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Journal of Nuclear Materials 248 (1997) 34–37

journal of nuclear materials

Effect of oxidation on thermal desorption of deuterium sorbed in graphite

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Abstract

By means of thermal desorption spectroscopy (TDS), effect of air oxidation on deuterium release from carbon fiber composite SEP N112-A and fine grain graphite POCO AXF-5Q has been studied. Carbon samples were loaded with deuterium by exposure to 133 Pa D_2 at 1170 K for 2 h. Thermal desorption from SEP proceeds over a wide range, 1200 to 1900 K, without any sharp peaks. There are two distinct release stages visible in spectra of POCO. A minor portion of deuterium is evolved in a relatively narrow peak at 1350 K, while the rest is in the wide peak centered at 1800 K. Air oxidation of loaded samples at 1000 K to a weight-loss of ~ 5% leads to a disappearance of the low temperature part of spectra while the amounts of deuterium released above 1600 K remain unchanged. It is suggested that air oxygen removes chemisorbed deuterium from the walls of pores accessible to O_2 molecules. The rest of the sorbed deuterium is apparently trapped at the sites accessible to D atoms only, not to D_2 and O_2, and therefore is stable at the initial stage of oxidation.

1. Introduction

Carbon fiber composites (CFC) are presently the most attractive materials under consideration for the ITER divertor high heat flux components because of its excellent thermal resistance properties [1]. Unfortunately, the presence of carbon within the torus can drastically affect the parameters of in-vessel tritium inventory. It is agreed that tritium retained in the codeposited layers will be occasionally removed by a special technique. The issue on tritium inventory in the bulk of plasma facing carbon-based materials is less clear.

As a first approximation, tritium inventory in plasma facing graphites can be evaluated from experiments on hydrogen loading by gaseous charging [2]. It is known that a capacity of graphite and CFC for hydrogen absorption is essentially modified by fast neutron irradiation [3–5]. As armor erosion and thermal fatigue/radiation damage resistance will set an upper limit for the lifetime of ITER divertor [1], tritium inventory in divertor cassettes before replacing them might be governed by both the neutron fluence achieved and the tritium sorption kinetics.

One further point concerns a mobilization of retained tritium. It is well established that hydrogen absorbed in graphite during gaseous charging is stable in vacuum up to ~ 1100 K [6]. Because of this, no tritium release will occur between the pulses as far as normal operation is considered. A different situation arises when active gases are admitted into the torus either to remove tritium from codeposited layers or in case of an accident. In this connection tritium behavior in carbon during C–O_2, C–H_2O reactions should be understood. In the present paper, using the thermal desorption spectroscopy (TDS), the effect of air oxidation on deuterium release from graphites has been studied.

2. Experimental

Carbon fiber composite SEP N112-A and fine grain graphite POCO AXF-5Q (hereafter denoted as SEP and POCO, respectively) were used. Specimens of $2 \times 2 \times 1$ mm^3 in size were cut from larger plates and annealed in vacuum ~ 10^{-5} Pa at 2000 K for 10 min. Deuterium

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PII S0022-3115(97)00205-5

loading was performed as follows. The specimens were placed inside a graphite tube made of POCO AXF-5Q. Both the tube openings were closed with graphite caps that were being hold against the tube by Mo electrodes. The tube was resistively heated in D_2. Oxidation was done by heating deuterium loaded specimens in the air, dried with a liquid nitrogen trap at a pressure of 0.08 MPa.

TDS measurements were carried out in an UHV chamber with a background pressure of 10^{-6} Pa. Specimens were held between Mo electrodes and resistively heated to 2000 K. For regulation of the heating a tantalum strip was connected parallel with the carbon specimen. As close correlation was observed between tantalum and carbon temperatures, linear ramping of both the strip and the specimen was provided by an electronic programmer equipped with a W–Re thermocouple spot-welded to the strip while the specimen temperature was measured with an optical pyrometer. Deuterium release in the form of D_2 and HD molecules was monitored with a calibrated quadruple mass-spectrometer.

3. Results and discussion

3.1. Deuterium thermal desorption from as-loaded specimens

Release spectra of deuterium from SEP and POCO exposed to 133 Pa D_2 at 1170 K for 2 h are shown in Fig. 1. Thermal desorption from SEP proceeds over a wide range, 1200 to 1900 K, without any sharp peaks. In contrast, there are two distinct release stages in spectra of POCO: a minor portion of deuterium evolved under heating to 2000 K is released in a relatively narrow peak at 1350 K, while the rest is in the wide peak centered at 1800 K.

