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Multiscale study of the porosity of carbon deposits collected in Tore Supra

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Abstract

Carbon deposits collected in Tore Supra, on the neutralisers and on the toroidal pump limiter, are analysed by adsorption isotherm measurements and electron microscopy. Both techniques are suitable to study the porosity in a multiscale range and allow the characterisation of the volume and the structure of the pore network. The neutraliser deposits show an oval shape structure and a high specific surface area. This area corresponds to microporosity, i.e. pores with a typical size lower than 2 nm, (∼11%), mesoporosity (∼5%) and macroporosity, i.e. pores with a typical size more than 50 nm. Surprisingly, transmission electron microscopy performed on thin foils cut from an oval reveals a regular network of parallel slit-shaped mesopores (size ∼ 10 nm) and macropores (size ∼ 100 nm), with a well-defined orientation with respect to the oval axis.

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1. Introduction

Particle control is a key issue in next step fusion devices for the exhaust flux, plasma contamination and tritium retention. Particle balance analysis of long discharges in Tore Supra (TS) [1] has revealed deuterium retention whose extrapolation to ITER leads to an unacceptable value for tritium. Low D/C ratio (less than 10%) have been measured in carbon deposits collected in TS plasma facing components (PFCs) [2], and neither implantation nor codeposition could quantitatively explain the stationary retention which is observed during the discharges [1]. Absorption, diffusion and re-emission of deuterium in both PFCs and deposits may play a key role in this particle balance and should be very dependent on their structure, texture and porosity [3,4]. The aim here is to quantitatively characterise the pore volume, shape and size in the range from 1 nm to 1 μm for TS carbon deposits. Samples collected on neutraliser (TS-NTR) and toroidal pump limiter (TS-TPL) are compared to the carbon fiber composite (CFC) which is the original PFC.

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We present here results of volumetric measurements through adsorption isotherms and of structural measurements through scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Adsorption isotherms give global information on the sample structure and porosity; various procedures or theories have been developed during the last years to characterise the whole porosity of materials, i.e. micropores (size lower than 2 nm), mesopores (size between 2 and 50 nm) and macropores (size larger than 50 nm) [5]. Besides, TEM gives local information on the crystallographic structure at the atomic scale, and on the texture and porosity, from a few nm to a few μm scales. Adsorption isotherms of methane and nitrogen at 77 K as well as SEM have been performed on the raw carbon deposits, whereas TEM has been performed on thin foils cut within an oval using focus ion beam (FIB).

2. Experimental part and methods

2.1. Samples

TS-NTR deposits were collected on the leading edge of the neutralisers located under the TPL; they are ∼200 μm thick rough layers with oval shapes (Fig. 1) whose self-similarity were previously characterised by a fractal dimension of 2.15 [6]. TS-TPL flakes were collected on the upper side of the TPL; they are ∼100 μm thick flakes and are less rough than TS-NTR. Deuterium measurements [2] have shown that their D/C ratio was low (less than 1% and 10% for TS-NTR and TS-LIM, respectively). CFC consists in carbon fibers embedded in a carbon pyrolytic matrix and is mainly graphitic and non-microporous; it was used in this work as a reference material.

2.2. Adsorption

Adsorption isotherms were measured step by step on a home-made set-up composed of a quartz cell cooled at 77 K and connected to a stainless steel calibrated volume equipped with pressure gauges (MKS Baratron manometer capacitance) in the 10^{-4}–1000 mbar range. Gas puffs were introduced in the sample cell, and adsorbed amount, V_{ads}, was plotted versus relative pressure, $p_{\mathrm{r}} = p/p_0$, where p and p_0 were equilibrium and saturation pressure, respectively. Before each isotherm, samples were outgassed during more than 6 h at 900 K under 10^{-7} mbar. The measurement reproducibility was checked; nevertheless, their analysis led to accuracy on adsorbed amount values of ∼10%. We used the BET method [5,7] as a standard procedure to determine equivalent specific surface area, a_{BET}. Furthermore, the α_{s}-method [5,8] was used to distinguish between multilayer formation on flat surfaces (called external surface) and micropore filling. Reduced quantity α_{s} was the ratio $V_{\mathrm{ads}}/V_{0.4}$, where $V_{0.4}$ was the adsorbed volume at $p_{\mathrm{r}} = 0.4$, and α_{s}(TS) is plotted versus α_{s}(CFC), CFC being chosen here as the reference material.

