starts at CFC-Mo and Mo-W interfaces [14]. Close examination of the W coating before high heat flux (HHF) test revealed the presence in those zones of pores with size of 10–20 nm. They can be seen in Fig. 1. These zones, with a thickness of 400–500 nm, were identified as nano-porous W (np-W) and nano-porous Mo (np-Mo). This observation
has initiated research on two subjects: (i) elimination of the nano-porous zones from the W coating structure improving in this way the thermo-mechanical properties of the coatings and (ii) development of a new CMSII technology (np-CMSII) to produce on purpose nano-porous coatings for specific applications. In this paper only the second subject will be discussed. The deposition pressure was kept constant (0.66 Pa) during all experiments concerning pore formation and just the bias voltage was adjusted. Correlating the processing parameters during the deposition process with the formation of nano-porous structures led to conclusion that the energy of the ions striking the coating during its growth is responsible for pores formation. At low energy (at low bias voltage of 80 V) a compact, pores-free structure is obtained. With increasing the bias voltage toward 1000 V the structure becomes nano-porous. On the other hand a high voltage bias favors the sputtering of the coating reducing in this way the final deposition rate. At a bias voltage of 2000 V the sputtering rate is higher than the deposition rate and practically no coating is formed. Consequently the bias voltage should be chosen so a porous structure to be formed with a reasonable deposition rate.

The gases are usually retained at the grain boundaries so the capability of a coating to retain gases increases when the grain size decreases. In addition, this capability is significant higher in a nano-porous structure than in a compact, pore-free structure. The CMSII is a very flexible technique. Coatings with the grain size in the range of 1–10 nm but also in the range of 30–100 nm can be produced by changing the rotation device. On the other hand other gases such as He or D can be introduced in the deposition atmosphere together with Ar. In this way coatings with He or D can be obtained by optimizing the ratio between the flow rates of the auxiliary gases and Ar. Since He and D are light gases Ar is necessary in the deposition atmosphere to keep the sputtering rate at a reasonable level.
For this study a number of 10 samples were produced with the CMSII industrial coating unit in three runs. Details about the samples are given in Table 1. In the coating run no. 1 standard, pore-free W coatings (W), were produced. Argon containing nano-porous W coatings (Ar-np-W) were produced in the coating run no. 2 and deuterium containing W coatings (D-np-W) in the coating run no. 3.

Table 1

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Coating run</th>
<th>Type of coating</th>
<th>Substrate</th>
<th>Thickness (µm)</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>W (standard)</td>
<td>W</td>
<td>1.2</td>
<td>STEM</td>
</tr>
<tr>
<td>2</td>
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<td>Ar-np-W</td>
<td>W</td>
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<td>STEM</td>
</tr>
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<td>Ar-np-W annealed</td>
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<td>0.8</td>
<td>STEM</td>
</tr>
<tr>
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<td>RBS</td>
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<tr>
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<tr>
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<td>Ti</td>
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<td>EDX</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>W (standard)</td>
<td>Ti</td>
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<td>TDS</td>
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</tr>
<tr>
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<td>3</td>
<td>D-np-W</td>
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<td>6.4</td>
<td>TDS</td>
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<td>10</td>
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<td>D-np-W</td>
<td>Mo</td>
<td>6.4</td>
<td>GDOES</td>
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</table>

3. CHARACTERIZATION OF THE NANO-POREOUS COATINGS

The coatings structure was investigated by Scanning Transmission Electron Microscopy (STEM Hitachi HD-2700, 200 kV, c-corrected). The STEM analyses provide complimentary information for the same area where BF STEM (Bright Field STEM) image is associated with diffraction contrast, HAADF STEM (High-Angle Annular Dark Field STEM) image reveals Z-contrast coming from the atomic number and SE (Secondary Electrons) image is associated with topography. The lamellae for STEM observations were prepared using a Focused Ion Beam technique (FIB/SEM integrated system Hitachi NB5000).