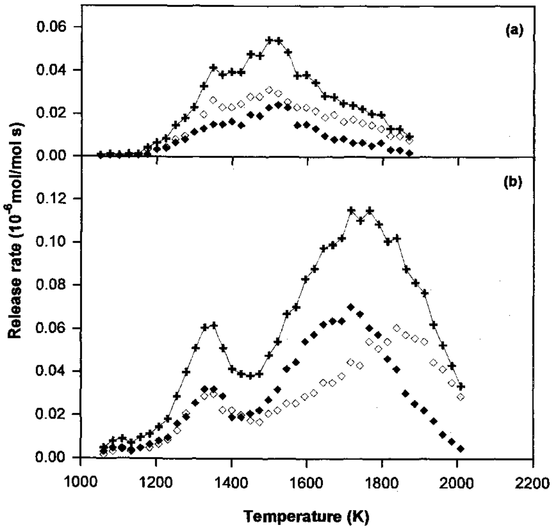

Fig. 1. Thermal desorption of deuterium as D_2 and HD molecules (closed and open symbols, respectively) and the net deuterium (D_2 + HD) release (solid curves) from SEP N112-A (a) and POCO AXF-5Q (b) exposed to 133 Pa D_2 at 1170 K for 2 h. Heating rate 8 K/s.

Table 1
Amounts of deuterium released from graphites under heating to 1600 K and from 1600 to 2000 K. Deuterium loading: 133 Pa D_2 at 1170 K for 2 h; oxidation: 0.08 MPa dried air at 1000 K for 10 min.

Material	Treatment	Net (D_2 + HD) deuterium release μmol D_2 /mol C		
		$T \leq 1600$ K	$T > 1600$ K	total
SEP	D_2	1.8	0.7	2.5
	D_2 + air	0.6	0.7	1.3
POCO	D_2	2.6	4.5	7.1
	D_2 + air	1.8	4.4	6.2

It is of interest to compare the amounts of deuterium released from the materials at lower and higher temperatures, for example, to the point of 1600 K and above that. The results of integration of the spectra are collected in Table 1. The great fraction of deuterium retained in SEP is escaped at 1600 K. In opposite, a heating above 1600 K is required to liberate deuterium from POCO.

As known, a release of deuterium sorbed in porous graphites might proceed in several steps: liberation from traps, volume and grain (crystallite) boundary diffusion of D atoms followed by recombination on the internal surfaces and migration of formed molecules along micropores out of the specimen [2]. Clearly the second stage may be omitted for release of chemisorbed deuterium. All artificial graphites contain some amounts of residual protium [7], this can result in a mixed recombination to form HD molecules. The fraction of deuterium released as HD seems to be a function of the D/H concentration ratio. It could also depend on mutual arrangement of sorbed deuterium and residual protium.

As seen in Fig. 1 a great release of HD molecules occurs even at the maximum heating temperatures of 1900 and 2000 K used for SEP and POCO, respectively, whereas the D_2 desorption rate goes to zero. At lower temperatures, however, HD and D_2 desorption rates are of the same order in magnitude. All this indicates that a major fraction of residual protium is more deeply bound in graphites than sorbed deuterium. Consequently, at high temperatures the internal surfaces are covered mainly with protium resulting in the release of the remaining deuterium preferentially in the form of HD molecules.

It is known that thermal desorption of chemisorbed hydrogen from carbon surfaces proceeds in a range from 1100 to 1600 K [6]. This suggests that the low temperature part of the spectra measured in the present study is attributed to the release of deuterium adsorbed on the walls

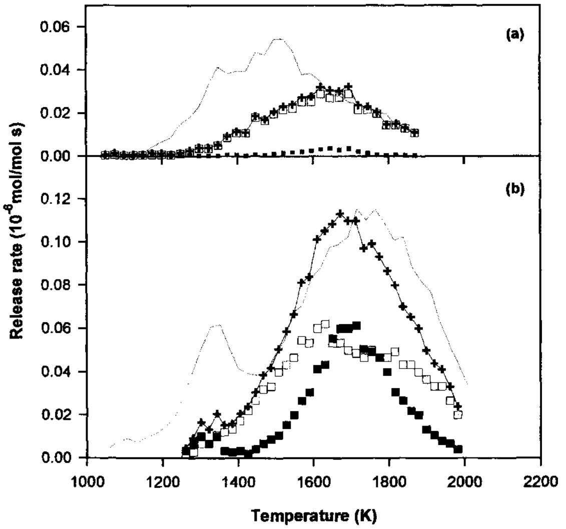

Fig. 2. Thermal desorption of deuterium as D_2 and HD molecules (closed and open symbols, respectively) and the net deuterium (D_2 + HD) release (solid curves) from SEP N112-A (a) and POCO AXF-5Q (b) exposed to 133 Pa D_2 at 1170 K for 2 h followed by oxidation in 0.08 MPa dried air at 1000 K for 10 min to weight losses of 5%. Dashed curves show the net release from as-loaded specimens for comparison. Heating rate 8 K/s.

of pores, diffusion of D_2 molecules from these is sufficiently rapid. (Obviously, such pores are readily accessible also to nitrogen molecules and therefore contribute to a value of specific surface determined by the Brunauer–Emmett–Teller (BET) method.) This explanation correlates well with our oxidation results. The latter are presented below along with a discussion on the high temperature part of spectra.

