

Deuterium retention in TiC and TaC doped tungsten at high temperatures

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Abstract

Samples made of tungsten doped either with titanium carbide (W-1.1TiC) or tantalum carbide (W-3.3TaC) were either exposed to D₂ gas at a pressure of 100 kPa at 800–963 K or irradiated by 38 eV/D ions at 800 K. The deuterium (D) inventory in the samples was examined by nuclear reaction analysis and thermal desorption spectroscopy. The D bulk concentration and total retention in W-3.3TaC were comparable in all cases to that in pure polycrystalline W. The D bulk concentration in W-1.1TiC was more than one order of magnitude higher than that in pure W after exposure to D₂ gas, and was also several times higher than that in W-1.1TiC after irradiation at 800 K. It is suggested that D trapping inside the carbide precipitates in W-1.1TiC becomes essential at high temperatures.

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1. Introduction

Tungsten (W) is proposed for use as a plasma-facing material in the divertor region in ITER and future fusion devices. Widely discussed disadvantages of tungsten are its poor thermo-mechanical properties, such as high ductile-to-brittle transition temperature, cracking under high-heat cyclic loads, and embrittlement after recrystallization and irradiation [1]. Toughened, fine-grained, recrystallized (TFGR) tungsten-based materials doped either with titanium carbide (TiC) or tantalum carbide (TaC) are promising for use as plasma-facing or structural materials because of their improved ductility at low temperatures, high resistance against radiation damages, and good resistance to crack formation [2]. However [3-5], these materials have shown a tendency to retain higher amounts of D at elevated temperatures (>450 K) than pure polycrystalline W. The divertor plates in fusion reactors will operate at high temperatures, e.g., the expected surface temperature around the strike points in ITER is about 1300 K on the outer divertor and about 800 K on the inner divertor [6]. Therefore, this paper is devoted to investigation of trapping effects in the carbide doped W at higher temperatures.

2. Experimental details

Samples made of toughened, fine-grain recrystallized tungsten doped either with 1.1 wt.% (3.3 at.%) TiC (W-1.1TiC) or with 3.3 wt.% (3.2 at.%) TaC (W-3.3TaC) with dimensions of $10 \times 10 \times 1.2 \text{ mm}^3$ manufactured at Tohoku University (Japan) were used. The sample fabrication procedure consisted of several steps: (1) mechanical alloying of W and TiC (or TaC) powders in H_2 atmosphere; (2) degassing of the alloyed powder; (3) encapsulation of the powder in a steel capsule in vacuum; (4) hot isostatic pressing at 1350 °C; (5) grain boundary sliding-based microstructural modification (GSMM) - a deformation process at 1650 °C in vacuum. The materials are composed of W grains with dimensions in the range of 0.5-5 μm and carbide

precipitates with dimensions in the range of 0.05-1 μm , which are located both inside the W grains and at the grain boundaries [2-3]. In addition, samples made of hot-rolled pure polycrystalline W with dimensions of $10\times 10\times 0.8\text{ mm}^3$ and purity of 99.97 wt.% supplied by PLANSEE (Austria) were used as reference material (called “polycrystalline W” in the text). Those samples had flattened elongated grains with a length in the range of 1-5 μm [7]. All the samples were polished to a mirror-like finish and then annealed in vacuum at 1223 K for 2 hours to remove residual hydrogen and relieve stresses. The samples were exposed either to gas (first series of the experiments) or to plasma (second series).

The first series was made to investigate interaction of D with intrinsic trapping sites in the materials. The samples were exposed to D_2 gas at a pressure of 100 kPa at temperatures of 800 K, 873 K, and 963 K for 24 hours. The samples of all types (polished from both sides) were simultaneously placed in a stainless steel tube connected to a vacuum system. The tube was heated by an external electric furnace. Before the exposure, the system was pumped and baked until the background pressure decreased down to 1×10^{-5} Pa. Then the pump was closed, and the chamber was filled with D_2 gas with a purity of 99.9%. The real sample temperature was calibrated versus the measured oven temperature with a test sample measured in an independent experiment by a thermocouple spot-welded to the sample. After the exposure, the samples were quickly cooled down (<1 minute) to room temperature in D_2 atmosphere.

The second series of experiments was made to investigate features of trapping under irradiation by low-energy D ions at high temperatures. The samples of all types were simultaneously exposed to a D plasma in the PlaQ plasma device (IPP, Garching) [8]. D ions (mainly D_3^+) with the mean energy of 38 eV/D were extracted from an electron-cyclotron resonance plasma by applying a DC bias of -100 V to the externally heated sample holder. The

ion flux was about 9×10^{19} D/m²s, and the fluence ranged from 6×10^{24} D/m² to 1.8×10^{25} D/m². The temperature of the samples was 800 K. After the irradiation, the samples were cooled down to room temperature in about 30 minutes in D₂ atmosphere at a pressure of 0.5 kPa.

