



# Behaviour of Si and Ti doped carbon composites under exposure to the deuterium plasma

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## Abstract

Studies of the deuterium interaction with carbon-based substrates were performed for graphite doped either with SiC or with TiC (5% or 10% of Si or Ti) and carbon fibre composites doped with SiC (2.5; 8; 40% of carbide). Non-doped CFC and graphite were used as reference materials. The materials were exposed to the deuterium plasma in a tokamak or in simulators of plasma-surface interactions. The main emphasis was on the determination of the deuterium retention in the near surface region and in the bulk of the composites. Characterisation of the non-exposed and deuterium irradiated substrates was accomplished by means of RBS, NRA, EDS, laser profilometry and ultra-high resolution microscopies. The most important observations are connected with the penetration of the deposited deuterium into the bulk of composites – even a few millimetres beneath the surface. The rate of the process was found to be related to the structure of materials and, to a certain extent, to the content of dopants. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Over recent years there have been observed considerable interest in studies of doped carbon-based composites as potential candidates for plasma facing materials in future fusion devices [1,2]. A large number of composites containing boron, silicon or titanium have been produced and tested under various conditions, including the tests performed in tokamaks [3,4]. It has been observed that doping with B, Si or Ti leads to a reduced chemical erosion of carbon-based materials due to the suppressed formation of hydrocarbons under the bombardment with ions of hydrogen isotopes [5–10]. The improvement of the oxidation resistance has also been observed [11]. However, there are also certain deficiencies associated with doping; especially thermal

conductivity of multicomponent composites is usually lower than that of sole graphite materials. This influences poor thermomechanical properties under high heat loads which lead to the severe erosion of composites used as plasma facing components or tested in thermal shock simulators [12]. Porous structure enables the hydrogen isotopes to migrate into the bulk of materials and eventually the increased retention of fuel atoms is observed in the near surface region and in the bulk, even a few millimetres beneath the surface [13,14].

This work is mainly focused on the deuterium deposition and retention in silicon and titanium doped graphite and multidirectional carbon fibres. The aim of the investigation was to recognise the influence of the material structure – in particular the distribution of dopants – on the deuterium uptake.

## 2. Experimental

The investigation was carried out with carbon fibres doped with SiC (containing nominally 2.5; 8.0; 40.0

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vol.%) and with graphite doped either with SiC (LS5 and LS10 containing 5 or 10 at.% of Si, respectively) or TiC (LT5 and LT10 with 5 or 10 at.% of Ti, respectively). The doped graphites were produced by CEREM. Isotropic graphite (IG-110U, Toyo Tanso) and non-doped CFC (SEPCarb N112) were used as reference materials. The substrates were exposed to the deuterium in either rf-assisted glow discharge plasma (ion dose up to  $1 \times 10^{18} \text{ cm}^{-2}$ , target temperature  $60^\circ\text{C}$ ) or in a magnetron discharge, dose up to  $1 \times 10^{21} \text{ cm}^{-2}$ , target temperature  $700^\circ\text{C}$ . The third set of samples was exposed to the scrape-off layer plasma in the TEXTOR-94 tokamak. For the exposure they were mounted on the holder of the collector probe system, introduced to the vessel, positioned a few millimeters from the last closed flux surface and then exposed to a number (2 to 6) of ohmic and NBI heated discharges fuelled with deuterium; the typical pulse length was about 7 s. The samples were kept at the TEXTOR liner temperature ( $260^\circ\text{C}$ ) but during the pulse the temperature increase to approximately  $370^\circ\text{C}$  was observed.

The composites were examined by a number of complementary analytical methods before (both “as delivered” and machined samples) and after the exposure to the plasma in order to recognise their initial morphology (structure and composition) and the influence of the exposure on the change of the morphology. The characterisation of the non-exposed materials was essential to check possible discrepancies between the nominal and the real composition, as it was the case observed for some composites investigated previously. Rutherford backscattering spectroscopy (RBS) and energy dispersive X-ray spectroscopy (EDS) were applied to study the qualitative and quantitative composition of

the materials. The determination of the deuterium content in the surface and in the bulk was accomplished by means of the nuclear reaction analysis (NRA) using a He-3 beam [ $^3\text{He}(\text{d,p})^4\text{He}$ ] at energy of either 770 or 1500 keV. Analyses of the deuterium which migrated into the bulk were performed on surfaces freshly open by cleaving. Precautions were taken to avoid the contamination of those surfaces by the deuterium deposited on the exposed surfaces; the procedure of the sample preparation has been described previously [13]. Topography studies were performed using scanning electron (SEM) and atomic force microscopes (AFM).