EDX microanalysis was performed with a Si(Li) X-ray detector using an ultra-thin polymeric window from EDAX Inc. The system is installed on a Scanning Electron Microscope (FEI Inspect S model). The spectra analysis was performed with EDAX Genesis software using ZAF standardless model with automatic background subtraction.

Thermo-Desorption Spectroscopy (TDS) was performed using a quadrupole mass spectrometer (HAL 200) provided by Hiden Analytical Ltd. The samples are heated up in a quartz tube (Φ25 × 550 mm) that is connected with the mass spectrometer and the turbomolecular pump. This technique was used to determine the total amount of gas retained in the coating. Ar concentration into the coating was also determined by Rutherford Backscattering Spectroscopy (RBS) using a Van de Graaff accelerator and three detectors. The standard detector was installed
at 140° and the other two (pin-diode detectors) were located symmetrical each other, both at 165°. Spectra were collected for 2 MeV $^4$He$^+$ and 2.1 MeV $^1$H$^+$. Angle of incidence was 0° (normal incidence). The RBS data were analysed with the IBA DataFurnace NDF v9.6d [15, 16].

In some cases Glow Discharge Optical Emission Spectrometry (GDOES) was used for depth profiling of the constituents across the coating.

### 3.1. STRUCTURE OF THE COATINGS

Since Ar is used in the production of W coatings, the first gas containing porous coating was an Ar containing W coating (Ar-np-W). This coating was produced with the industrial CMSII equipment described in ref. [7]. It was investigated in comparison with the standard W coating (Sample no. 1) deposited also by CMSII on a W substrate (12 × 12 × 1 mm). The standard coating with a thickness of 1.2 μm has a columnar structure with the width of the columns in the range of 30–100 nm (Fig. 2a). A small porous zone of about 10 nm is formed at the substrate-coating interface (Fig. 2b). The pores with a size in the range of 1–5 nm are produced at the beginning of the deposition process when the bias voltage is relatively high. This regime is intentionally applied with the aim to clean the substrate by sputtering and improve the adhesion between coating and substrate. A small amount of Ar (< 1 at %), probably most at the interface, is retained in the standard W coating [12].

![Image](image_url)

**Fig. 2** – HAADF STEM images of standard W coating deposited by CMSII on bulk W substrate (Sample no. 1): a) columnar structure; b) substrate-coating interface.

Using the np-CMSII technique a nano-porous D-np-W coating (Sample no. 10) was deposited on W substrate (12 × 12 × 1 mm). GDOES depth profile of W for a
D-np-W can be seen in Fig. 3. A small contamination of C is also present at the surface and at the W-Mo interface.

![GDOES depth profiles for a D-np-W coating (Sample 10).](image)

Using the same np-CMSII technique a nano-porous W coating (Sample no. 2) was deposited. The structure of the nano-porous W coating (Sample no. 2) can be seen in Fig. 4. The pores are visible at the interface, but also in the entire structure. Some bubbles can be also seen at the surface. The porosity of this coating is clearly higher than that of standard CMSII coatings. The pores are better revealed by heating of the W coating at high temperatures. In Fig. 5 the BF STEM images of the W layer (Sample no. 3) annealed at 950°C for 30 min, are shown. The pores size increased from 1–5 nm to 7–30 nm. Responsible for pore enlargement a diffusion mechanism combined with a recrystallization process induced by heating seems to be the answer [17].

![BF STEM images of Ar containing nano-porous W coating (Sample no.2); porosity into the coating (a), and at the interface (b).](image)
3.2. GAS CONTENT INTO THE COATINGS

The gas content into the W coatings was determined by three methods: RBS, EDX and TDS. RBS analysis was performed on Sample no. 4. One 1H and one 4He spectra are shown in Fig. 6. The W signal and the step where the W concentration is reduced due to the presence of Ar are clearly seen. The fit is made with W 87.3 at % and Ar 12.7 at %. The areal density is \( 4720 \times 10^{15} \) at/cm\(^2\) which would correspond to 809 nm taking into account the averaged bulk densities. This value is in good agreement with 790 nm measured by STEM (Fig. 4a). EDX analysis has been performed comparatively for standard W coating (Sample no. 5) and nano-porous W coating (Sample no. 6). The substrate was Ti in both cases.
The EDX spectra, enlarged in the region of Ar peak, are shown in Fig. 7. The presence of Ar in the second sample is clearly seen while no Ar was detected on the standard W coating.