Deuterium depth distributions in the samples were measured by nuclear reaction analysis (NRA) using the D(³He,p)α reaction at the 3 MV tandem accelerator (IPP, Garching). Spectra of protons and α particles from the reaction were transformed into D concentration profiles using the NRADC programme [9] with SIMNRA [10] and cross-section data from [11]. Thermal desorption spectra (TDS) were measured in the TESS installation (IPP, Garching) [12]. The samples were placed in a quartz tube, which was linearly heated up to a temperature of 1275 K with a heating rate of 0.25 K/s at a background pressure of about 1×10^{-6} Pa. The sample temperature was measured in independent experiments in TESS by a thermocouple spot-welded to the sample. The release of 12 masses was monitored by a quadrupole mass spectrometer (QMS). Deuterium release in TDS was calculated taking into account D₂ and HD molecules, which are always observed in experiments with deuterium. QMS signals for masses 3 (HD) and 4 (D₂) were calibrated using NIST calibrated leaks (for details see [13]).

3. Results

The experiments with gas exposure demonstrated significant differences between the materials used. The NRA measurements revealed constant D concentration within the analysis range (≤ 7 μm) in W-1.1TiC after exposure to D₂ gas. The highest D concentration ($\sim 2.5 \times 10^{-4}$ at. fr.) was observed after exposure at 800 K, whereas at higher exposure temperatures the concentrations were about 2 times lower. The average D concentration taken from TDS (calculated by dividing the total amount of retained D by the sample thickness) and the near

surface concentration taken from NRA were similar at 963 K, whilst the TDS data were less than the NRA data at 800 K and 873 K. One can conclude that the sample was almost homogeneously filled with D only at 963 K, while the concentration decreased with depth at lower temperatures.

TDS measurements from W-3.3TaC and from polycrystalline W after exposure to gas demonstrated much smaller amounts of D in the samples than in W-1.1TiC at all temperatures used. NRA measurements showed that the deuterium concentrations in W-3.3TaC and in polycrystalline W were below the sensitivity limit ($\leq 10^{-5}$ at. fr.) at all temperatures used.

Fig. 1 shows TDS after exposure of W-1.1TiC and W-3.3TaC to D₂ gas. The spectra of the two materials are very different. The D release maxima in the spectra from W-1.1TiC were located at temperatures above 1000 K, the shape of TDS varied with the temperature of exposure, and the amount of deuterium trapped increased with temperature. Contrary, the spectra from W-3.3TaC contained only one peak at about 1000 K, and TDS was practically independent of the temperature of exposure.

In experiments with plasma irradiation, the D retention was smaller than in the case of exposure to gas. In NRA measurements in W-1.1TiC irradiated at 800 K to the highest fluence of 1.8×10^{25} D/m², deuterium was visible only in the near-surface layer (≤ 0.2 μ m), the concentration in deeper layers was close to the sensitivity limit of the method (at least several times lower than that after experiments with gas at 800 K). D concentrations in W-3.3TaC and in polycrystalline W were below the sensitivity limit of NRA.

TDS spectra from all the irradiated samples consisted of a single peak with the maximum at temperatures above 950 K (**Fig. 2**). The peak shifted towards higher temperatures and broadened with increasing fluence. The amounts of retained D in all materials obtained by TDS varied with

the incident fluence Φ slower than $\Phi^{1/2}$, i.e. not like in the ideal case of diffusion-limited retention (**Fig. 3**). The D inventories in W-3.3TaC and in pure polycrystalline W were similar, and both were several times smaller than the inventory in W-1.1TiC, which in turn was still several times lower than the values obtained in [3] after irradiation at 300 K and 600 K.