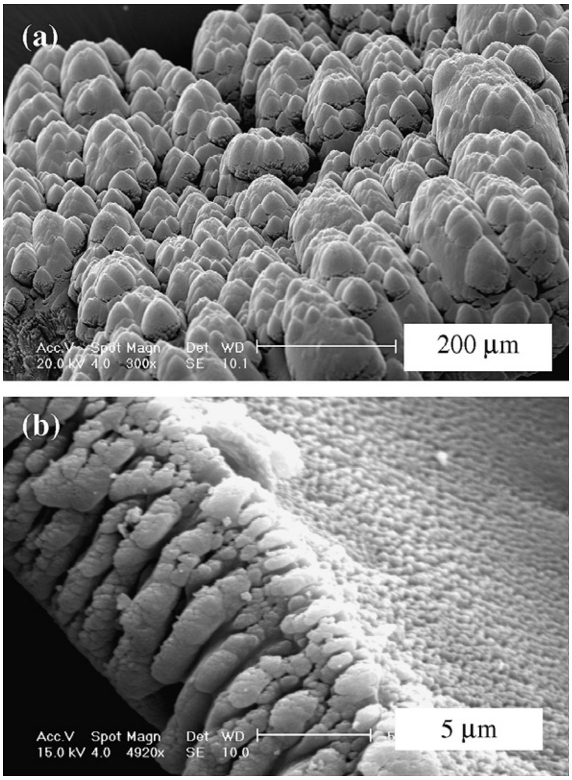

Fig. 1. Scanning electron microscopy micrographs of TS samples: (a) TS-NTR and (b) TS-TPL.

2.3. Electron microscopy

SEM was carried out at the Microscopy Centre (Université de Provence, France) using a ESEM Philips XL 30 microscope with a 5 nm resolution. TEM was carried out at the CP2M laboratory (Marseille, France) using a JEOL 2010 F field emission microscope, with a 0.18 nm structural resolution and a 0.2 nm spot size. FIB was carried out at the same laboratory using a Philips FIB 200

TEM with a 5 nm spatial resolution and equipped with a platinum gas injector. FIB proved to be very suitable for localisation of a relevant zone within our samples and for preparation of high quality thin foils for TEM analysis.

3. Results and discussion

Methane adsorption isotherms and their α_s-plot are displayed in Fig. 2(a) and (b), respectively. TS isotherm shapes are similar to those of microporous samples (i.e. type I according to the IUPAC classification [9]) whereas CFC isotherm shape is similar to those of non-porous sample (i.e. type II). Table 1 shows that BET area are 190 $m^2\,g^{-1}$ for TS-NTR and 120 $m^2\,g^{-1}$ for TS-TPL, much higher than that of CFC sample (2 $m^2\,g^{-1}$). The type I/type II difference is clearly seen by plotting the isotherm normalized at the BET area (not shown here) or by doing α_s-plot. Therefore, both isotherm shape and BET area consistently prove the existence of microporosity. The linear part of the α_s-plot (observed for $\alpha_s(\mathrm{CFC}) > 0.3$) is due to multilayer adsorption on the external surface and corresponds to the following equation: $\alpha_s(\mathrm{TS}) = B\alpha_s(\mathrm{CFC}) + C$. Slope B gives external surface area (a_{ext}) ratio between TS and CFC samples; $a_{\mathrm{ext}} = B\ a_{\mathrm{ext}}(\mathrm{CFC})V_{0.4}(\mathrm{TS})/V_{0.4}(\mathrm{CFC})$. The steepest parts (observed for $\alpha_s(\mathrm{CFC}) < 0.3$) are due to the strongest gas-surface interactions, like those induced by micropore confinement. Micropore STP volume, V_μ, is deduced from the C intercept value; $V_\mu = CV_{0.4}$. Using the solid methane density of 1.8×10^{22} molecule g^{-1}, we then deduce a micropore volume of 0.06 and 0.04 $cm^3\,g^{-1}$ for TS-NTR and TS-TPL, which corresponds (using an approximate density of 2.2 g cm^{-3}) to a volume ratio of 11% and 8%, respectively. It should be noted that these volume values are only indicative because they depend on carbon deposit properties which are not well-known like its actual density, the presence of close porosity or the presence of metallic impurities. Two steps are observed, corresponding to two types of micropore filling: the first is in the 0–0.1 α_s(CFC) range and corresponds to the filling of ultra-micropores ($d < 1.3$ nm), while the second is in the 0.2–0.4 α_s(CFC) range and corresponds to the filling of super-micropores (1.3 nm $< d <$ 2 nm) [5]. The curve in between these two steps corresponds to the monolayer formation on the super-micropore walls and we can thus estimate that the relative part of ultra-micropore is similar for the two samples (57% for TS-NTR and 65% for TS-TPL, Table 1).

