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Raman spectroscopy and X-ray diffraction studies of some deposited carbon layers in Tore Supra

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Abstract

Carbon deposited layers collected in Tore Supra on the neutralizers, on the toroidal pumped limiter and on the vertical outboard limiter have been analysed by X-ray diffraction and Raman spectroscopy. Both techniques show that these samples are highly disordered, mainly consisting of graphite-like nanoparticles. They are not similar to amorphous or hydrogenated amorphous carbons: this is consistent with the low amount of deuterium found trapped inside. Their structure can be related to their vicinity to plasma, particle bombardment inducing high temperature and preventing full amorphization. Samples exposed to the highest fluency in the machine show the largest degree of disorder, with probably a minor contribution of three-dimensional disorder, which may be due to the formation of bonds with deuterium.

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1. Introduction

In all the fusion devices using carbonaceous walls, plasma surface interactions are the cause of emission of carbon atoms and hydrocarbon molecules that deposit in regions shadowed from the direct plasma out flux. When their temperature remains low, these deposits can contain a significant amount of hydrogenated species whose extrapolation to ITER leads to an unacceptable value of the tritium retention [1]. In Tore Supra (TS) the presence of an actively-cooled first wall (with a pressurized water loop at 120 °C) is a unique opportunity to study the physical structure of deposits formed in conditions close to those which will prevail in a reactor. After the last experimental campaign, deposits were sampled from different parts of the vacuum chamber and the aim here is to do a comparative analysis of reference samples: highly oriented pyrolytic graphite (HOPG), carbon fiber composite (CFC), pyrolytic graphite (PYRO) with some of these TS samples. The first was scrapped on August 2002 from the leading edge (LE) of the neutralizers that are located under the toroidal pumped limiter (TPL) (labelled in what follows TS-NTR-LE) [2]. The second was collected at the same date and comes from the upper side of the TPL

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(TS-TPL-US). The third and fourth samples were scrapped on August 2003 from the lateral faces of the CFC armor tiles of the vertical outboard limiter (TS-VOL-CFC) and from its cooling copper base (TS-VOL-Cu), respectively. All the TS samples more or less look like powder and therefore both CFC and PYRO have been powdered in a mortar to be studied in the same manner.

We present here results of X-ray diffraction and Raman spectroscopy: X-ray diffraction gives straightforward information on the long-range order of the powder grains whereas Raman spectroscopy gives information on the physical and chemical environment through the vibrational structure. This latter technique is widely used to discriminate the various phases of carbon: graphitic, disordered, amorphous, diamond-like ... Generally speaking, these phases are discussed in terms of sp^2 (planar) or sp^3 (tetrahedral) bonding, carbon atoms being therefore threefold or fourfold coordinated. sp^2 or sp^3 character can originate from pure C–C bonding as well as from bonding of C with heteroatoms as H. Irradiation of graphite has shown that different stages of damage can be distinguished: first, from graphite to nanocrystallites (nc-C), second, from nc-C to amorphous carbon (a-C, mainly sp^2) and third, from a-C to sp^3 amorphous carbon (ta-C, mainly sp^3) [3–5]. HOPG displays a single narrow band at $\sim 1580\,\mathrm{cm}^{-1}$ whereas crystalline carbons display three characteristic bands: at 1580–$1590\,\mathrm{cm}^{-1}$ labelled G, at 1330–$1360\,\mathrm{cm}^{-1}$ labelled D, and at 1610–$1625\,\mathrm{cm}^{-1}$ labelled D′. The G (graphite-like) band is assigned to C–C stretching vibration of sp^2 C atoms whereas the assignment of the D band is more complex. It can originate from a symmetry loss due to the finite size of crystallites (label D is for disordered graphite) [6–8] or from C–C stretching vibration of C atoms presenting a mixed sp^2–sp^3 character [9]. Bands appearing in the 1500 and $1200\,\mathrm{cm}^{-1}$ region characterize amorphous or highly disordered samples [7], the disorder being possibly induced by heteroatoms or by nanopores [10].

2. Experimental results

2.1. Diffraction

Diffraction measurements have been done with a standard Inel Debye–Scherrer diffractometer with a Cu K_α source (XRG 3000) and a curved (120°) ionisation detector. Fig. 1 shows the 002 diffraction peak obtained for PYRO, CFC, TS-NTR-LE and TS-TPL-US samples. Table 1 summarizes the values of the angular position and the full width at half maximum measured by merely fitting this peak with a Gaussian line. Line shape asymmetry is observed in the case of CFC, probably due to both fibber and pyrolytic components and the value given here is a mean value. The interplane distance is deduced from the position by the diffraction relation and the coherence length related to interplane distances is deduced from the width of the 002 peaks by the Laue–Scherrer formula. The reticular distance d_{002} measured for TS samples is in the range 0.340–0.345 nm, significantly differing from the expected graphite value of 0.335 nm, and corresponds to distance between adjacent sheets in poorly graphitised carbons. Consistently, the coherence length of TS samples (25 sheets) is reduced compared to that of CFC (220 sheets) and the diffraction peak intensity is also drastically reduced, indicating a high degree of disorder. It should be noted that only a graphite-like signature has been measured, excluding a large amorphous contribution.

