X-ray diffraction study of a tungsten-based material for the first wall of ITER

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Abstract. Methods of X-ray diffraction (XRD), Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy were applied to POLEMA W sample after He plasma irradiation. The W reflections of the plasma treated sample exhibit an evident asymmetry characterized by a negative asymmetry parameter. Using the Williamson-Hall Plot technique the XRD reflection asymmetry has been successfully quantitatively described in frame of a model with two W phases with slightly different unit cell parameters and essentially different crystallite size and microstrain values.

1. Introduction

Due to its superior thermophysical and mechanical properties, tungsten is considered promising as plasma facing material, a material of the first wall components for ITER divertor in particular [1].

Recently, the changes of surface morphology of W samples after plasma irradiation with H [2-9], D (deuterium) [2-3], He [2], Ar [4] of fluence up to $\sim 10^{27}$ m$^{-2}$ has been studied by Scanning Electron Microscopy (SEM) [2, 4-9], Optical Microscopy (OM) [4, 7] or Atomic Force Microscopy (AFM) [7]. Various types of surface defects were observed, such as macro- [2] and micro-cracks [6-9], holes [7], blisters, bubbles and pores [2, 4, 7, 9], columnar structures [2] etc.

The elemental composition of the W sample surface after exposure to plasma has been investigated using Energy Dispersive X-ray Spectroscopy (EDXS) [4], X-ray Photoelectron Spectroscopy (XPS) [3] or Secondary Ion Mass Spectrometry (SIMS) [2, 9], providing the information about the impurity elements on the sample surface induced by sample mechanical and plasma processing.

X-ray diffraction (XRD) analysis has been recently applied to study the W facing materials after plasma treatment [2-9]. XRD data are mainly used for calculation of W unit cell parameter or interplane distances in the material [2-4, 6-7]. No calculation and discussion of the crystallite sizes is performed in the most of works [3-9]. Formation of microstrain $\delta s$ in W sample after plasma treatment due to difference of unit cell parameters from the table value of the W unit cell parameter is discussed in [3-4, 7]. Evaluation of $\delta s$ and average crystallite (regions of coherent X-ray scattering, RCS) size $D$ values of W by means of a crystallographic evaluation program has been performed in [2].

An asymmetry of W reflections was observed in [2, 5, 8]. The asymmetry was qualitatively interpreted in [5, 8] within the framework of the point defect model. In this model, an asymmetry parameter $\delta B$ is introduced [5] as $\delta B = (FWHM_{\text{left}} - FWHM_{\text{right}})/(FWHM_{\text{left}} + FWHM_{\text{right}}) \times 100\%$, where $FWHM_{\text{left}}$ and $FWHM_{\text{right}}$ are left and right parts of the Full width at half maximum of the reflection (see Figure 1 for illustration). The $\delta B$ parameter is connected with type of the point defects in the...
structure. In the case of the asymmetry parameter $\delta B > 0$, the vacancies are present in the structure. Contrary, if $\delta B < 0$, the interstitial atoms are observed in the structure. In [2, 5, 8], the asymmetry of W reflections of the negative sign is observed after the plasma treatment. A conclusion is drawn [5, 8] that in the W structure after the plasma treatment the point defects in the form of interstitial atoms are present.

Thus, the W samples are mainly examined and interpreted by means of qualitative or semi-quantitative techniques. The asymmetry of the XRD reflections of the W facing material after the plasma treatment is discussed in frames of qualitative point defect theory. We have made an attempt to analyze quantitatively the observed asymmetry of the W XRD reflections after plasma irradiation by means of Williamson-Hall Plot (WHP) technique in framework of a model with two phases with slightly different unit cell parameters.

2. Experimental details

The 20x20x7 mm³ tungsten (W) sample (inset in Figure 2) was prepared by POLEMA JSC (Russia). One side of the sample was irradiated with He ion plasma (fluence $\sim 10^{24}$ He/m², 300 pulses, distance to target 250 mm, energy density $\sim 0.4$ MJ·m⁻², heat load factor 100 MJ·m⁻²·s⁻¹/2).