### 3. Results and discussion

Fig. 1 shows backscattered electron (BE) images which illustrate the surface features of the CFC + SiC 8% composite in the “as delivered” state (Fig. 1(a)) and after machining and removing the outermost layer (Fig. 1(b)). In the first case the surface is fairly smooth with a “glazed” appearance and no fibrous structure can be perceived. Moreover, this BE image does not show any mass contrast which would indicate the existence of different phases, i.e. C and SiC. The phases can easily be distinguished after the machining of the sample (Fig. 1(b)); the bright areas correspond to the distribution of silicon carbide. The results of the RBS analysis of both the phases are exemplified in the spectra in Fig. 2. The “as delivered” surface (Fig. 2(a)) contains in principle only carbon atoms and no significant amount of Si could be detected whereas the machined sample contains on average 4% of Si which agrees well with the nominal composition of the composite: 8% vol. of SiC. This

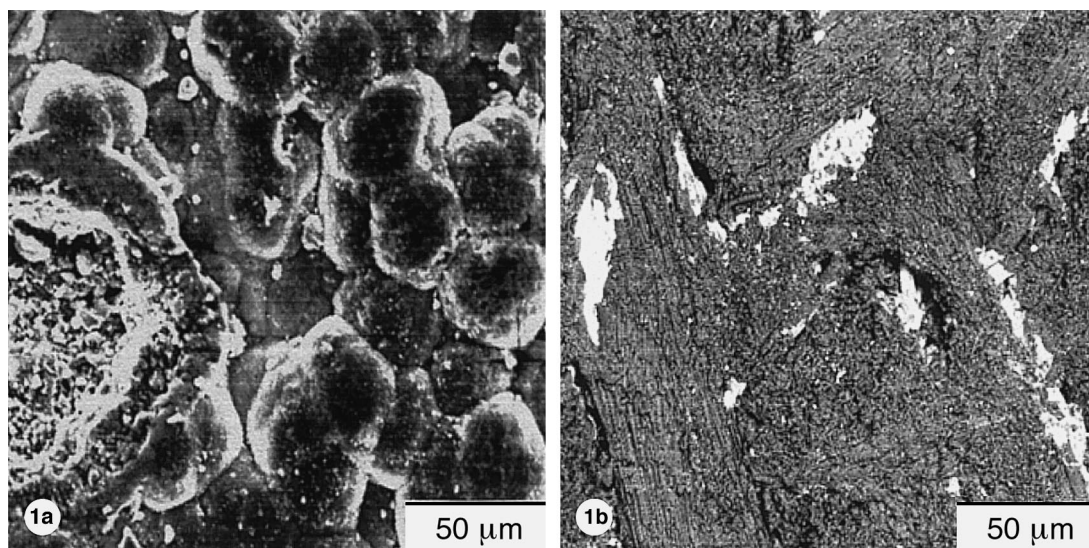


Fig. 1. Backscattered electron images of the non-exposed CFC with 8% of SiC: (a) “as delivered” surface; (b) surface after machining.