Table 1
Methane adsorption isotherms (77 K) on CFC and TS samples

	a_{BET}	a_{ext}	V_μ	η_{ultra}	ε_μ
TS-NTR	190	60	0.06	57	11
TS-TPL	120	30	0.04	65	8
CFC	2	2	–	–	–

BET specific surface area, a_{BET} ($m^2\,g^{-1}$), external surface area, a_{ext} ($m^2\,g^{-1}$), micropore volume, V_μ ($cm^3\,g^{-1}$), ultra-micropore ratio, $\eta_{\mathrm{ultra}} = V_{\mathrm{ultra}}/V_\mu$ (%), and volume ratio of micropores, $\varepsilon_\mu = V_\mu/V_{\mathrm{sample}}$ (%).

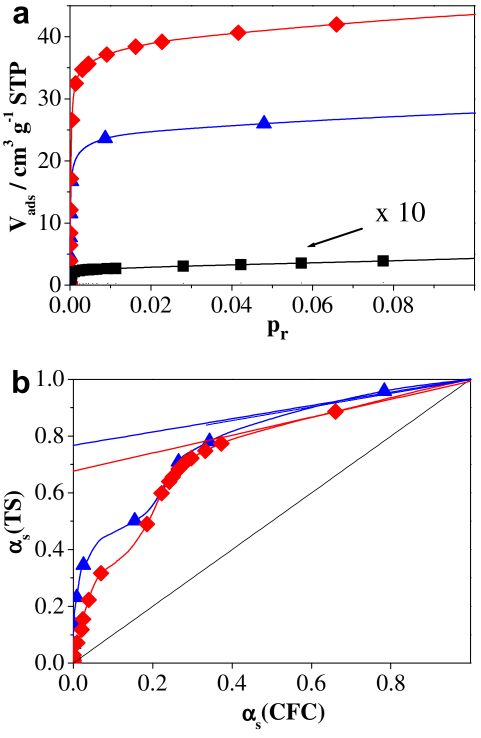

Fig. 2. Methane adsorption at 77 K on (■) CFC (▲) TS-TPL and (◆) TS-NTR samples: (a) adsorption isotherms and (b) α_s-plots.

An adsorption isotherm of nitrogen has been measured on TS-NTR (Fig. 3) which shows a hysteresis loop in the capillary condensation p_r range. This indicates the existence of mesoporosity which is estimated here at ~0.01 $cm^3\,g^{-1}$ (i.e. corresponding to a 5% volume ratio). The hysteresis loop shape is similar to those observed for pillared clays [10,11] and could therefore be due to slit-shaped pores and/or to an 'ink bottle' shape. In fact, in both cases, desorption occurs later due to a meniscus effect in the first case, and due to a constriction effect in the second case. It should be remarked that this constriction effect, and more generally the global pore network connectivity, can play a role in transient retention and diffusion processes.

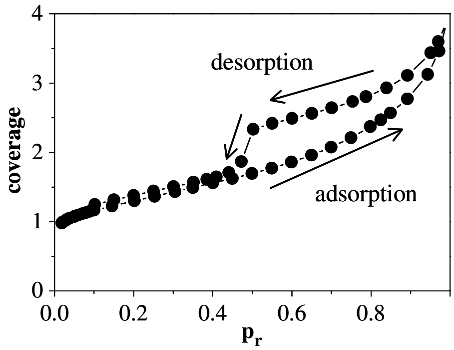

Fig. 3. Nitrogen adsorption isotherm at 77 K on TS-NTR sample showing the hysteresis loop.

