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Overview of EU CFCs development for plasma facing materials

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Abstract

To improve the properties of carbon materials, the tritium inventory should be reduced, chemical erosion and RES have to be suppressed to increase the resistance to water/oxygen at elevated temperatures. In addition, in the next generation devices, i.e., the International Thermonuclear Experimental Reactor (ITER), plasma disruption, slow transients, and ELMs, which can occur as off-normal events as the result of a transition from detached divertor operation to attached operation causes extremely high heat loading to carbon protection material. Therefore, Carbon fiber composites (CFCs) with high thermal conductivity (300 W m^{-1} K^{-1} at 20°C, 145 W m^{-1} K^{-1} at 800°C) are favourable. In framework of European Fusion Technology program, a great effort has been made to develop CFCs to meet all requirements. This paper presents an overview in progress of EU CFCs development. The characteristics of CFCs with respect to thermal-mechanical properties, erosion by plasma, tritium retention, H_2O/O_2 reactions, and neutron irradiation effects were reported.

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1. Introduction

Carbon-based materials are considered as attractive choices for the plasma facing components, because of their low atomic number which leads to favourable plasma compatibility. Carbon-based materials pose excellent thermal shock resistance and therefore they are indispensable for high heat flux components in forthcoming fusion devices. In the next generation devices, i.e., the International Thermonuclear Experimental Reactor (ITER), plasma disruption, slow transients, and ELMs, which can occur as off-normal events as a result of a transition from detached divertor operation to attached operation causes extremely high heat loading to carbon protection material. Therefore, carbon fiber composites (CFCs) with high thermal conductivity (300 W m^{-1} K^{-1} at 20°C, 145 W m^{-1} K^{-1} at 800°C) are favourable.

In addition, as next generation devices, i.e., the ITER will produce intense neutron fluxes [1], substantial R & D is needed to elucidate the effects of neutron-induced damage on the microstructure and critical properties of these materials, e.g. thermal conductivity, swelling and tritium trapping, because they could limit the utilization of these materials in fusion devices. The crucial problems which need to be better understood is the behavior of thermal–mechanical properties, swelling and tritium retention in materials subjected crystallographic damage and microstructural changes induced by neutrons.

This paper presents an overview in progress of EU CFCs development. The characteristics of CFCs with respect to thermal–mechanical properties, erosion by plasma, tritium retention, H_2O/O_2 reactions, and neutron irradiation effects were reported.

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2. CFCs development

A systematic development of high thermal conductivity CFCs has been carried out in framework of European Fusion R & D Program. In the early stage, for purpose of investigation on high heat flux behaviours, neutron effect on thermal conductivity, mechanical properties, tritium retention, oxygen reactivity and plasma compatibility, a series of commercial available CFCs were used. Based on the data obtained from those CFCs, several 3D CFCs have been developed.

2.1. The R & D on CFCs materials

2.1.1. Early stage CFC materials [2]

The investigated materials are the seven following carbon fiber composites (CFCs):

A 05: A 2D felt-type CFC supplied by Le Carbone Lorraine. The elementary carbon fibers made from polyacrylonitrile (PAN) precursor, are randomly distributed in a plane. The volumic fraction of fibers is 25%. This felt undergoes needing which orientates in percentage of fibers in the perpendicular direction to the plane. The matrix densification is by chemical deposition of pyrocarbon from the vapor phase followed by a pitch impregnation. The final heat treatment of graphitization is at about 2500°C.

CX 2002U: A 2D felt-type supplied by Toyo–Tanso. This CFC constituted of ex-PAN fibers randomly distributed in a plane is densified by chemical deposition of pyrocarbon from the vapor phase; then it is graphitized at high temperature.

DMS 678: A 2D woven CFC supplied by DUNLOP. It is constituted of layers of ex-PAN fibers woven in a plane. The densification is by chemical vapor deposition of pyrocarbon.

N112: A 2D CFC supplied by Société Européenne de Propulsion. This CFC is constituted by an ex-PAN NOVOLTEX preform; that is to say layers of carbon fibers woven in a plane, with carbon felt inserted between two layers of woven carbon fibers. Then there is a needling which gives some fibers an orientation in the direction perpendicular to the plane. The volumetric fraction of fibers is about 30%. The densification is by chemical infiltration of pyrocarbon followed by a heat treatment at high temperature. The last phase of densification is operated by a pitch impergnation at 1000 bars/1000°C followed by a heat treatment at 2200°C.