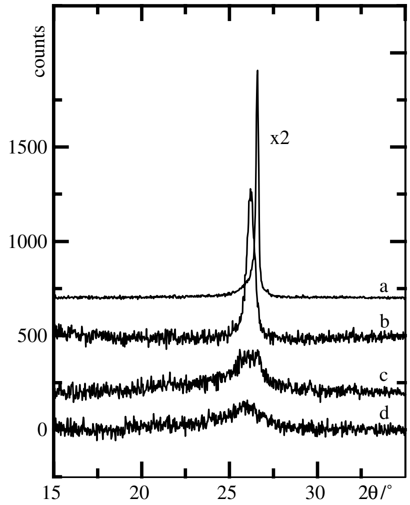

Fig. 1. 002 X-ray diffraction peak of (a) CFC, (b) PYRO, (c) TS-TPL-US and (d) TS-NTR-LE.

Table 1
X-ray diffraction data for the 002 peak of some reference and TS samples: position 2θ/deg, interplane distance d/Å, width $\delta(2\theta)$/deg and coherence length deduced from the Laue–Scherrer formula L_c/Å

	2θ	d	$\delta(2\theta)$	L_c
CFC	26.54	3.36	0.23	740
PYRO	26.21	3.40	0.47	360
TS-TPL-US	26.10	3.41	1.58	110
TS-NTR-LE	25.86	3.45	2.01	85

2.2. Raman spectroscopy

A Jobin-Yvon-Horiba (France) Raman LabRAM 'Infinity' micro-spectrometer equipped with back-illuminated Peltier effect cooled Spex CCD matrices

(2000 × 256 pixels) and with a doubled Nd/YAG laser (532 nm) was used in this study, the resolution being around 2 cm^{-1}. It also included a Notch filter and the excitation power was ∼0.3 mW in order to avoid any thermal effect. The laser spot was ∼1 μm^2 and several parts of each sample have been tested. The probe depth depends on the resonant nature of the transition and is estimated less than 100 nm.

Fig. 2 shows spectra obtained for HOPG, PYRO and CFC (left), TS-NTR-LE, TS-TPL-US, TS-VOL-CFC and TS-VOL-Cu (right) samples. Raman micro-spectrometry has revealed that samples were heterogeneous and these spectra are examples of what can be observed. As expected for crystalline carbons, CFC and PYRO samples exhibit the three bands G, D and D′ whereas only the G band is observed for HOPG. For TS samples, both G and D bands are broadened but still clearly assignable, the latter being the largest, while the D′ band is no longer observed. These spectra clearly cannot be attributed to amorphous or hydrogenated amorphous carbon [7,11] and are similar to those observed for disordered carbon, containing a majority of sp^2 bonds.

The spectra have been fitted by a sum of three Lorentzian lines centred at ∼1350, 1585 and 1620 cm^{-1} for reference samples, and a sum of three Lorentzian lines centred at ∼1350, 1500 and 1240 cm^{-1} and one Gaussian line centred at ∼1590 cm^{-1} for TS samples (Table 2). When going from reference to TS samples, the G band broadens and slightly shifts upwards, the D band broadens and increases: this is characteristic of transition from graphite to disordered graphite as nc-C [6,7,12]. Two additional broad bands centred in the range 1485–1545 (called in what follows central band) and 1145–1248 cm^{-1}, respectively (called in what follows red band) are necessary to fit the spectra. These bands characterize a higher level of disorder than that evidenced by merely a broadening of G and D and could reveal of a nc-C → a-C transition. Analysing Table 2 shows two categories for TS samples: (i) NTR-LE, VOL-CFC and VOL-Cu samples having a low-width G band (52–70 cm^{-1}), a high-frequency central band (1524–1545 cm^{-1}), a high-intensity D band (55–58%) and a low-intensity red band (0–5%), and (ii) TPL-US samples, having a high-width G band (88–123 cm^{-1}), a low-frequency central band (1478–1505 cm^{-1}), a low-intensity D band (25–32%) and a high-intensity red band (21–44%). In addition, one of the TPL-US samples shows a low G band frequency (1576 cm^{-1}), lower than that of HOPG. The red shift and the broadening of the G band, the lowering of the D band intensity and the presence of the red band indicate alteration of the average bond angle or presence of fourfold coordinate bonding, i.e. three-dimensional disorder involving sp^3 bonds [3–5,12]. Our analysis shows therefore that all the TS samples are composed of highly disordered sp^2 nanoparticles, TS-TPL-US samples probably having a small additional sp^3 component.