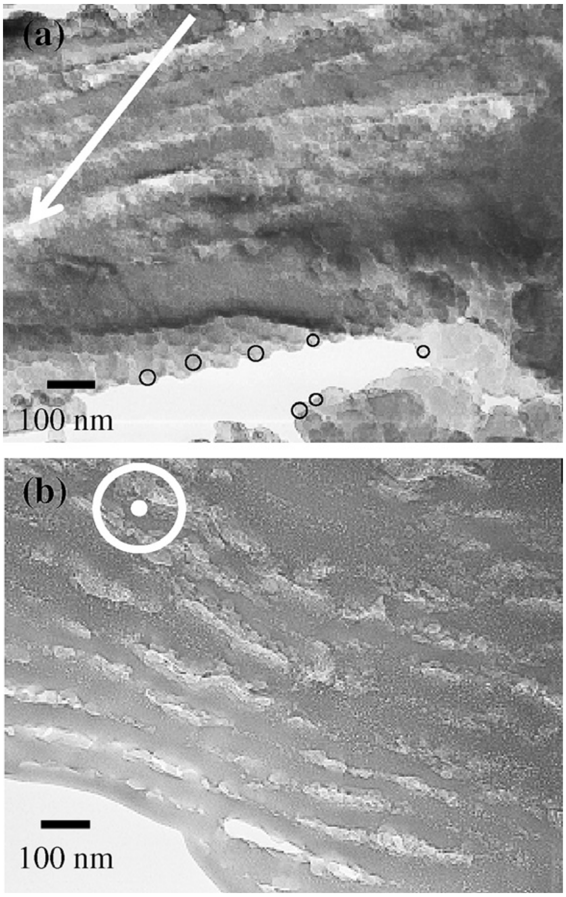

Fig. 4. Transmission electron microscopy micrographs of TS-NTR thin foil prepared using focussed ion beam: (a) parallel, and (b) perpendicular, to the oval axis. This axis is schematically indicated by the arrows. Dark circles highlight some spherical particles of typically 20 nm diameter.

Fig. 4(a) and (b) shows TEM images of thin foils prepared by FIB, parallel or perpendicular to the oval axis, respectively. Roughly speaking, contrasts are due to the density of the carbon foil and here, the light and wavy lines indicate void spaces through the foil thickness. These images clearly show a regular network of parallel mesopores, ~10 nm wide and ~45° tilted with respect to the oval axis. This mesopore network configuration is consistent with slit-shaped pores, in agreement with what has been deduced from volumetric measurements. In addition, open macropores, ~100 nm wide, are observed in the parallel foil, probably contributing to the external surface area deduced from volumetric measurements. Fig. 4 also shows that the sample contains spherical particles of ~20 nm diameter (highlighted in Fig. 4(a) using dark circles) and that it is probably formed by clustering of such particles. The microstructure of these samples has been analysed in a previous work using X-ray diffraction, Raman spectroscopy [12], and high resolution TEM [13]; this has shown that the granules consist of small graphite-like crystallites whose typical sizes are 2–4 nm and 7–9 nm, parallel and perpendicular to the graphene planes, respectively. The microporosity measured by volumetric measurements may thus originate from inter-crystallite stacking defects.

4. Conclusion

We have done both volumetric and structural measurements by means of adsorption isotherms and electron microscopy, respectively, to determine the main features of the multiscale porosity of Tore Supra carbon deposits. Results clearly show the existence of the three types of pores, i.e. micro-, meso-, and macro-pores; the first type of pores is very attractive and could play a role in D retention, whereas the latter type gives ways for rapid diffusion within the bulk. Generally speaking, surfaces may also provide active sites and a large amount of porosity will clearly favour reactivity phenomena. Studying their whole structure and connectivity can therefore help in understanding retention/diffusion processes. In addition, a regular network of slit-shaped parallel mesopores with a well-defined arrangement with respect to the deposit growth axis has been evidenced, which can certainly bring valuable information on the growth processes. These studies are currently in progress.

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