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Deuterium retention in codeposited layers and carbon materials exposed to high flux D-plasma

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Abstract

A ceramic BCN target with samples of dense RG–Ti–91 without boron, RG–Ti–B with boron (0.1 at.%) and porous POCO AXF-5Q graphites was exposed in a stationary D-plasma of the 'Lenta' device with an ion energy of 200 eV and an ion flux of $(3-6) \times 10^{17}$ D/cm^{2}s at 1040 and 1400 K to a fluence of $\sim 1 \times 10^{22}$ D/cm^2. Codeposited layers were obtained for comparison on the target surface. Thermal desorption spectroscopy (TDS) showed that the amount of deuterium in RG–Ti after exposure at 1040 K was more than an order of magnitude higher than in POCO (9×10^{17} and 7×10^{16} D/cm^2, respectively). The retention took place preferentially in a surface layer about 100 μm thick. The bulk deuterium concentration in both RG–Ti and POCO was lower than 1 appm. The irradiated RG–Ti surface was subjected to strong erosion and consisted of 'columnar' grains covered with TiC at their tips. The deuterium in RG–Ti irradiated at 1400 K was located in the surface layer (1.5×10^{16} D/cm^2). The value of the bulk concentration did not exceed 0.1 appm while in POCO it was equal to about 20 appm. TDS for deuterium in RG–Ti demonstrated a spectrum similar to that for codeposited layers on a target surface. The differences in deuterium retention in the graphites are explained on the basis of structural differences. Considering tritium inventory assessment for ITER, dense graphites like RG–Ti are preferred for working divertor plates at high temperatures.

1. Introduction

Divertor plates of carbon materials in future fusion reactors such as the ITER will be affected by high heat loads up to 10–20 MW/m^2 [1]. Therefore, the materials must have a high thermal conductivity in order to remove the deposited energy. In addition, the materials must have a low erosion yield and low hydrogen isotope trapping. The retention of hydrogen in carbon materials is of great importance, because it affects fuel recycling and tritium inventory. The carbon erosion, both physical and chemical, under plasma bombardment must be low in order to prevent contamination of the plasma with carbon atoms, excessive thinning of the divertor plates and codeposition of carbon and hydrogen.

Porous fine grain graphites have a relatively low thermal conductivity of the order of 100 W/mK at 300 K [2]. Therefore, carbon fiber composites with higher thermal conductivity (380–240 W/mK at temperatures 300–600 K for CX2002U, for example) are now commonly used [3]. However, the disadvantage of fine grain carbon materials can be overcome by doping the carbon.

With respect to the thermal conductivity, titanium (Ti) doped (∼2 at.%) recrystallized graphite such as RG–Ti–91 shows very favourable properties (order of 600–200 W/mK at temperatures of 300–1000 K) [4]. According to Ref. [5], RG–Ti–91 appears to be a promising material for high heat flux areas of fusion devices. Indeed, this material has shown good performance in the divertor of tokamak ASDEX-Upgrade

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during the 1994–1995 discharge period [6]. The maximum heat flux to the RG–Ti–91 tiles was about 6 MW/m^2 and the maximum surface temperature increase of up to 700 K. No significant damage was found.

Doping of the graphite with Ti and a small amount of boron (~0.1 at.%) leads to a decrease in the chemical erosion and hydrogen trapping [7,8].

In a previous study [8] of deuterium (D) retention in RG–Ti–91 and POCO AXF-5Q graphites, samples were exposed to the D-plasma at 1400 K. It was shown that the amounts of deuterium in the graphites at fluences up to $\sim 4 \times 10^{20}$ D/cm^2 were approximately the same, and the deuterium was accumulated in a surface layer. At fluences in the range of $4 \times 10^{20} - 7 \times 10^{21}$ D/cm^2, the deuterium concentration in the bulk of POCO increased and reached about 18 appm while the bulk retention in RG–Ti was negligible. Dense RG–Ti graphite has an advantage for sorption parameters compared with porous POCO graphite at 1400 K which corresponds to the upper temperature limit for a graphite ITER divertor. However, data on deuterium accumulation at about 1000 K (the divertor plate working temperature) as well as correlation between deuterium retention and erosion were not presented.

