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Sequential oxidation and reduction of tungsten/tungsten oxide

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ABSTRACT

The reduction of oxide films on the surface of tungsten was studied. The oxide films were created by briefly exposing smooth W foils to oxygen plasma generated using a microwave discharge at 500 W and an oxygen pressure of 40 Pa. Oxidation resulted in the formation of a WO_3 film with a thickness of approximately 1700 nm. The oxidised samples were then exposed to hydrogen plasma that was generated using the same conditions as the oxygen plasma and simultaneously heated by concentrated solar radiation. Several peaks were observed in the plot of the recorded sample temperature versus hydrogen plasma treatment time, indicating surface reactions. The treated samples were characterised using scanning electron microscopy, Auger electron spectroscopy, X-ray photoelectron spectroscopy and X-ray diffraction. The first step in the reduction process was the transformation of WO_3 to $\text{W}_{18}\text{O}_{49}$ which was followed by the rapid and complete reduction of the entire oxide film. The surface morphology changed upon reduction of the oxide film, and nanostructured tungsten remained on the surface, particularly after three sequential oxidation/reduction cycles. The reduction by hydrogen plasma was accomplished in a few seconds at approximately 1100 K, indicating the interaction of reactive hydrogen species, such as hydrogen atoms, with the $\text{W}_{18}\text{O}_{49}$ compound with a rich morphology. Treatment in equilibrium hydrogen at the same pressure without igniting plasma required a considerably higher reduction temperature of approximately 1400 K and an order of magnitude longer reduction time.

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1. Introduction

Selecting the correct plasma-facing materials is a very important task in the construction of the International Thermonuclear Experimental Fusion Reactor (ITER) [1]. During the running of fusion plasma in ITER, the materials will be exposed to extreme conditions, e.g., high particle fluxes and temperatures, which can lead to material erosion [2]. Because low-Z materials have high sputtering yields and thus short erosion lifetimes, the best candidates for plasma-facing materials are high-Z materials. One such candidate is tungsten, which is a promising material for the construction of divertors [3–6]. Furthermore, tungsten is also used in the ASDEX Upgrade (Axially Symmetric Divertor Experiment tokamak) as a full W-coated first wall [7]. In addition to a low sputtering yield, tungsten also possesses other superior properties, such as a high melting point and good thermal conductivity, among others [8]. Although hydrogen plasma is used in fusion reactors, under certain scenarios, the tungsten surface may come into contact with oxygen. These scenarios can include a loss of coolant accident, air leakage due to failure of vessel integrity [8] or the eventual use of oxygen glow discharge for cleaning [9–12]. When tungsten is exposed to an oxygen-containing atmosphere, it will oxidise. The temperature of tungsten components in fusion devices, which can be several hundred degrees Celsius, can have

an additional influence on the oxidation kinetics of tungsten. The mechanisms for the oxidation of tungsten in dry air in the temperature range between 600 and 800 °C have been studied by Cifuentes et al. [8]. First, a protective layer of $\text{W}_{18}\text{O}_{49}$ was formed. At higher temperatures, local cracking and the formation of $\text{WO}_{2.92}$, which was ultimately transformed to WO_3 , were observed [8]. WO_3 is very volatile at high temperatures (greater than 1300 K [13]), and its volatilisation is highly dependent on temperature and oxygen pressure [14,15]. Druyts et al. [16] studied the oxidation rates of tungsten in air as a function of time in the temperature range of 300–700 °C. They observed a transition between protective oxidation at lower temperatures, where the oxidation followed a parabolic law, and non-protective oxidation at higher temperatures, where the oxidation kinetics was approximately linear. This transition was observed in the range of 500–550 °C. At temperatures of 600 °C and greater, the volatile yellow-green oxide WO_3 was formed, but at temperatures greater than 1000 °C, the volatilisation led to a net weight loss. To reduce the oxidation rate of tungsten, self-passivating tungsten alloys were proposed, such as W–Cr–Si (12 wt.% Cr, 8 wt.% Si) and W–Cr–Ti (18 wt.% Cr, 2 wt.% Ti) [13,17]. In the case of an accident, such alloys can form a protective Cr_2O_3 layer at the surface, which leads to a reduction in the oxidation rate of approximately three to four orders of magnitude compared to that of pure tungsten [13]. Hopf et al. [10] investigated the oxidation of tungsten in ECR plasma generated in He/O_2 plasma, which was a part of the work performed during preparation of oxygen glow discharge experiments in the ASDEX Upgrade. They used an additional bias voltage