N11: It is same CFC as N112 but is has not undergone the last phase of densification by a pitch impregnation.

FMI A27-130: A 3D CFC constituted of P130 high modules fibers. This material contains 5.5% in volume of fibers in the y and z directions and 36% in volume of fibers in the x direction (the x direction is perpendicular to the plane y, z) which is the direction of high thermal conductivity.

MKC: A 1D CFC fabricated by MITSUBISHI KAGAKU from its pitch based K321 fibres; the fibers volume fraction is 60%.

2.1.2. New developed CFCS [3]

DUNLOP CONCEPT 1: It is a 3D CFC constituted of long fibers woven in the plane, with ex-pitch fibres (P120-P130) in x direction and ex-PAN fibers in y direction; then there is a needing giving an orientation of fibers in the perpendicular direction (z direction). The volumic fraction of fibers is 30%. The densification is operated by three cycles of Chemical Vapor Infiltration (CVI) of pyrocarbon. The density of this CFC is about 1.85.

DUNLOP CONCEPT 2: It is the same material as DUNLOP CONCEPT 1 but with a fibers volumic fraction of 38%. The densification is operated by three cycles of pyrocarbon CVI and the density is about 1.86.

DUNLOP CONCEPT 3: It is a 2D CFC constituted of long fibers woven in the plane with ex-pitch fibers P120 in the s direction and P25 in the y direction. The volumic fraction of fibers is 40%. The densification is operated by three cycles of pyrocarbon CV1. The density of this CFC is about 1.88.

Three kinds of high thermal conductivity CFCs and one Si doped CFC have been manufactured by SEP:

N 312 A: It is a 3D woven CFC with the ex-pitch fiber P25. The volumic fraction of fibers is 35% (22% in x direction, 8% in y direction, 5% in z direction). Then there is a densification operated by chemical infiltration of pyrocarbon at 1000°C followed by a heat treatment at about 2800°C. The last phase of densification is made by chemical infiltration of pyrocarbon at 1000°C, followed by a pitch impregnation at 1000 bars/1000°C. The density of this CFC is about 1.90.

N 312 B: It is a 3D CFC constituted by a NOVOLTEX preform, with P25 ex-pitch fibers in s direction and ex-PAN fibers in y direction, then a needling to give an orientation in z direction. The volume fraction of fibers is 35% (27% in x direction, 4% in y and z directions). Then there is a densification by chemical infiltration of pyrocarbon at 1000°C followed by a heat treatment at 2800°C. The last phase of densification is made by chemical infiltration of pyrocarbon at 1000°C followed by a pitch impregnation at 1000 bars/1000°C. The density of this CFC is about 1.95.

N 312 C: It is a 3D CFC, N11 type, which has undergone a final infiltration of liquid silicon leading partly to the formation of silicon carbide (0/12 at.% Si). The porosity of this material is very low (1%) and its density is about 2.09.

NS31 is a 3D CFC constituted of P55 ex-pitch fibers (80 vol.%) in one direction and ex-PAN fibres (20 vol.%) in the perpendicular direction; this CFC undergoes a subsequent needling which gives a fibres orientation in the third direction (z direction). The high thermal

Table 1
Thermal properties of the CFCs

		MKC (‖)	A05 (‖)	CX2002U (‖)	DMS678 (‖)	N11 (‖)	N112 (‖)	FMI A27-130 (‖)
Thermal conductivity	25°C	618	324	283	110	248	220	309
(W/m K)	800°C	252	118	101	62	103	97	136
CTE (20–1000°C) (10^{-6}/K)		−0.10	0.95	2.16	0.69	1.34	0.55	1.17
Heat capacity	25°C	669	665	652	669	673	669	668
(J/kg K)	800°C	1685	1670	1654	1674	1685	1669	1670
Density (G/cm^3)		1.97	1.81	1.64	1.72	1.79	2.01	2.03

conductivity direction is that of the P55 ex-pitch fibers. NS31 is densified by chemical infiltration of pyrocarbon and heat treated at a temperature >2500°C. At last, liquid silicon is injected under pressure leading partly to the formation of silicon carbide (SiC). NS31 contains about 8–10 at.% of silicon and its porosity is about 3–5%.