The goal of the present study was to compare erosion and deuterium retention in RG–Ti and POCO graphite materials after exposure to high-flux D-plasma at 1040 and 1400 K to fluences of about 10^{22} D/cm^2 (equal to the particle dose on a divertor during one working ITER pulse) as well as to estimate the deuterium to carbon ratio in the codeposited layers.

2. Experimental

The experiments were carried out on compact anisotropic graphite RG–Ti–91 without boron and RG–Ti–B with boron (0.1 at.%) and porous isotropic graphite POCO AXF-5Q. RG–Ti–91, manufactured by hot pressing, is a strong dense graphite (2.2 g/cm^3) containing 1.7% Ti [8]. It has an axial texture or laminated microstructure [9]. The widely used commercial POCO AXF-5Q graphite was chosen as a reference material [2]. Samples of the graphites were exposed to a stationary deuterium plasma in the 'Lenta' device [8]. The exposure conditions were as follows: ion energy of 200 to 220 eV; sample temperature 1040 and 1400 K at ion fluxes of 3.2×10^{17} and 6.0×10^{17} D/cm^{2}s, respectively; residual gas pressure of 0.25 Pa and total fluence of $\sim 1 \times 10^{22}$ D/cm^2.

Cylindrical samples 25 mm in diameter and 10 mm thick were mechanically polished and then cleaned in an ultrasonic bath with alcohol. The direction of maximum thermal conductivity of the RG–Ti samples was used when the long dimension of grains was oriented normal to the surface which faced the plasma. The samples were mounted on a water-cooled target manufactured from high temperature BCN ceramics. Codeposited layers were also obtained on the target surface. The target surface was kept at a floating potential of −40 V. The temperatures of the samples and the ceramic target during exposure to the plasma were measured by optical pyrometer and thermocouple. After exposure, the samples were transported in air to the surface analysis station and then examined by means of scanning electron microscope (SEM) and reflection high energy electron diffraction (RHEED). The weight loss of the samples was measured using a microbalance. For TDS analysis from the near-surface layer of graphite cylinders and the BCN ceramic, cubes were cut with $1.5 \times 1.5 \times 1.5$ mm^3 dimensions. The cubes were ultrasonically cleaned in alcohol before TDS. TD measurements were performed in an UHV chamber at a pressure of 10^{-6} Pa.

Deuterium retention in the samples was studied by TDS during heating to 2150 K. Desorbed HD and D_2 molecules were detected with a calibrated quadrupole mass spectrometer (QMS). A QMS sensitivity correction was applied to the HD signals. HD molecules were assumed to form in the specimen due to an initial hydrogen presence from manufacturing. The deuterium concentration was calculated assuming D_2 to be 2 D atoms and HD to be 1 D atom. Mechanical removal of the surface layer (with a knife) was used to distinguish between the bulk and surface fractions of retained deuterium. The thickness of the layer (about 100 μm) was calculated from the weight loss of the samples. The surface structure of the deuterium-irradiated graphite was studied by SEM and RHEED. The thickness of the codeposited layer on a BCN ceramic surface was measured with an optical microscope.

After exposure to the D-plasma, no differences were found in the erosion rate, composition, structure and amount of retained deuterium between RG–Ti specimens with and without boron. Therefore, the term "RG–Ti" will be used throughout the text for definition of both types of graphites.

3. Results and discussion

The results and discussion are described in two parts – 1040 K lower temperature response and 1400 K higher temperature response.

3.1. Exposure to D-plasma at $T = 1040$ K

The irradiated surface of RG–Ti consisted of 'columnar' carbon grains which were about 10 μm in cross-section and 100 μm long. The grains were stacked normal to the surface. Also, the grain tips were covered by a layer of titanium carbide (TiC) of not less than 10 nm thickness. Authors [4] in a related study found that the 'columnar' structure was formed from carbide particles. Most likely, the carbide particles protect the underlying carbon material from erosion until a columnar structure evolves. The surface of the POCO graphite remained uniform and relatively smooth. The scale of the inhomogeneities was about 10 μm. At the same time, in the course of erosion measurements it was found that the POCO graphite had been subjected to greater chemical erosion than was RG–Ti (see Fig. 1). The average erosion rate for POCO was five times higher than that for RG–Ti (0.4 and 0.08 atom C/ion D, respectively).