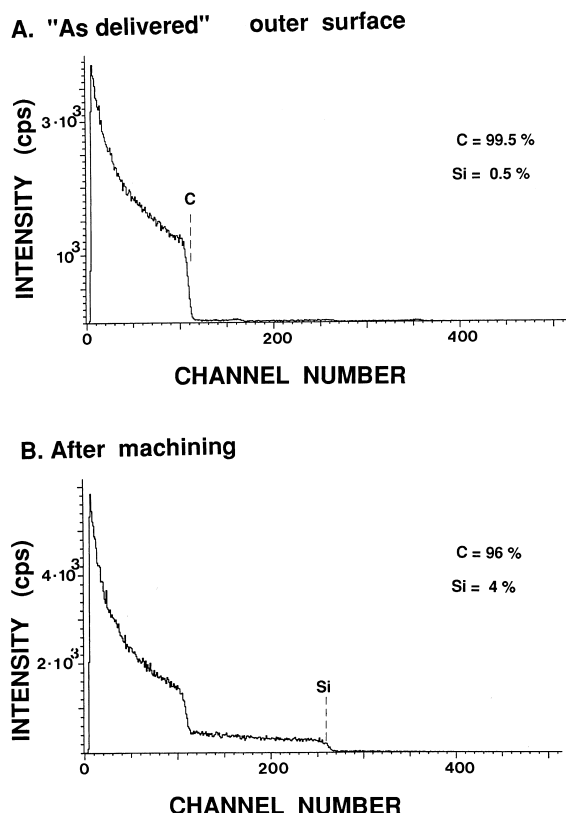


Fig. 2. RBS spectra of the non-exposed surface of the non-exposed CFC with 8% of SiC: (a) "as delivered" surface; (b) surface after machining.

result has been confirmed with the quantitative analysis performed by means of EDS. Moreover, the local EDS analysis confirmed the Si to C concentration ratio being 1:1 in the bright areas, indicating the stoichiometric SiC. Also for other composites pronounced differences have been detected when comparing the "as delivered" and machined surfaces. For instance, the initial surface of CFC doped with 2.5 vol.% of SiC contained over 40% of Si in the outermost layer. Therefore, machined samples of the fibre composites were used for exposures to the deuterium plasmas.

While the "as delivered" SiC doped carbon fibres were found fairly clean, the initial surfaces of the LS and LT composites were covered with uniformly distributed precipitates containing sodium and chlorine. These materials were cleaned in an ultrasound water-alcohol bath. Fig. 3 exemplifies the secondary electron image of surface features of the LT10 material after cleaning; this image is representative also for the other LS and LT composites. In the ultrasound cleaned samples no significant amounts of impurity atoms have been detected by EDS and RBS.

Exposures to the plasma and studies of the deuterium deposition, retention and in-depth migration were preceded by the determination of the deuterium background level in the bulk of the composites. The background was determined using the NRA technique; the measurements were made with a 1500 keV  $^3\text{He}^+$  beam (information depth approx. 4.5  $\mu\text{m}$ ) and the surface concentrations were converted to bulk concentrations expressed in ppm units, where 1 ppm is the

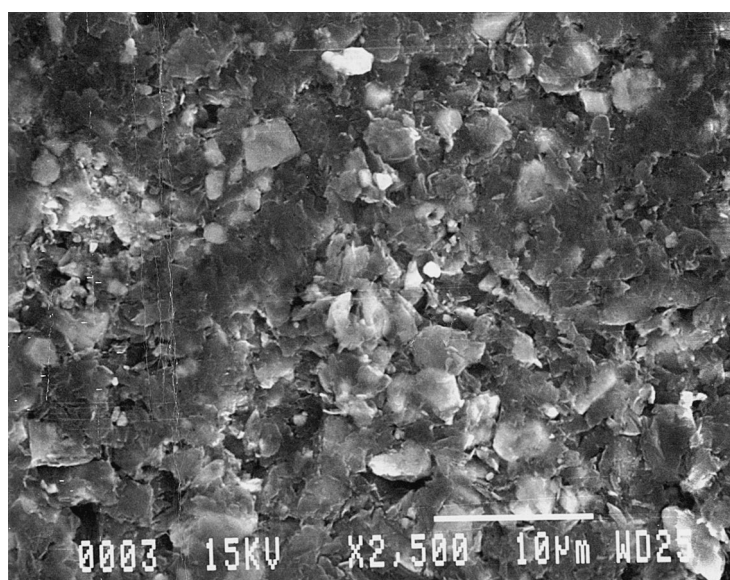


Fig. 3. Surface topography of the non-exposed LT10 composite.