2.2. Neutron irradiation effects

Investigation on neutron irradiation effects on the thermal–mechanical properties of several CFCs materials have been carried out. The thermal properties of the CFCs before irradiation are given in Table 1. To investigate the neutron irradiation effects on properties of carbon materials, three main irradiation experiments were performed, namely, CERAM D217-15, CERAM D217/18/19 and MACIF. The irradiation temperature are: CERM D217-15, 1500°C, CERAM D217/18/19, 600°C, 800°C, 1000°C and MACIF 400°C, respectively. The dpa *g* values were calculated by HFR-TEDDI program. The CERAM irradiations have been performed in the High Flux Reactor (HFR), Petten, whilst the MACIF irradiation has been carried out in the OSIRIS reactor at Saclay (France). The damage dose of Petten HFR irradiations are ranging from 0.8 to 5 dpa *g* and 0.35 to 0.85 for MACIF irradiations.

2.2.1. Neutron effects on thermal conductivity

Neutron irradiation induces degradation of thermal conductivity. For example, after irradiation temperature of 420°C and damage dose of 0.83 dpa *g*, the degradation of thermal conductivities has been observed for all investigated CFCs. The normalized thermal conductivities at 400°C, $(K_i/K_o)_{400°C}$ were between 0.28 and 0.38. Neutron irradiation induces carbon displacement from their initial position in the lattice to interstitial position between two basal plane. Thus, large dislocation loops or defect clusters are created especially at low irradiation temperature. The low irradiation temperature (400°C) prevents annealing of these defects, and the propagation of the phonons along the basal plane is slowed down, inducing a decrease in the thermal conductivity. The average normalized thermal conductivities of all investigated CFCs as a function of irradiation temperature for 1 dpa *g* are given in Table 2. The results show that the neutron induced degradation of thermal conductivity decreases with increasing irradiation temperature. There is almost no degradation of thermal conductivity, if the irradiation temperature is higher than 1000°C for neutron damage of 1 dpa *g*. It is obvious that there is a beneficial effect of high irradiation temperature (⩾ 1000°C), allowing an annealing during irradiation, so that the carbon atom displaced from their lattice sites can return to their initial position. The results also show, that the neutron induced degradation of thermal conductivity is lower for those CFCs with lower initial thermal conductivity.

2.2.2. Dimensional changes

The dimensional changes (dL/L_o) of 2D and 3D CFCs irradiated in the temperature ranges 385–420°C, 0.41–0.83 dpa *g* are very small in both parallel (‖) and perpendicular (⊥) directions. Generally, dimensional changes of ex-PAN fibers CFCs are negative in both directions. Contrary, the dimensional changes of ex-pitch fibers CFCs are always positive on both directions and almost close to nil. After irradiation at 600°C/1 dpa *g*, the dimensional changes are almost the same as at 400°C [2].

2.2.3. Irradiation effects on the tritium retention in carbon

Before loading, the unirradiated specimens were conditioned for 1 h at 850°C under vacuum to remove

Table 2
Thermal conductivity changes as a function of damage and temperature

Temperature (°C)	$(K_i/K_0)T_{irr}$, 1 dpa	
	High K_0 CFC	LOW K_0 CFC
400	0.30–0.35	0.30–0.35
600	0.55–0.60	0.60–0.65
800	0.75–0.80	0.85–0.90
1000	0.80–0.85	0.95–1
1500	1	1

High K_0: ⩾ 300 W/m K at 25°C; ⩾ 120 W/m K at 800°C. Low K_0: ⩾ 100 W/mK at 25°C; ⩾ 50 W/mK at 800°C.