According to the results of TDS analysis, the amount of deuterium in the damaged surface layers of RG–Ti graphite was about one order of magnitude higher than that of POCO (9×10^{17} and 7×10^{16} D/cm^2, respectively). The bulk concentration of the deuterium in the RG–Ti graphite was below the detection limit (0.1 appm), while in POCO, it did not exceed 1 appm.

Deuterium release from RG–Ti graphite occurred in the form of D_2 molecules starting at 1000 K and reached a maximum at 1100 K.

The TD spectrum of D_2 molecules from POCO was characterized by three peaks at 1000, 1200 and 1400 K. The TD spectrum for HD molecules was shifted approximately 100 K to higher temperatures (see Fig. 2).

After exposure to the D-plasma, the BCN ceramic target near the graphite samples was covered by a carbon deposit 10 μm thick. The maximum rate of deuterium release from this layer took place at a temperature of 1000 K. The deuterium to carbon ratio in the codeposited layers on the target was approximately 5×10^{-4}. We believe that the peak for deuterium evolution established for RG–Ti and POCO graphites at 1000 K can be attributed to the gas escape from the thin codeposited deuterium-rich carbon layer present on the surface of irradiated specimens.

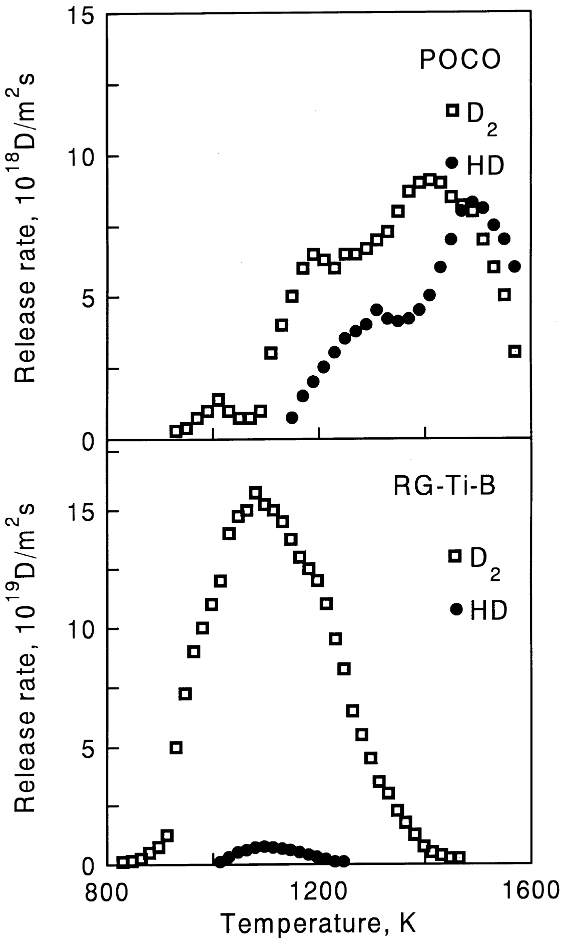

Fig. 2. Thermal desorption of D_2 and HD molecules from POCO AXF-5Q and RG–Ti–B with 0.1 at.% boron graphites exposed to deuterium plasma (sample temperature 1040 K, ion flux 3.2×10^{17} D/cm^2 s, exposure time 9 h). The heating rate was 6 K/s.

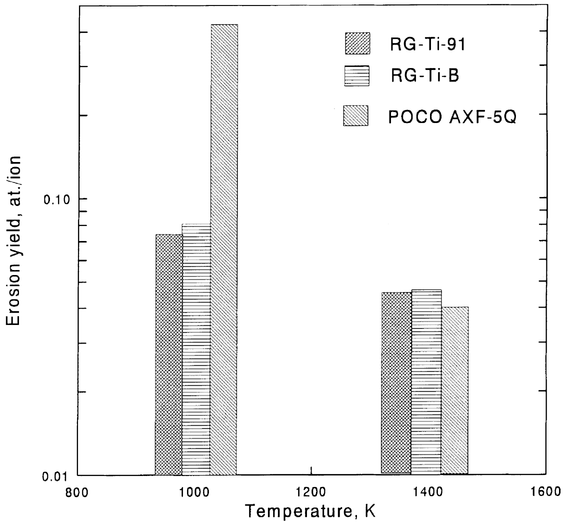

Fig. 1. The erosion yield of RG–Ti–91 (1.7 at.% Ti), RG–Ti–B with boron (0.1 at.%) and POCO AXF-5 Q graphites exposed to the deuterium plasma at 1040 and 1400 K.