SEM investigations and elemental EDX microanalysis were carried out using scanning electron microscope JSM 7001F (JEOL Ltd., Japan) equipped with energy-dispersive X-ray spectrometer INCA PentaFETx (Oxford Instruments, England).

XRD patterns of the plasma irradiated side of the sample were registered using a powder diffractometer D2 Phaser (Bruker AXS, Germany) designed in vertical Bregg-Brentano $\theta$-$\theta$ geometry and equipped with semiconductor linear position-sensitive detector LYNXEYE with opening angle of 5°. The measurements were performed in symmetric $\theta$-2$\theta$ scan mode using Cu-$K\alpha$ radiation monochromatized by Ni filter. To reduce the influence of the possible effect of preferential orientation of crystallites, during the measurements the sample was rotated around the sample holder axis coinciding with the axis of the diffractometer goniometer. Additional measurements were carried out to correct the XRD patterns to zero shift $\Delta\theta_{zero}$ of the detector and to evaluate the displacement angle correction $\Delta\theta_{disp}$ for WHP and unit cell parameter calculations ($2\theta = 2\theta + \Delta\theta_{zero} + \Delta\theta_{disp} \cdot \cos(\theta)$). For these measurements, the sample was mounted together with the Si640d X-ray powder standard (NIST, USA) in such a way that the sample surface was at one level with the Si powder surface. The
Si reflections of these measurements were used as internal standard for correction of the reflection angle positions of the sample. In turn the reflections of high intensity of the sample from these measurements were used as an external standard to correct the XRD reflection angle positions in the subsequent measurements of the sample.

X-ray phase analysis of the XRD patterns was performed by means of program EVA [12]. Powder Diffraction File-2 (PDF-2) [13] was used for the phase analysis. To evaluate the reflection parameters, the XRD pattern was first corrected for the background and Cu-Kα₂ contributions using the program EVA. After that, the expected 2θ angle positions of the reflections were set on the XRD pattern in automatic and/or manual modes. To evaluate the parameters of the strongly overlapped set reflections, for each of the observed experimental reflections independently of the others, parameters of the pseudo-Voigt (pV) profiles of the set reflections were refined by means of the TOPAS program [14] to describe the experimental reflection profiles.

Using the program SizeCr, which includes [15] the WHP method modified for pseudo-Voigt (pV) reflections, an WHP was constructed for the main observed crystal phases showing a sufficient number of reflections with a sufficiently high intensity. The pV type of the reflections observed was confirmed following the criterion $0.64 < \text{FWHM}/B_{\text{int}} < 0.94$ [16] for the pV reflections, where FWHM is observed full width at half maximum of the reflections and $B_{\text{int}}$ is their integral breadth for the crystalline phase considered. The FWHM values were corrected for instrumental broadening following the procedure for pV reflections [17] resulting in corrected values $FWHM_{\text{corr}}$, which were used for the calculations. During the WHP calculations, the Scherrer’s coefficient $k_{\text{Scherrer}} = 0.94$ [18] in the equation of Scherrer and Stokes’s coefficient $k_{\text{strain}} = 4$ [19] in the Stokes equation were utilized. The average values of the crystallite size $D$ and microstrain $s$ are obtained, correspondingly, from the intersection $A$ of the linear WHP graph $y = A + B \cdot x$ with y axis and slope $B$ of the graph as $D = k_{\text{Scherrer}} \cdot \lambda / A$ and $s (\%) = B^{1/2} \cdot 100 \%$, where $\lambda$ is wave length of the X-ray radiation used [15]. All checks, corrections and calculations were carried out by means of SizeCr.

The unit cell parameters of the detected crystal phases were calculated using the Celsiz [20] program by the method of least squares from the values of the Bragg angles 2θ of the observed reflections of the corresponding compounds with experimental corrections for $\Delta 2\theta_{\text{zero}}$ and $\Delta 2\theta_{\text{displ}}$.