air and moisture. For the irradiated specimens the conditioning temperature was adapted to the irradiation temperature. Tritium loading was done under a H_2 + 2 ppm T_2. After loading the surface adsorbed tritium was removed by purging at room temperature. The retained tritium is determined by heating the specimens with 5°C min^{-1} to 1050°C and purging with He + 0.1% H_2. The released tritium is measured with an ionization chamber and finally trapped in bubblers. The details of experiment were described elsewhere [4]. It was observed that about 10% of retained tritium was not released by heating to 1050°C. To determine the total retained tritium the samples were normally afterwards oxidized in oxygen at 850°C. The tritium trapped in the bubblers was determined by liquid scintillation counting. The most systematic investigation of neutron effects has been carried out for graphite S1611. The results show that the tritium retention increases with increasing neutron damage and it seems to achieve above about 0.1 dpa a saturation value. The fact, that equilibrium is obtained for both unirradiated and irradiated samples within 10 h at 850°C loading, which indicates the fast tritium transport and fast adsorption kinetics. Moreover, because essentially all trap sites should be occupied, the retained tritium should correspond to the total number of trap sites. From the data obtained, it is reasonable to estimate, that the saturation value ($\geqslant 0.1$ dpa) of trap sites of neutron irradiated samples should be about 1000 appm.

In the tokamaks, the neutron irradiation and process of tritium interaction occurs at the same temperature. Therefore, the tritium loading at a temperature which corresponds to the irradiation temperature are assumed to be more representative. As it has been mentioned, the amount of retained tritium increases with loading temperature up to 850°C. Compared to the values at 850°C, the retained tritium at 600°C to about 60% and at 400°C to 10–20%. Evidently the transport and adsorption processes are so low at the lower temperatures that only a fraction of the traps is occupied during the 10 h loading. Clearly, an estimation of the retained tritium under tokamak conditions requires that a set of representative conditions is established.

2.2.4. Oxidation behavior of CFCs and doped CFCs

Oxidation resistance is an important criterion in selection of PFC's due to the fact, that PFC-oxidation may cause severe consequence in loss of vacuum accidents and loss of coolant into vacuum accidents (water/steam ingress into the vacuum vessel). Facilities and first results of oxidation of carbon based doped (Ti, Si) and doped CFCs in steam and air are described elsewhere [4]. Comparing steam and air it was found, that oxidation rates in air are roughly of the same size at 700°C as in steam at about 1000°C; furthermore, sequences of oxidation resistance of different materials in steam are not the same as in air. In general, undoped CFCs have the same oxidation resistance as nuclear carbons V483T and A3. Highly SiC doped INOX A14 (40 vol.% SiC) revealed an oxidation resistance in steam about 2–3 orders of magnitude better than undoped materials; doping with Ti however does not improve oxidation resistance. From experimental results, it can be seen, reduction of Si contains to 8–10 at.% decreases oxidation resistance in comparison with INOX A14 (40 vol.% SiC), which however remains still better than for undoped carbons by a factor of about 4.

Most probably, the low oxidation rates of Si-doped carbon materials are caused by formation of a SiO_2-layer, which is known to have very low diffusion permeability for steam and oxygen at temperatures <1400°C and, accordingly carbon zones covered with SiO_2 are protected from oxidation. However, as theoretical examinations indicate, SiO_2 is formed only if oxidant pressure is sufficiently high, whereas at low pressures volatile SiO can be formed [5].

2.2.5. Outgassing behavior of CFCs

Investigation of outgassing for doped and undoped CFCs, a systematic investigation of outgassing behavior of doped CFCs and undoped CFCs was carried out in terms of temperature dependence and temperature pretreatment. The experimental and evaluation procedures have been described in details elsewhere [6]. For comparative investigation, the characteristics of 5 materials; Sep Carb N112 (3D), Dunlop V(2D), SiC 2.5%, SiC 8% doped CFCs(2D), 3D Novotex (No3) and NS31 (Si-doped 3D) have been investigated. In order to obtain appropriate comparison, all pre-treated samples (1000°C, 20 h) were exposed to air for two weeks before the outgassing test. In general the total amount of outgassing of Si-doped CFC is 1–2 order of magnitude lower than that of other carbon based materials tested. The results also indicate, that the release temperature of H_2O of Si-doped CFC is about 100°C lower than other carbon based materials.