The release of a considerable amount of deuterium from RG–Ti at 1100 K is probably related to the formation (due to active chemical erosion of the carbon) of the 'columnar' structure which represents a large newly created surface area characterized by a large sorption capacity. At the same time, deuterium is not able to penetrate into the bulk of this graphite.

The accumulation of deuterium in POCO graphite proceeds also on the surface layers of the samples (~3×10^{16} D/cm^2). However, the presence of a high HD signal in TD spectra points out that the gas evolution takes place not only from the surface reached by deuterium, but also from a bulk with a lower deuterium concentration in the neighborhood of the surface. A high temperature shift of the HD signal is assumed to be the result of a delay in gas escape related to the time needed for diffusion of HD molecules from the bulk to the surface.

3.2. Exposure to D-plasma at T = 1400 K

In the course of experiments on RG–Ti and POCO graphites exposure to D-plasma at 1400 K, some peculiarities in the character of surface erosion and deuterium sorption were found compared to exposure at 1040 K. A relatively weak decrease in the erosion rate of RG–Ti specimens (by a factor of 1.5) was accompanied by considerable change in composition and morphology of surface. No titanium carbide was detected by RHEED analysis. The scale of the eroded surface roughness and crystal dimensions was of the same magnitude, 3–10 μm. The deuterium in the eroded RG–Ti graphite layer was significantly lower than that at 1040 K (~1.5 × 10^{16} D/cm^2 and 9 × 10^{17} D/cm^2, respectively). After removal of a layer about 100 μm thick, the deuterium concentration in the remaining specimen did not exceed 0.1 appm.

The codeposited layer on the BCN target surface was 20 μm thick and the D/C ratio was about 2 × 10^{-3}. The TD spectra of deuterium from RG–Ti and codeposited layers were characterized by a broad maximum at 1500 K which was obviously related to the gas evolution from a codeposited deuterium-rich carbon layer (see Figs. 3 and 4).

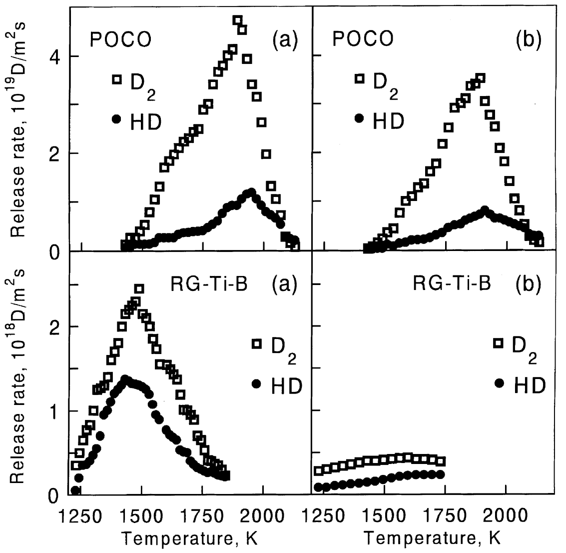

Fig. 3. Thermal desorption of D_2 and HD molecules from POCO AXF-5Q and RG–Ti–B with 0.1 at.% boron graphites exposed to deuterium plasma (sample temperature 1400 K, ion flux 6 × 10^{17} D/cm^2 s, exposure time 5 h) before (a) and after (b) mechanical removal of ~100 μm thick surface layer. The heating rate was 6 K/s.