3. Discussion

XANES experiments previously done at the K edge of carbon on CFC, PYRO, TS-NTR-US samples have shown close graphitic signatures for the three samples, evidenced by the presence of an intense 1s → π* peak at 285 eV and of characteristic multiple scattering features between 290 and 310 eV [13], indicating a medium (>1 nm) or long-range order parallel to the basal

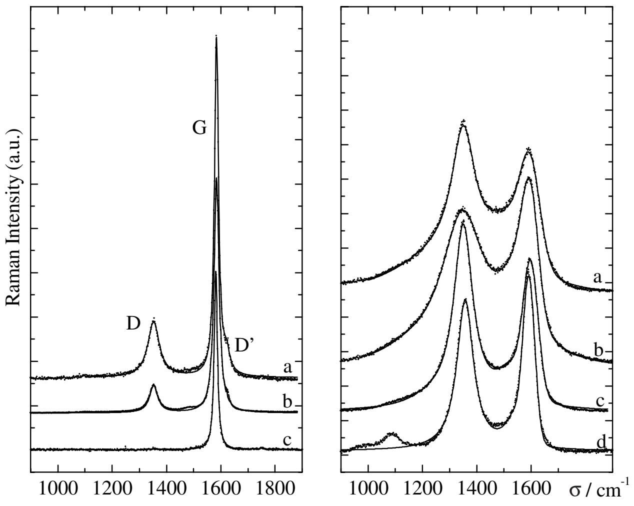

Fig. 2. Raman spectra of (left) reference samples: (a) CFC, (b) PYRO, (c) HOPG and (right) TS samples: (a) TPL-US, (b) VOL-Cu, (c) NTR-LE and (d) VOL-CFC. Points are experimental data and lines are fits.

Table 2
Decomposition of Raman spectra for reference and TS samples: position P/cm^{-1}, width (FWHH) w/cm^{-1}, relative height I/% and ratio I_D/I_G, α, D being the band at ~1350 cm^{-1} and G the band at ~1590 cm^{-1}

	P	w	I	P	w	I	P	w	I	P	w	I	α
HOPG	1582	14	100	–	–	0	–	–	0	–	–	0	–
PYRO	1584	22	82	1353	41	17	–	–	0	1625	8	1	0.2
CFC	1584	25	46	1351	52	45	–	–	0	1619	35	9	1.0
	1584	18	64	1353	52	30	–	–	0	1622	28	6	0.5
NTR-LE	1598	65	24	1350	87	55	1524	124	16	1226	186	5	2.3
VOL-Cu	1597	70	13	1347	196	58	1545	157	25	1145	253	5	4.5
VOL-CFC	1592	52	32	1357	74	57	1534	78	12	–	–	0	1.8
TPL-US	1595	88	16	1350	110	32	1505	179	23	1244	414	29	2.1
	1586	105	17	1354	130	25	1487	105	14	1248	472	44	1.5
	1576	123	24	1354	143	29	1478	150	26	1238	312	21	1.2

Different micro-Raman measurements are given for CFC and TPL-US samples, the first line corresponding to the spectrum shown in Fig. 2.

planes. The broadness of the Raman bands indicates that TS samples are clearly too disordered for the standard estimation of a coherence length (or grain size), which is probably lower than 4 nm [4–6,9,12]. We therefore believe that both types of experiments are in agreement and show that TS samples have an in-plane typical coherence length of the order of a few nanometers.

TS samples do not have the characteristics of hydrogenated amorphous layer (a-C:H) and this suggests a low amount of deuterium retention. Consistently, deuterium measurements done by nuclear reaction analysis (NRA) have shown that the total amount retained in NTR-LE deposits is low (around 0.5%) [14]. As a matter of fact, the temperature of this sample can reach 1200 °C because of fast electron flux impinging the leading edge of the neutralizer. In the case of the other samples, the low thermal conduction between the deposits and the actively-cooled elements of the limiters leads to temperature higher than 450 °C [15]. These high temperature values explain both the low amount of trapped deuterium and the non-amorphous nature of samples.

Our Raman spectral analysis allows us to distinguish TPL samples from the others, the former probably having a larger amount of three-dimensional defects. Only TPL continuously receives the largest flux of plasma particles (~10^{21} m^{-2} s^{-1}) and the related samples correspond then to the largest fluency: we thus believe that these defects appear for large fluency. This can be correlated to experiments of Niwase et al. [3] showing that three-dimensional amorphization occurs only for high fluency whereas only easily recoverable in-plane defects were observed for low fluency. On the other hand, volumetry experiments have shown that the NTR sample have a high porosity (80 times that of CFC) [13] and this can be the origin of the large disorder observed by Raman spectroscopy, as suggested by the predominance of the D band.

4. Conclusion

Raman spectroscopy and X-ray diffraction investigations have shown that the deposited layers in Tore Supra were neither amorphous, nor hydrogenated amorphous carbon. They are highly disordered carbons consisting in majority in sp^2 bonds, and do not contain a large amount of deuterium. These results can be related to the sample vicinity to plasma: they receive high flux of particles and reach high temperature and, consequently, they do not efficiently retain deuterium. We believe therefore that sources of deuterium retention can probably be searched for in other parts of the machine, more distant from plasma.

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