### 3. Results and discussion

SEM image of the sample surface and EDX spectrum taken from them are shown in Figure 3. After

![Figure 3. SEM image and EDX spectrum (yellow) of the plasma irradiated sample surface](image)

![Figure 4. WHP of the phases W₁ (a) and W₂ (b) of the plasma irradiated sample](image)
plasma treatment, the surface has a moon-like landscape with “islands” (lighter areas in Figure 3(a)) and “cavities” (darker areas) with sizes of tens µm. Similar SEM images for the plasma treated W sample surface were obtained in [2, 7]. EDX microanalysis revealed 14.11 at.% of W and impurity atoms of Ti (7.43 at.%) and a small amount of other impurity metallic atoms (0.32, 1.50, 1.67 and 2.78 at.% of Cr, Al, Fe and Mg, correspondingly). As well, a lot of non-metallic impurity atoms were detected (33.16, 20.8, 18.80 and 0.15 at.% of C, F, O and S). The atoms referred to here as the impurity appear to have hit the surface of the sample when it was manufactured and processed by plasma.

Using the EDX results, X-ray phase analysis was carried out. Results are presented at Figure 2. A lot of high-intensity XRD reflections with different Miller indices $hkl$ were attributed to polycrystalline body-centers cubic (bcc) α-W (W phase thereafter, PDF-2 00-004-0806) [10]. A limited number of very weak reflections of the impurity phase of AlCr$_2$C (PDF-2 00-058-0267) [11] was also detected. Other elements observed by EDX microanalysis exist, probably, only on the surface in composition of X-ray amorphous material, or are incorporated in the structure of the found phases as impurity substitution atoms.

A thorough inspection of the measured XRD patterns showed that similar to [2, 5, 8], the W reflections of the plasma-treated sample investigated exhibit a pronounced asymmetry of negative sign ($\delta B = -11 \%$, Figure 1). In the framework of the point defect theory discussed in [5] that means the presence of the interstitial atoms in the W structure. However, the observed asymmetry of the W X-ray reflections can also be explained by the formation of two W phases with slightly different parameters. We will denote these phases in the further text as W$_1$ and W$_2$ and try to get quantitative characteristics of these phases within the framework of the model with the two W phases.

Calculation of the unit cell parameters by means of program CelSiz results in a small difference between the unit cell parameters of these two W phases (cf. $a = 3.152(3)$ Å and $3.159(3)$ Å for the phases W$_1$ and W$_2$, respectively). The obtained values of the unit cell parameters of the phases are close to the values of the unit cell parameters of the W material after 100 and 1000 plasma gun shots in [2] ($a = 3.1658$ Å and $3.1592$ Å respectively) and somewhat less than the table value $a = 3.1648$ Å [10] for the W powder as it was expected from the shift of the experimental observed reflection positions from the theoretical table ones (Figure 2).

Figure 4 presents WHP graphs for the phases. The WHP graphs constructed for both phases clearly demonstrate a positive slope, which means that there are microstrains in the W-crystallites of both W-phases of the plasma-treated sample under study. Interestingly, the values of the crystallite sizes $D$ and microstrain $s$ noticeably different in the phases W$_1$ and W$_2$ (cf. $D = 67(17)$ nm, $s = 0.13(1) \%$ and $D = 129(37)$ nm, $s = 0.097(8) \%$). Probably, one of the phases belongs to the bulk of the sample, and the other to the near-surface area damaged by plasma shots.

However, at the current stage of the investigation it is not possible to attribute the W phases to the bulk or near-surface layer. According to the literature data there are contrary results concerning to the evolution of the microstructure parameters after the plasma treatment. According to [2], the $D$ of W crystallites decreases after plasma treatment, whereas the $s$ values increase. Nevertheless, the W reflection width after plasma treatment decreases in [6, 8], that corresponds to an increase of $D$. The development of tensile stress (which is connected with increasing the microstrain) at first stages of the plasma irradiation is detected in [6] following by relaxation (i.e. decrease of microstrain) after 400 plasma pulses.

4. Conclusions
A model of two W phases with slightly different unit cell parameters successfully describes the asymmetry of the W reflection profiles of the sample after plasma processing. WHP technique is applied for evaluation of the average microstructure parameters. The average size of the crystallites of one of the phases is about twice the size of the crystallites of the other W-phase. The value of the microstrain in larger crystallites is about 1.5 times less than in the W-phase with a smaller size of
crystallites. Further work on the other quantitative methods of XRD necessary for the development of the model is in progress.

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