4. Discussion

Thermal desorption from all the samples both after exposure to D₂ gas and plasma took place at high temperatures (>800 K), suggesting that trapping sites with a high detrapping energy are responsible for D retention both in pure W and doped W at high temperatures. It should be noted that TDS spectra from pure W samples irradiated at 773 K in [14] also showed D release in a similar temperature range. A much higher concentration of retained D in W-1.1TiC than that in pure W at high temperatures indicates a much higher concentration of such trapping sites in W-1.1TiC. One may suggest that the carbide precipitates determine the D retention in W-1.1TiC at high temperatures. In general, deuterium can be trapped both inside the precipitates and at the precipitate boundaries. The titanium carbide precipitates are non-stoichiometric (TiC_x) [2] and contain vacant sites in the carbon sublattice where deuterium can be trapped [15-16]. At moderate temperatures D can be trapped only at the carbide boundaries, as the diffusivity in TiC is low. At high temperatures, deuterium may diffuse in the bulk of TiC and be retained there. A similar explanation was proposed for hydrogen trapping in Ti-containing steel [17]. According to [18], the hydrogen diffusion coefficient in TiC at 773 K is 6×10^{-17} m²/s, therefore the D diffusion length during the exposure to D₂ gas (and irradiation to the highest fluence) is certainly longer than the carbide grains dimensions. The high temperature shoulder extending up to 1100 K was mentioned in experiments [3, 5] on irradiation of W-1.1TiC at about 600 K. Long high temperature tails are typical for diffusion limited release, and this might be an evidence of D

trapping in the bulk of the TiC precipitates already at 600 K. No such effect was observed for W-3.3TaC.

The difference in D retention at high temperatures between W-1.1TiC and W-3.3TaC may be related to the differences between the properties of the carbide precipitates in the materials. Firstly, it can be related to a different non-stoichiometry of the carbides. Titanium carbide has stable compositions ranging from $\text{TiC}_{0.47}$ to $\text{TiC}_{0.99}$ [19]. At the same time, tantalum carbide has stable compositions in a more narrow range from $\text{TaC}_{0.73}$ to $\text{TaC}_{0.99}$, and this may lead to smaller diffusivity and smaller number of trapping sites due to smaller number of C-vacancy sites. The strong influence of the degree of non-stoichiometry on D retention and diffusivity in TiC_x was experimentally observed in [16, 20] and confirmed by density functional theory calculations in [15]. However, no data on hydrogen solubility, diffusivity, and retention in TaC are available.

One also has to mention that TaC, W_2C , and Ta_2O precipitates were found in W-3.3TaC, while only TiC precipitates were found in W-1.1TiC [2]. This also might influence the D trapping.

The experiments with plasma exposure gave smaller concentrations of trapped deuterium than the experiments with gas exposure. A similar effect was observed for self-damaged W exposed at about 700 K to the low-energy, high-flux D plasma and D_2 gas at 100 kPa [21]. According to the diffusion-trapping model of hydrogen retention in metals [22], in the case of local equilibrium between trapped and solute hydrogen, the population of a certain trap type depends on binding energy, the concentration of solute hydrogen, and the temperature. In the case of exposure to gas, in the equilibrium state the solute D is homogeneously distributed in the sample and its concentration c obeys the Sieverts' law: $c = Sp^{1/2}$, where S – hydrogen solubility,

p – hydrogen partial pressure, whereas in the case of ion implantation, the concentration of solute D has a maximum at the ion range ($c = (1-r)I_0R_p/D$, where D – hydrogen diffusivity within the ion range, r – reflection coefficient of incident ions, I_0 – incident ion flux, R_p – ion range) and linearly decreases to almost zero at the sample surfaces (if the D release is not surface limited).

If diffusion within the ion range is not enhanced by ion implantation, the maximum D solute concentration during the ion implantation was about 8×10^{-10} at. fr. (assuming $r = 0.7$, $R_p = 2.6$ nm [23], and $D = 1.4 \times 10^{-9}$ m²/s [24]), which is about three times lower than that ($\sim 2.5 \times 10^{-9}$ at. fr.) in the case of exposure to D₂ gas (according to the data on solubility for pure W [24]). However, this difference can be even higher if ion enhanced diffusion takes place within the ion range and due to the uncertainties of the values used in the estimation. Taking into account the potentially large number of trapping sites in TiC precipitates (as the concentration of Ti in W-1.1TiC is about 3×10^{-2} at. fr. and their nonstoichiometry can be as high as 0.53) and dependence of trap population on the concentration of solute D, higher concentrations of retained D may be expected in a fusion reactor where incident ion fluxes will be much higher ($> 10^{24}$ D/m²s) than in the present study.

The difference between the results for the samples exposed to D₂ gas and irradiated by plasma can also be ascribed to the difference in the D losses during cooling the samples down to room temperature. However, calculations of these losses for a pure W sample using the diffusion-trapping code TESSIM [25] (with cooling-down rates close to the experimental ones) demonstrated that the main losses of trapped D occurred only close to the surface within depths below several μm and do not significantly affect the bulk of the samples.

Finally, the influence of impurities on the sample surface is also not likely as the analysis of the polycrystalline W samples exposed to D₂ gas using X-ray photoelectron spectroscopy (XPS) and NRA (using the ¹²C(³He,p₀)¹⁴N, ¹²C(³He,p₁)¹⁴N, and ¹²C(³He,p₂)¹⁴N reactions) did not show an increase in the amounts of carbon, oxygen and other impurities on the surface of the samples in comparison with unexposed (and irradiated) ones.