Table 1  
Deuterium background levels and surface roughness measured for carbon-based materials

Material	Bulk D content (ppm)	Surface roughness	
		$R_a$ ( $\mu\text{m}$ )	$R_z$ ( $\mu\text{m}$ )
Graphite	1	1.2	11.2
LS 5	Not measured	1.6	13.4
LS 10	2	1.5	13.1
LT 5	Not measured	1.4	12.9
LT 10	3	1.4	13.0
N112	3	7.7	49.2
2.5% Si	9	6.8	49.1
8% SiC	9	7.1	53.5
40% SiC	12	8.8	61.2

detection limit and it corresponds to  $9 \times 10^{16} \text{ cm}^{-3}$ . The results are collected in Table 1 and one may notice significant differences in the background level. For a given category of substrates, the lowest levels are found in non-doped materials, but the D level in fibre materials is distinctly greater than that in graphite based composites. The differences in the deuterium content are probably attributed to the roughness and porosity of the materials. The results of the surface roughness measurements are also included in the Table 1. The values  $R_a$  correspond to the average roughness on the area of  $1 \text{ cm}^{-2}$  and the  $R_z$  values represent the average of five highest amplitudes (top-to-valley) on the area under investigation. The fibre substrates are rough and porous and, when stored in air, uptake pronounced amounts of water vapour (including also 0.015% D-containing water) as checked with mass spectrometry during outgasing of the materials in vacuum.

In Table 2 are collected the deuterium concentrations determined on surfaces and in the bulk of materials exposed to the glow discharge plasma: 100 eV D ions, total dose  $1 \times 10^{18} \text{ cm}^{-2}$ . The surface concentrations were measured two days after the exposure, whereas the determination of D content in the bulk was done after storing the samples for two months. The results indicate

Table 2  
Deuterium concentrations on surfaces and in the bulk of materials after the exposure to the glow discharge plasma

Material	Surface ( $10^{17} \text{ cm}^{-2}$ )	Bulk (ppm)
Graphite	0.85	1
LS 5	0.94	Not measured
LS 10	1.26	11
LT 5	0.88	Not measured
LT 10	0.88	20
N112	1.87	8
CFC 2.5% SiC	1.30	95
CFC 8% SiC	2.13	133
CFC 40% SiC	2.35	122

that there is a certain relation between the surface roughness of the materials (see Table 1) and the amount retained on surfaces. As expected, greater concentrations are detected on the rough CFC surfaces than on graphite. However, the amount of deuterium retained on fibre substrates increases with the content of dopant whereas one would rather expect the decrease in concentration, because SiC is known to trap hydrogen less efficiently than carbon does. Therefore, the effect observed is probably attributed to the increasing surface roughness and defects on grain boundaries between carbon and silicon carbide. Such structural imperfections enable deuterium to penetrate not only to the near surface layers but also into the bulk. This statement is justified by the fact that the deuterium quantities distinctly exceeding the background level are found in the bulk of materials: approximately 1–1.5 mm beneath the exposed surfaces. Greater bulk concentrations of D are measured for the doped CFCs than for doped graphites. In the exposed fibres, even at the depth of 2.5–3 mm the deuterium content was slightly above the background level. The results are in agreement with those obtained in tritium loading experiments of neutron irradiated CFC materials including silicon doped fibres (2.5 and 8%) and SEP N112 [15].

Exposures performed in a magnetron device (target temperature  $700^\circ\text{C}$ , total dose up to  $10^{21} \text{ cm}^{-2}$ ) resulted in the retention of  $2\text{--}3 \times 10^{16} \text{ cm}^{-2}$  on graphite type substrates and  $4\text{--}5 \times 10^{16} \text{ cm}^{-2}$  on CFCs. However, no correlation was found between the dopant content and the amount of deuterium retained. Both types of the substrates were covered with a deposit containing deuterium; the layer thickness as inferred from the depth profiling based on the NRA spectra was 15–20 nm. Fairly uniformly distributed small bubbles (5–7 nm in diameter) were observed with AFM on surfaces of pure and doped graphites, as exemplified in Fig. 4. The structure of the deposit was similar to the one reported previously [16]. No bubbles were found on the fibre composites exposed under the same conditions. Only the structure of underlying fibres could be observed in AFM images; the surface features are shown in Fig. 5.