3.2. Oxidation effects

Referring to Fig. 2, an oxidation of deuterium loaded specimens in dried air affects the release spectra significantly. In a qualitative sense, SEP and POCO show similar behavior: oxidation at 1000 K for 10 min to a weight-loss of ~ 5% leads to a disappearance of the low temperature part of spectra while the net amounts of D_2 + HD released above 1600 K remain unchanged. It is interesting to note that the D_2 desorption rate from oxidized SEP is negligible throughout the measured spectrum (Fig. 2a). Air oxidation apparently promotes an increase in protium coverage of the internal surfaces and consequently a rise in the probability of mixed recombination. In contrast to SEP, no drastic changes are observed in the high temperature part of POCO spectra: D_2 and HD peaks are only slightly shifted along a temperature axis with no marked variations in amplitude.

It should be emphasized that the same changes in spectra were observed also, after oxidation in open air (humidity of ~ 60%). This indicates a minor role of water vapor in the observed effects. In relation to nitrogen, as the main component of air, Chiu et al. [8] found that nitrogen gas was completely ineffective in removing both implanted and chemisorbed deuterium. Thus, in the following, the reaction between oxygen and chemisorbed deuterium is considered. Because, in contrast to hydrogen, no oxygen diffusion in graphite bulk occurs even at high temperatures [9], this reaction proceeds, obviously, only on the walls of open pores. This means that the reactivity of retained D atoms located at the various traps towards air oxygen is understood by suggesting different accessibility of that to gases.

As evidenced, a part of the chemisorbed hydrogen on the graphite surface is removed by oxygen even at room temperature [8]. In contrast, hydrogen adsorbed on diamond powder is stable in oxygen at 300 K, with detectable oxygen adsorption being registered only above 700 K [10]. It is essential that the oxygen uptake was attended with the release of pre-adsorbed hydrogen. An upper limit for the thermal stability of sorbed hydrogen in oxygen atmosphere seems to be near 1120 K, at which a total tritium degassing of graphite has been obtained in Ref. [5]. In the present study the deuterium loaded specimens were exposed to air at a rather high temperature suggesting that oxidation is accompanied by removal of chemisorbed deuterium from the surfaces accessible to air oxygen.

The nature of air stability of deep trapped deuterium is less clear as no consistent data on deep hydrogen trapping in graphites can be found in the literature. Redmond et al. [11] pointed out that all synthetic graphites have a number of pores closed for gases at low temperatures. Using a small angle neutron scattering (SANS) method, Hoinkis et al. [12] revealed that closed porosity might be characterized by a large value of surface area, up to 30 m^2/g. A similar estimation for the total surface area of closed pores in CFC was done by Chernikov et al. [13] when studying their structure with transmission electron microscopy (TEM). At high temperatures a part of closed pores becomes accessible to hydrogen and therefore should be named 'potentially accessible' [6].

Hoinkis [6] observed that the major part of sorbed deuterium is released from A3-3 graphite in a high temperature peak centered at 1800 K, with only a minor fraction to 1400 K. He explained the peak at 1800 K by thermal desorption of deuterium chemisorbed on the walls of potentially accessible pores with the slow diffusion of formed D_2 molecules being a rate determining stage of the release. At the same time a pronounced increase in BET surface areas was found [14] for most graphites (including fine grain graphites and A3-3) oxidized in air to weigh loss of only 1–5%. This effect was proved to be attributed to the opening of previously inaccessible pores. Therefore, an abrupt release of sorbed deuterium could be expected just at the initial stage of oxidation. Otherwise, there is a need to assume that chemisorbed deuterium is stable in air even at high temperatures.

That a part of sorbed deuterium is in fact stable in air oxygen indicates that D atoms in POCO and to a lesser degree in SEP are retained to form the complexes which cannot be referred to surfaces ones. It is possible that there are some intracrystallite complexes as suggested in [2,15]. As evidenced in the present study the amounts of such complexes might depend on graphite microstructure. Alternatively, the differences in amounts of deep trapped deuterium between POCO and SEP might be attributed to kinetic peculiarities of deuterium retention in graphites tested.

3.3. Fusion application

Because of a short-run, rise in operating temperatures far above 1100 K is acceptable for carbon armor of ITER divertor [1], great weight losses of CFC under accidental air ingress into the vacuum vessel might be expected. In this regard there are at least two questions to be answered before proceeding to an assessment of tritium mobilization in case of an accident. First, what fraction of closed pores of CFCs becomes accessible to tritium during prolonged operation of the ITER divertor? Second, what part of sorbed tritium forms the stable intracrystallite complexes? As hydrogen sorption behavior and graphite microstructure are essentially modified under neutron irradiation, there is strong need to study the effect of oxidation on hydrogen mobilization in damaged CFC.

4. Conclusion

The effect of air oxidation on thermal desorption of deuterium from carbon fiber composite SEP N112-A and fine grain graphite POCO AXF-5Q has been studied. It is observed that a specific fraction of sorbed deuterium is easily removed from both materials just at the initial stage of oxidation. This deuterium seems to be related to D atoms chemisorbed on the walls of the pores readily accessible to air oxygen. The rest deuterium is absorbed to form the complexes which cannot be referred to surface ones and therefore are stable at the initial stage of oxidation.

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