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of -200 or -400 V applied to the substrate holder to obtain ion energies similar to those in an ASDEX Upgrade DC glow discharge. They observed increased oxygen content on the surface that extended to approximately 5 nm into the surface. No information about the type of oxide was reported.

Because the appearance of oxides on the surfaces of plasma-facing materials is extremely undesirable, these oxides will have to be removed from the surface of the tungsten material. This can be performed using hydrogen plasma [10,18]. However, the changes that occur to the structure of the surface when oxidation followed by reduction is sequentially repeated several times remain unknown. In this work, we investigated the formation and reduction of oxide films on the surface of tungsten upon several cycles of sequential treatments with oxygen and hydrogen plasma at elevated temperatures.

2. Experimental details

2.1. Plasma treatment

Samples of tungsten sheets from Goodfellow Ltd. were cut to small squares with a size of 1 cm^2 . To form a thin oxide film and to investigate the reduction of the oxide film, the samples were mounted separately in a plasma reactor, which has been described in detail elsewhere [19,20]. The reactor consists of a quartz glass tube mounted perpendicular to a waveguide. The source of microwaves is a magnetron operating at adjustable powers. For our particular experimental conditions, the power was set to 500 W. The region of the most intense plasma was in the centre of the 5-cm-wide quartz tube. The samples were placed on a porous zirconia sample holder inside the region of the most intense plasma and heated independently from plasma parameters using concentrated solar radiation [19]. There is an adjustable opening shutter between the concentrator and the sample that allows for adjusting the solar heat flux independently from the position of the sun during the day and weather conditions as the experiments are only conducted during sunny days without clouds. For experiments reported in this paper, the direct solar radiation was almost constant over the entire surface of the square sample (1 cm^2) and the mean measured value is around 950 W/m^2 . The sample temperature was measured using a monochromatic ($5\text{ }\mu\text{m}$) optical pyrometer (Ircon, Modline Plus 7000, special series), which requires the knowledge of the normal emissivity at this wavelength to determine the real surface temperature. We selected a value 0.85 for oxidised tungsten [21]. Its lower detection limit is approximately 800 K (corresponding to 0 mV), and the upper detection limit is approximately 3000 K. The plasma reactor was first evacuated using a two-stage rotary pump. Then, the processing gas was leaked continuously through a flowmeter, resulting in a stable pressure of 40 Pa.

First, oxygen gas was used to oxidise the tungsten samples. The oxygen plasma was ignited simultaneously when the samples were exposed to concentrated solar radiation. When the sample temperature during oxidation reached approximately 1200 K (which occurred in a few seconds), both the plasma and solar radiation heating were turned off. The temperature evolution versus time is shown in Fig. 1. Some samples were only oxidised and stored for characterisation, but most of the samples were also treated with hydrogen plasma, as follows. After oxidation, the oxygen gas in the plasma reactor was pumped away and hydrogen gas was introduced into the reactor using the same pressure as for oxygen. Again, hydrogen plasma and concentrated solar radiation were simultaneously turned on, and the sample temperature during reduction of the oxide with hydrogen plasma was monitored using the pyrometer. This process allowed us to obtain information regarding the initiation of reduction because a considerable change in the pyrometer signal was observed due to changes in the emissivity (the spectral emissivity at $5\text{ }\mu\text{m}$ of pure tungsten is considerably lower (approximately 0.15) than that of the oxide). The samples were treated with hydrogen plasma for different lengths of times, from a few seconds to half a minute. Some samples were sequentially oxidised and reduced by treatment with