5. Conclusions

D retention in toughened, fine-grain, and recrystallized tungsten doped either with 1.1 wt.% TiC or with 3.3 wt.% TaC was investigated in the temperatures range of 800-963 K. The samples were either exposed to D₂ gas at a pressure of 100 kPa at 800–963 K for 24 h or irradiated by 38 eV/D ions at 800 K to fluences in the range of $6 \times 10^{24} - 1.8 \times 10^{25}$ D/m². The D inventory in W-3.3TaC was very low in all cases and comparable with that in pure polycrystalline W. The D concentration close to the surface and the total amount of D trapped in W-1.1TiC after exposure to D₂ gas was more than one order of magnitude higher than that in W-3.3TaC and in pure W at all temperatures used. The D concentration near the surface in W-1.1TiC after exposure to gas was maximal at 800 K ($\sim 2.5 \times 10^{-4}$ at. fr.), and was several times higher than that after plasma irradiation. The maximum release of retained D during TDS from all the materials was observed at temperatures above 950 K indicating that traps with a high detrapping energy were responsible for D retention. It was concluded that the concentration of such trapping sites in W-1.1TiC was much higher than that in W-3.3TaC and pure W. It is suggested that D trapping in vacancies inside non-stoichiometric carbide precipitates in W-1.1TiC becomes essential at high temperatures. The difference of D retention in W-1.1TiC and W-3.3TaC may be attributed to differences in sizes and amounts of the precipitates, their stoichiometry and D diffusivity in them.

The difference between accumulation in W-1.1TiC after irradiation by low-energy D ions and exposure to D₂ gas may be due to the difference in D solute concentrations in the two cases.

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Figure captions

Fig. 1. Thermal desorption spectra of D₂ molecules from (a) W-1.1TiC and (b) W-3.3TaC exposed to D₂ gas at a pressure of 100 kPa for 24 hours at various temperatures.

Fig. 2. Thermal desorption spectra of D₂ molecules from W-1.1TiC, W-3.3TaC, and pure polycrystalline W irradiated by 38 eV/D ions at 800 K to the fluence of 6×10^{24} D/m².

Fig. 3. Fluence dependences of D inventory obtained by TDS in W-1.1TiC, W-3.3TaC, and pure polycrystalline W irradiated by 38 eV/D ions at 800 K.

