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Hydrogen accumulation in nanostructured as compared to the coarse-grained tungsten

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HIGHLIGHTS

- Study of the hydrogen behaviour in nanostructured as compare to coarse grained tungsten samples.
- Comparison between single (H), sequentially (C plus H) and simultaneously (C and H) implanted samples.
- Study of the stability of the nanostructures after implantation at different temperatures.
- Implantation energies for H and C above the displacement damage threshold.
- Study of the hydrogen behaviour as a function of the implantation temperature.

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ABSTRACT

We report on the influence of sample microstructure and of irradiation conditions on the H behaviour in Tungsten (W). For this purpose, commercial coarse grained (CGW) and nanostructured W (NW) samples were implanted with (i) H at room temperature (RT), (ii) sequentially with C and H at RT, and (iii) simultaneously (co-implanted) with C and H at RT. To study the possible effect of implantation temperature on H behaviour, a CGW sample and a NW sample were sequentially implanted with C at RT and with H at 673 K. The H and C implantation fluence was $5 \times 10^{20}\ \mathrm{m}^{-2}$ and the implantation energies were 160 keV for H and 650 keV for C which are above the displacement damage threshold. Scanning electron microscopy images show that nanostructured samples consist of columns with an average diameter of about 100 nm. These nanocolumns are stable under the studied implantations conditions. Moreover, surface modification is absent in all studied samples. X-ray diffraction data illustrate that all samples are mono-phase (α-W phase) and that none of the implantations led to the appearance of secondary phases. Resonant nuclear reaction analysis data show that the H retention in NW samples is larger than in CGW and that synergistic effect has a significant influence on the H retention in CGW samples but not in NW samples.

1. Introduction

Due to its properties tungsten is considered nowadays the best candidate for plasma facing materials (PFM) applications, in both magnetic confinement (MC) and inertial (laser) confinement nuclear fusion reactors (IC) [1–5]. However, some difficulties have been identified in coarse grained W (from now on CGW) which have to be overcome in order to fulfill specifications [6,7]. In particular, special attention should be paid to the high capacity for light species retention. Light species in CGW tend to nucleate in vacancy clusters forming overpressurized bubbles that lead, among other effects, to surface blistering and exfoliation [8–10]. In view of this, the light species behaviour in W has been experimentally studied [11–15] and modelled [16,17] by many groups all over the world.

Most of these studies were devoted to analyse the W behaviour under irradiation conditions taking place in magnetic fusion reactors. In these reactors, PFM will be mainly exposed to H-isotopes, He and plasma impurity ions such as carbon, all of them impinging into the PFM with energies below the displacement damage

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threshold. On this frame, the data on H behaviour reported so far evidence that H retention (i) is quite large in W [18], especially in samples containing radiation induced defects that even delay the H transport [19]. (ii) H retention strongly depends on irradiation conditions (single beam versus multiple beams, sample temperature and ion flux) [20,21] as well as on sample microstructure [22,23].

In laser confinement fusion, light species are generated after the explosion of the (deuterium–tritium) pellets. In this fusion approach, the energy of the light species impinging into the PFM strongly depends on the target illumination mode: direct or indirect. In reactors like HiPER, [24–26], operating with direct drive targets, ions are expected to reach PFM with energies well above the displacement threshold. Thus, the radiation-induced damage configuration, in laser fusion reactors with direct targets will be quite different from that expected in MC reactors. Therefore, the hydrogen behaviour in PFM in laser fusion reactors with direct targets cannot be reliably extrapolated from the results obtained for the evaluation of W under MC conditions.

One alternative to delay the appearance of blistering and exfoliation effects is the use of materials with a grain size in the nanometer range, so called nanostructured materials [27–29]. The behaviour of these materials under irradiation is very much dominated by the large density of grain boundaries (GBs), which at room temperature (RT) act as (i) annihilation centres for Frenkel pairs (self-healing behaviour) [30,31] and (ii) pinning centres for light species [32,33]. These two facts may drive the delay (shift to higher irradiation fluences) for the formation of overpressurized bubbles. Moreover, if as reported by von Toussaint et al. [17], the trapping energy for H at the grain boundaries is smaller than that at the radiation-induced defects, GBs may favour H release, performing as effective diffusion channels. Nevertheless, the behaviour of light species and in particular of H in nanostructured materials has not been sufficiently addressed, especially from the experimental point of view. Indeed, most part of the present conclusions have been deduced from computer simulation data in which a small number of atoms and a low number of ideal grain boundaries have been considered [34,35]. Because of the notable differences in microstructure and defect configuration between modelled and real nanostructured samples, the results of computer simulations must be carefully validated. Nowadays, to the best of our knowledge, only few works have been devoted to this topic. On the other hand the scarce experimental work devoted to the characterisation of nanostructured materials under irradiation has been performed on materials consisting of a metallic matrix (i.e. steel) with embedded oxide-based nanoinclusions (oxide dispersion strengthened steels, ODS) [36–38]. In these systems, the large amount of different phenomena, in particular phase segregation and chemical bonding, taking place at the GBs hamper a fundamental understanding of the role of GBs in the final radiation-induced defect configuration. To overcome these problems and to have a more fundamental picture of the influence of GBs on the radiation behaviour, especially designed samples consisting of immiscible multilayers of pure elements have been deposited and studied. The obtained results show that the interface play a role in defect reduction [39].