2.2.6. Chemical erosion and stability of Si dopant

The measurements of chemical erosion were carried out in two different facilities: (a) Plasma Generator Device PSI-1 (flux density 10^{18} cm^{-2} s^{-1}); (b) High Current Ion Beam Source (flux density 3×10^{15} D^+ cm^{-2} s^{-1}).

At plasma Generator Device PSI-1, the chemical sputtering yield was measured dynamically (during temperature rise) with a calibrated mass spectrometer and the CH-band intensity as well as by the weight loss method. The results of mass spectrometry agree well with the values obtained by weight loss method. It is seen, that the maximum chemical sputtering of Si-doped CFC(NS31) is at least factor 2 lower than that of undoped CFC(DUNLOP 3D) [7].

Table 3
Thermal stability of NS31

Sample	Material	Diffusivity before heat treatment, at 100°C (cm^2/s)	Heat treatment	Diffusivity after heat treatment, at 100°C (cm^2/s)
1	NS 31	1.4281	1200°C – 1 h	1.3039
2	NS 31	1.4477	1600°C – 2 h	1.409
3	NS 31	1.4253	1600°C – 20 s	1.4309

At high Current Beam Source, the chemical sputtering yield was determined by weight loss method. It is clear that the yield of Si-doped CFC is about factor of 2–3 lower than that of undoped carbon.

To investigate the stability of Si dopant, surface composition of specimens was analysed pre- and post-heat treatment. Before the heat treatment, the Si concentration at surface is quite inhomogeneous. After the sample has been heated up to 1800 K for 2 h, a loss 1–5% of Si has been investigated and Si concentration is near homogeneous. A significant enhancement of Si concentration has been observed after heat treatment. The chemical sputtering yield of heat treated sample at 800 K is about a factor of 3–5 smaller.

2.2.7. *Stability of thermal property*

To investigate the thermal stability, samples have undergone several temperature treatments. The thermal diffusivity has been measured before and after temperature treatments. The results are given in Table 3. Three samples were used for each set of experiment. The diffusivities presented in table are the average of three measurements. Surprisingly, the decrease in thermal diffusivity, even heated up to 1600°C, 1 h, is less than 3%. It implies, that the thermal conductivity of NS31 will sustain through high temperature operation [8].

2.2.8. *High heat flux test of CFCs*

The modules (flat tile or monoblock design) have been manufactured with different heat sink materials. For monoblock CFC modules have been produced by active metal casting and subsequent brazing using a Ti braze.

The tests have been performed under quasi-stationary heat loads. The maximum absorbed heat fluxes of 20 MWm^{-2} have been applied. All tested modules show a rather good and uniform heat removal efficiency.

Thermal fatigue tests have been performed on several types of divertor modules; a total of 1000 cycles has been applied at absorbed heat fluxes of 20 MWm^{-2} (10 s pulse duration, 10 s cooling down). During thermal cycling no degradation of heat removal has been observed [9].

3. Conclusion

In the present study, a systematic investigation on the properties of CFCs, new CFCs and advanced silicon doped CFC is performed and the following conclusions can be made:

(a) Detailed results of neutron effects on thermal conductivity, dimensional changes and tritium retention have been obtained as a function of neutron doses and irradiation temperature.
(b) Experimental investigation on the behaviors of oxidation and outgassing has been performed.
(c) Systematic high heat flux test has been performed for CFC monoblock module type.
(d) New CFCs as well as Si-doped advanced have been developed.
(e) The thermal conductivity of Si-doped 3D CFC is as high as 300 W m^{-1} K^{-1} at 300 K.
(f) It has been demonstrated that doping of Si/SiC can increase the oxidation resistance in steam about 2–3 orders of magnitude.
(g) It seems that doping of silicon decrease the total tritium retention.
(h) The outgassing rates of gaseous species, H_2, CH_4, H_2O, CO and CO_2 of Si doped carbon materials are higher than those of undoped carbon materials. The release temperature of H_2 and H_2O is lower for Si doped CFCs.
(e) The chemical erosion yield of Si-doped CFC(NS31) material decreased by a factor 2–3.
(f) The thermal conductivity of NS31 remains almost constant under gone high temperature 1600°C operation.
(g) It seems that doping of silicon decrease the total tritium retention.

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