Figures

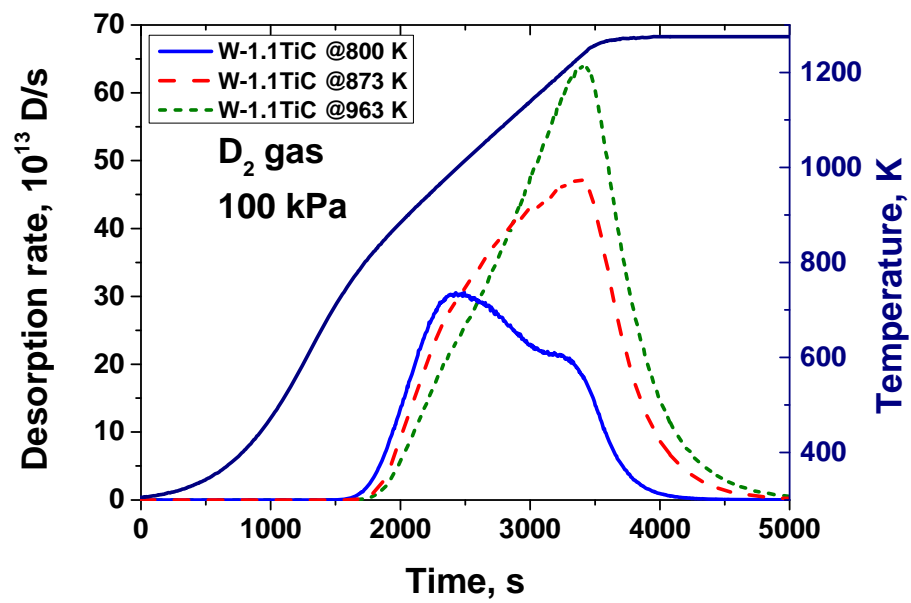


Fig. 1 a

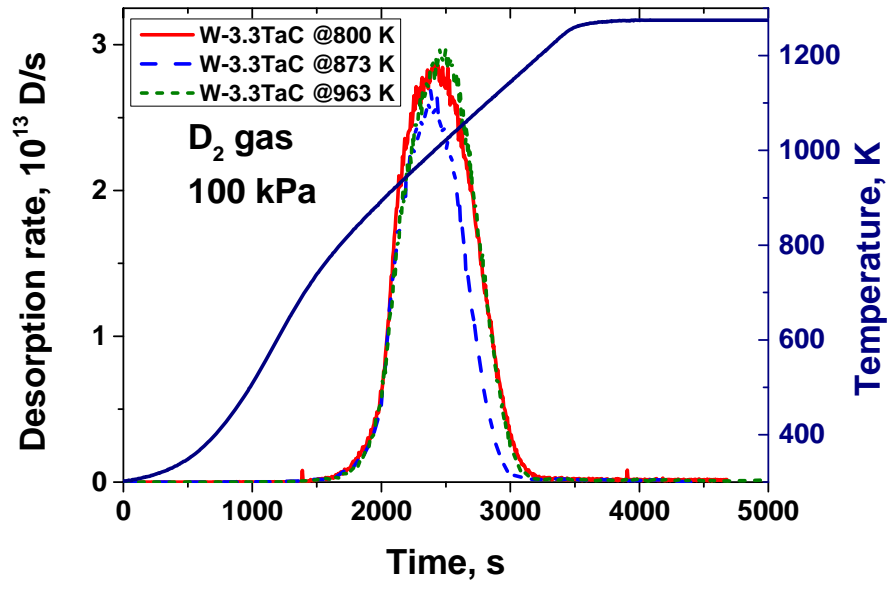


Fig. 1 b

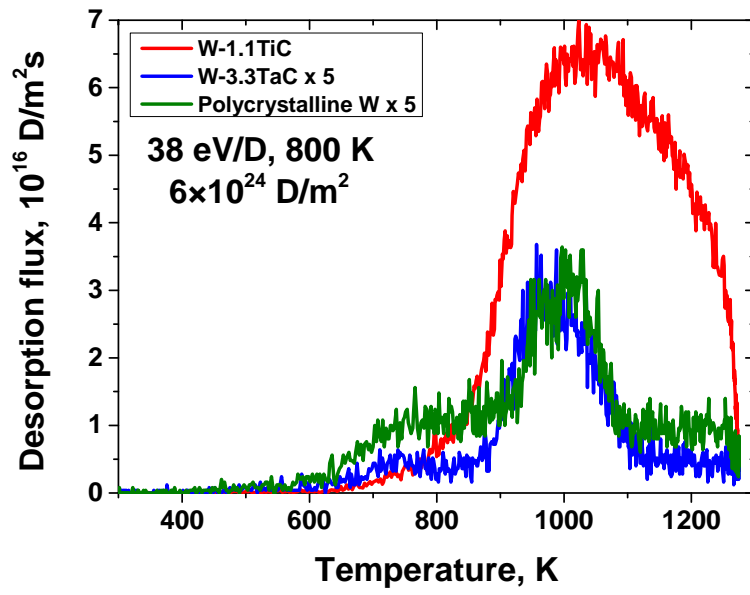


Fig. 2

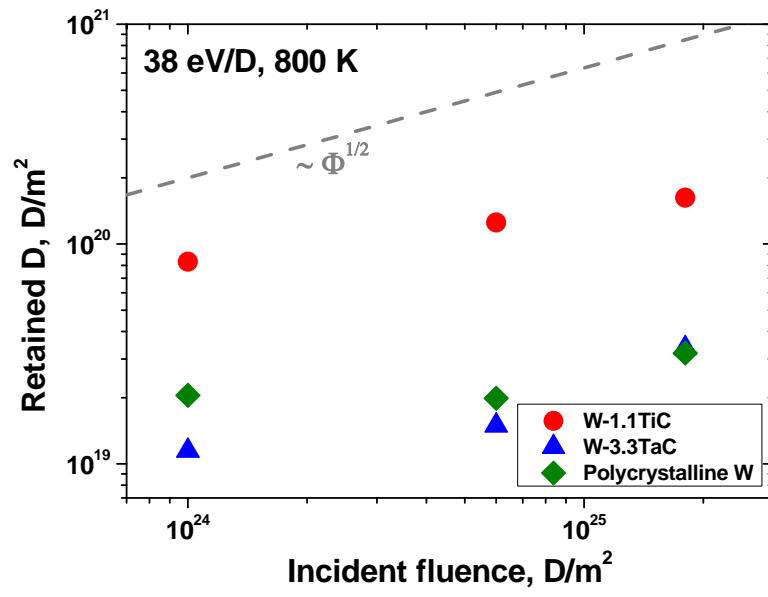


Fig. 3