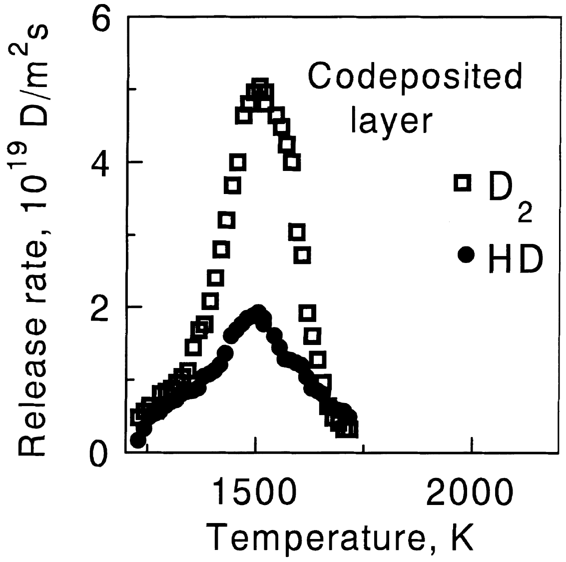

Fig. 4. Thermal desorption of D_2 and HD molecules from codeposited layers on the BCN ceramic target (target temperature ⩽ 1400 K, thickness 20 μm). The heating rate was 6 K/s.

The erosion rate of the POCO graphite decreased by an order of magnitude compared to that at 1040 K (see Fig. 1). It can be understood as a decrease in methane formation at higher temperatures (see Fig. 5 in Ref. [10]). At the same time, no marked change in surface roughness was observed by SEM: the scale of inhomogeneities was about 10 μm. The accumulated deuterium was found to be quite uniformly distributed through the specimen, about 1.5 mm thick. The amount of deuterium in the surface layer (about 100 μm thick) was somewhat higher compared to that in the bulk where it was found to be about 20 appm (taking into account a near-surface layer, 24 appm). The TD spectrum of D_2 and HD molecules from the POCO specimen had two peaks (at 1700 and 1900 K) which are attributed in the literature to the liberation of deuterium from deep traps with a binding energy of 4.5 eV [11] and/or closed micropores [12].

4. Conclusions

Deuterium retention in dense RG–Ti–91 without boron, RG–Ti–B with boron (0.1 at.%) and porous POCO graphites was studied after exposure to a high-flux D-plasma in the 'Lenta' device at 1040 and 1400 K. No differences were found in the erosion rate, composition, structure and retained deuterium levels between RG–Ti specimens with and without boron.

At 1040 K, TDS analysis showed that deuterium content in RG–Ti graphite was more than an order of magnitude higher than in POCO (9×10^{17} and 7×10^{16} D/cm^2, respectively). Deuterium was trapped in a near-surface layer about 100 μm thick. Bulk deuterium concentration in the RG–Ti was less than the experimental detection limit (<0.1 appm). The study of surface composition and morphology indicated that high deuterium content in the surface layer ($\sim 9 \times 10^{17}$ D/cm^2) was caused by chemical erosion peculiarities of RG–Ti. The surface consisted of 'columnar' carbon grains with TiC at their tips which were stacked normal to the surface. The average erosion rate for POCO was five times higher than that for RG–Ti (0.4 and 0.08 atom C/ion D, respectively). POCO was homogeneous and had a relatively smooth surface (∼10 μm). The deuterium content in the POCO near-surface layer was low ($\sim 3 \times 10^{16}$ D/cm^2) and the bulk concentration did not exceed 1 appm.

At 1400 K, the deuterium content in RG–Ti was significantly lower than that at 1040 K (1.5×10^{16} and 9×10^{17} D/cm^2, respectively). Deuterium was present locally in a near-surface layer and was absent in the bulk. Deuterium retention in POCO took place mainly in the sample bulk at a concentration of about 20 appm. The contribution of the surface layer in the deuterium accumulation was low (taking into account a near-surface layer, 24 appm). The erosion rate of these graphites was about 0.04 atom C/ion D.

Considering tritium inventory assessment for ITER, it is necessary to consider that at working divertor temperatures (up to 1000 K) most of the adsorbed tritium will be contained in the eroded near-surface layer 10–100 μm thick, independent of graphite porosity. At divertor temperatures higher than 1000 K, the porous graphite materials can accumulate tritium very effectively in the bulk. From this point of view, the dense graphites, e.g. like RG–Ti, are preferred (up to neutron fluences of about 0.1 dpa). For the temperature range studied (1000–1400 K), thick codeposited layers can accumulate considerable quantities of tritium (∼1000 appm).

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