In this paper, we analyse the role of GBs on the H behaviour for pure nanostructured W samples. For this purpose, commercial coarse grained W and home-deposited nanostructured W samples were single- (with H), sequentially- (with C plus H) and simultaneously- (with C and H) implanted. The stability of the nanostructures under irradiation, the sample surface and the phase composition of the samples are characterised by comparing scanning electron microscopy images and X-ray diffraction patterns measured prior to and after implantation. The H depth profiles for samples with different microstructure implanted under diverse conditions is characterised by resonant nuclear reaction analysis (RNRA). RNRA results show that the H behaviour in NW samples is dominated by the presence of native defects.

2. Experimental

W coatings with a thickness of ~1.2 μm were deposited by DC triode sputtering from a pure W commercial target (99.95%) at a normal incidence angle on single-side polished Si (100) substrate. The deposition setup consists of a high vacuum chamber with a base pressure in the 10^{-8} mbar range which is equipped with a 5 cm diameter magnetron designed and manufactured by Nano4Energy SL [40]. Deposition took place in the presence of a pure argon atmosphere (99.9999%) at room temperature. The Ar pressure was 8×10^{-3} mbar, the plasma power was 45 W and the target–substrate distance was 8 cm. More details about sample fabrication are reported in Ref. [41]. In order to study the influence of the sample microstructure on H behaviour, two samples, one with a columnar structure with an average diameter of ~100 nm (from now on NW) and a commercial coarse grained W with a grain size in the μ-m range (CGW) were implanted with H at room temperature (RT). In order to investigate the influence of radiation-induced damage and of the microstructure on H behaviour a second set of samples (one NW and one CGW) were sequentially implanted first with C at RT and then with H at RT. A third set of samples was simultaneously implanted (co-implanted) with C and H at RT, to assess the effect of synergistic effects. To study the possible influence of the implantation temperature on the H behaviour in predamaged samples, a fourth set of samples was implanted with C at RT and with H at 673 K. To mimic IC energies in HiPER, the implantation energies were selected to be 170 and 665 keV for H and for C, respectively [42]. The implantation fluence for both H and C was 5×10^{20} m^{-2}. This fluence was selected as a compromise between a high value and a reasonable implantation time to ensure stable implantation conditions, especially for the simultaneously implanted samples. All implantations were performed at the ion implanter located at the Helmholtz Zentrum Rossendorf Dresden. A brief overview of sample codes and implantations conditions is presented in Table 1.

Prior to implantation and in order to achieve a higher depth resolution in RNRA experiments, the CGW samples were mechanically polished by using napless synthetic cloth. For the first rough polishing step a 0.5 μm colloidal alumina was used. The second polishing was done by using a 0.03 μm colloidal alumina. The CGW samples were not heated either before or after polishing. The NW samples did not undergo any treatment (neither polishing nor heating) before implantation because their root mean square (rms) roughness was lower than 3 nm.

The sample morphology was characterised prior to and after implantation by high resolution scanning electron microscopy (FEG-SEM) using a ZEISS AURIGA microscope (Carl Zeiss, Oberkochen, Germany) operated at different acceleration voltages from 1 to 3 kV. The chemical analysis of microscopic regions within the samples was carried out with an energy dispersive spectrometer (EDS) from Bruker model XFlash 5030 with an active area size of 30 mm^2.

The microstructural characterisation of the samples prior to and after implantation was investigated by XRD using a Philips X-PERT four cycle diffractometer with a Cu Kα radiation source. The XRD measurements were performed in Bragg–Brentano geometry.

The H depth profiles were characterised by resonance nuclear reaction analysis (RNRA). RNRA experiments were carried out by using the $H(^{15}N,He\gamma)^{12}C$ [43] nuclear reaction with a N^{2+} beam impinging onto the sample surface at normal incidence. This reaction has a sharp resonance at 6.385 MeV. The beam energy was varied in the range from 6.425 to 11.033 MeV. The 4.43 MeV γ-rays