Another set of samples was exposed to the deuterium fuelled discharges at the TEXTOR-94 tokamak. Exposures performed 5–6 mm from the last closed flux surface resulted in the formation of co-deposited layers containing deuterium together with plasma impurity atoms like carbon, boron and heavier species (inconel alloy components) originating from the machine wall. The amount of the co-deposited deuterium differed between both categories of the substrates. They were in the range  $1.8\text{--}2.1 \times 10^{17} \text{ cm}^{-2}$  for graphites and  $2.7\text{--}3.0 \times 10^{17} \text{ cm}^{-2}$  for fibre materials. One may suggest that the differences were related rather to the surface roughness of the samples than to their chemical composition. The analyses performed on cleaved samples

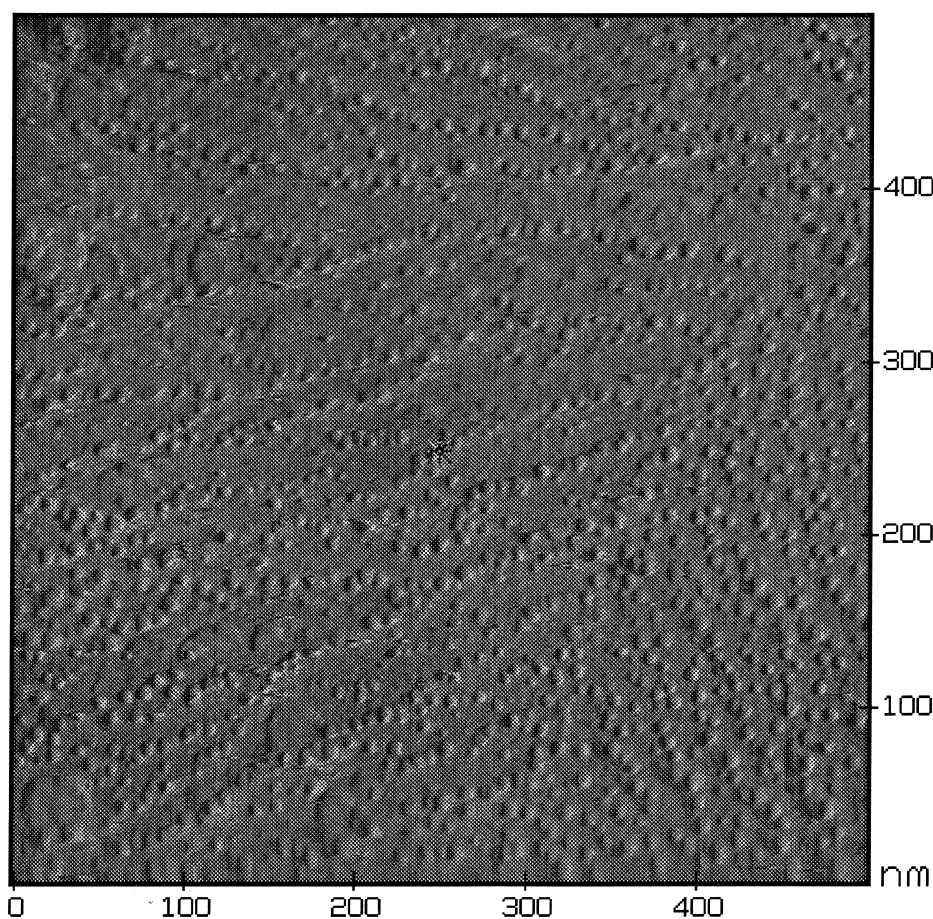


Fig. 4. AFM image of the deuterium containing deposit on the graphite surface.