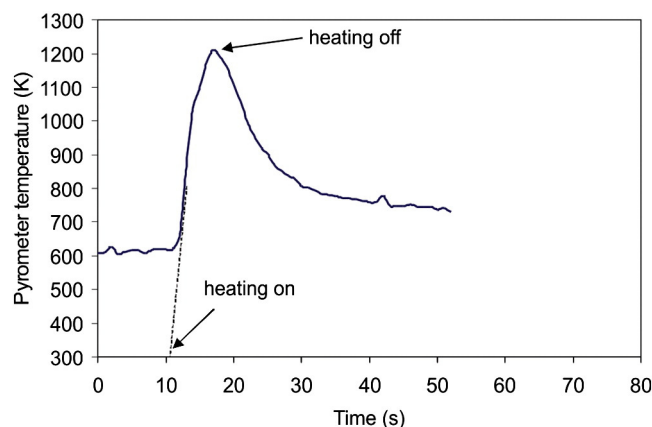


Fig. 1. Temperature of the tungsten sample using a normal spectral ($5\text{ }\mu\text{m}$) emissivity of 0.85 during oxidation in oxygen plasma (sample #1).

oxygen and hydrogen plasma three times. The surface of selected samples was analysed to monitor the appearance of any changes in morphology, composition and structure. All samples treated with hydrogen plasma were allowed to cool in H_2 gas to prevent any additional surface oxidation after exposing the samples to air. A list of the thoroughly characterised samples with the corresponding treatment conditions is presented in Table 1.

2.2. Surface characterisation

The samples were characterised using scanning electron microscopy (SEM), Auger electron spectroscopy depth profiling (AES), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

We used a JEOL FEG-SEM 7600F field-emission scanning electron microscope. Secondary electron images were recorded at magnifications of $5000\times$ and $20\,000\times$. The accelerating voltage was 15 kV.

AES depth profiling was performed using a PHI SAM 545A spectrometer. The samples were excited using a 3 keV electron beam with a current of $1.0\text{ }\mu\text{A}$ and a spot size of $40\text{ }\mu\text{m}$. To obtain depth profiles, the samples were sputtered using two symmetrically inclined Ar ion guns. Ions with a kinetic energy of 3 keV were rastered over a spot area of $3.5\text{ mm} \times 3.5\text{ mm}$. The etching rate was measured on standard Cr/Ni multilayer structures and was 10 nm/min . Concentration profiles were evaluated by using relative sensitivity factors from the manufacturer's handbook. The Auger peak-to-peak heights of C (272 eV), O (510 eV) and W (179 eV) were measured. The following sensitivity factors were used: C (0.18), O (0.50) and W (0.113).

XRD analysis was performed using a PANalytical X'Pert Pro diffractometer (MPD) operating at 40 kV and 20 mA (Cu $K\alpha$ radiation, $\lambda = 0.15418\text{ nm}$). The X-ray diffraction measurements of θ – θ symmetrical scans are made in the range 10 – 100° . The step size and the time per step are respectively fixed at 0.01° and 5 s. The X-ray diffraction spectra

Table 1

List of samples along with treatment details.

Sample	Description
#0	Reference (as-received sample)
#1	Oxidation in oxygen plasma only
#2	First oxidation, then partial reduction of oxide (both H_2 plasma and heating were turned off after reaching the maximum temperature—see Fig. 2a)
#3	First oxidation, then almost complete reduction (both plasma and heating were turned off just before reaching the minimum temperature—see Fig. 2a)
#4	Oxidation followed by full reduction in H_2 plasma (see Fig. 2a)
#5	Oxidation followed by full reduction, both repeated 3-times (Fig. 2b)
#6	Oxidation, then reduction by heating in H_2 gas without using plasma (Fig. 2c)

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