![EDX spectra for W coating](image)

![EDX spectra for W+Ar coating](image)

Fig. 7 – EDX spectra (detail on the Ar peak) for standard W coating (Sample no. 5) (a), and Ar-np-W coating (Sample no. 6) (b) deposited on Ti substrate.

The Ar concentrations measured by EDX are 0.8 ± 0.1 at % in the standard W coating and 5.7 ± 0.1 at % in the Ar-np-W coating. These values are estimated for a shallow zone (around 100 nm) from the coating surface. Taking into account the pores structure shown in Fig. 4 the Ar concentration into the depth of the W coating and particularly at the substrate-W coating interface might be significant higher.

Typical desorption curves for standard W coating (Sample no. 7) and for Ar-np-W coating (Sample no. 8) deposited on Ti substrate, correlated with the temperature of the samples measured inside the quartz tube are shown in Fig. 8.

![Desorption curves for standard W coating](image)

![Desorption curves for Ar-np-W coating](image)

Fig. 8 – Desorption curves for standard W coating (a), and for W + Ar coating (b).

The temperature was increased up to 950°C with a rate of about 2°C/s in both cases. The TDS spectrum for standard W coating shows three peaks. The first two peaks appeared at the temperatures of 630°C and 760°C and they might be associated with the Ar atoms released from the grain boundaries and defects.
The third peak with higher intensity is at the temperature of 850°C and seems to be produced by the Ar atoms trapped into the porosity mainly at the substrate-coating interface. The same peaks can be seen for Ar-np-W coating (Fig. 8b) at the same temperatures, but the intensity of the third peak is much higher than that of standard W coating. This is certainly due to the Ar atoms released from the pores of the Ar-np-W coating. By integration the TDS curves shown in Fig. 8 the total amount of Ar released from the W coating can be estimated. A value of $3.9 \cdot 10^{20}$ atom/m$^2$ was found for Ar-np-W coating and only $0.27 \cdot 10^{20}$ atom/m$^2$ for standard W coating. The amount of Ar retained in the nano-porous W coating is more than 10 times higher than that retained in the standard W coating.

3.3. DEUTERIUM CONTAINING W COATINGS

If deuterium (D) is added to the Ar in the deposition atmosphere D containing coatings can be obtained when the np-CMSII technique is used. By optimizing the D and Ar flow rates tungsten coatings with a thickness of 6.4 μm and relative high deuterium content were produced. The TDS spectrum of this coating shown in Fig. 9 indicates a very good ratio between D and Ar amounts into the coating. Ar cannot be fully removed from the W coating, but D is clearly the dominant gas.

The total amount of D into the W coating estimated from TDS spectrum is $2.5 \cdot 10^{20}$ D atom/m$^2$. This value is relevant for fusion plasma in a tokamak. As it can be seen in Fig. 9 deuterium is released at lower temperatures (610°C – 880°C) than argon. The Ar is mostly released at 900°C. This means that the bonding energy of D in the nano-porous W coating is lower than that corresponding to Ar.

4. CONCLUSIONS

A new technique (np-CMSII) and specific coating technologies were developed to produce Ar and D containing W coatings. The gas inclusions are accommodated
within porosity induced within the coatings. It has been observed that an increase of the substrate bias voltage during coating deposition leads to an increase of porosity. In this respect conventional coating deposition (CMSII-standard) leads to the formation of nanopores with dimensions of 1–5 nm whereas an increase of the bias voltage (CMSII-np technology) to 1000 V leads to an increase of the pore dimensions up to 7–30 nm. Consequently, due to the increase of pores dimensions, the gas content trapped within coatings during deposition process increased. The EDX, RBS and TDS measurements confirmed the relation between pore dimensions and trapped gas content.

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REFERENCES