revealed fairly small quantities of deuterium (above the background level) in the bulk of doped graphites and no change in the D content in the bulk of the non-doped one. For the SiC containing fibres the background level was exceeded by a factor 3 for the materials with 2.5% and 40% and by a factor of 5 for the composite with 8% of SiC. Therefore, like in the case of the exposures to the glow discharge plasma a relatively greater amount of D was detected in the CFC - 8% SiC material than in other fibre composites. However, the quantities were small and it is rather difficult to judge if the result obtained was related to the difference in the material structure or to the particular conditions during the exposure itself; for instance heat loads to the sample. When comparing the deuterium bulk concentrations following the both types of exposures (i.e. laboratory and tokamak plasma) one perceives that greater bulk contents were detected in the first case (see Table 2). The result may suggest that the plasma impurity atoms “stabilize” the hydrogen species in the co-deposits and – to some extent – inhibit their migration to the bulk. This suggestion is partly

justified by previous results showing that the distinct in-depth migration of D occurred into a 2-directional CFC exposed in a high flux simulator of plasma-surface interactions [13], whereas smaller amounts of deuterium, (10–150 appm) were also found in the bulk (1 mm beneath the surface) of the JET divertor tiles covered with a thick co-deposited layer containing more than  $4 \times 10^{19}$  D atoms  $\text{cm}^{-2}$  [17].

#### 4. Summary

Carbon based composites doped either with SiC or TiC were studied in order to characterize their initial state and the behaviour under the exposure to deuterium plasmas. Comparative investigation was performed for non-doped materials: graphite and CFC. The results indicate that the in-depth migration of deuterium from the deposited layer to the bulk is more pronounced for the doped materials than for the non-doped ones. This is probably related to the structural defects introduced by

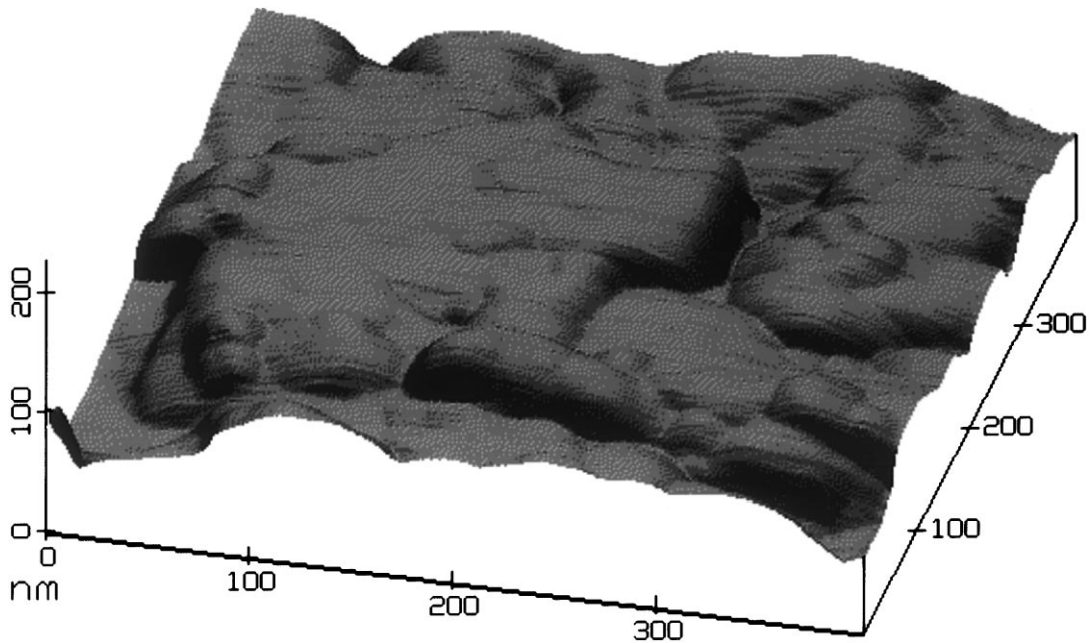


Fig. 5. AFM image of the deuterium containing deposit on the CFC - 2.5% SiC surface.

doping. There are differences observed in the efficiency of D migration from the deposits obtained under laboratory conditions and those formed under tokamak discharges. Comparatively less deuterium is detected in the bulk of composites facing the tokamak plasma. This may suggest that the presence of the plasma impurity atoms in co-deposits decrease the mobility of hydrogen species.

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