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The effect of low temperature neutron irradiation and annealing on the thermal conductivity of advanced carbon-based materials

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Abstract

Several carbon-based materials (carbon fibre composites NB 31, NS 31 and UAM-92, doped graphite RGTi-91), were irradiated at about 90 °C in the damage dose range 0.0021–0.13 dpa. Significant reduction of the thermal conductivity of all materials was observed (e.g. at damage dose of ~0.13 dpa the thermal conductivity degraded up to level of ~2–3% of the initial values). However, saturation of this effect was observed starting at a dose of ~0.06 dpa. The effect of annealing at 250 and 350 °C on the recovery of thermal conductivity of NB 31 and NS 31 was studied and it was shown this annealing can significantly improve thermal conductivity (~2.5–3 times). The data on the degradation of the thermal conductivity after additional irradiation after annealing is also reported.

1. Introduction

Carbon-based materials are being considered as armour for the divertor in next-step fusion devices, e.g. ITER. The main reasons are low *Z*, resistance against thermal shock, absence of melting, and excellent thermal performance as part of an actively cooled plasma facing components. In ITER, carbon fibre composite (CFC) armour is used in the divertor area at the strike point, [1], where a high heat flux of ~20 MW/m^2 during normal operation and disruption loads up to 30 MJ/m^2 are expected. Due to the relatively low temperature of the water coolant (~100 °C) in the ITER divertor, the irradiation temperature for CFC armour is in the range of ~150–1500 °C, and the anticipated maximum displacement damage dose is ~0.1 dpa. During operation it is planned that divertor components will be annealed several times at approximately 240–350 °C during baking procedures, and this thermal treatment could improve the thermal conductivity of irradiated material.

It is well known that the thermal conductivity of carbon-based materials degrades under neutron irradiation, (see for example [2,3]). Irradiation decreases the thermal conductivity of CFCs at damage doses as low as ~10^{-3} dpa, at irradiation temperature of 400 °C, [4].

Data on the effect of neutron irradiation on thermal conductivity of recently developed advanced CFCs, especially for low irradiation temperature ($\leqslant 200$ °C) are very limited. The effects of low temperatures (~250–350 °C) annealing on the recovery of the thermal conductivity and the further changes of the thermal conductivity from subsequent irradiation are also not known. This paper presents the data on neutron irradiation effects on the thermal conductivity of several advanced carbon-based materials at irradiation temperature of ~90 °C and at displacement damage doses in the range of 0.0021–0.13 dpa, including the effect of annealing at 250 and 350 °C on the recovery of the thermal conductivity.

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2. Experimental

2.1. Materials

The following materials have been selected for this study:

CFC NB 31, produced by Société Européene de Propulsion (SEP), France, [5]. This is a 3D CFC with P55 ex-pitch fibres in the *x* direction (which is the direction of the higher thermal conductivity) and ex-PAN fibres in other directions. This 3D structure is densified with pyrocarbon through a chemical vapour infiltration process and heat treated at very high temperatures to maximize the thermal conductivity. The last phase of densification is made through a chemical vapour infiltration of pyrocarbon, followed by a pitch impregnation at 1000 bars/1000 °C. The density of this material is ~1900 kg/m^3, porosity is ~8%, average room temperature thermal conductivity (in *x* direction) is ~350 W/mK.

CFC NS 31, produced by SEP, France [5]. This material is produced in a similar way to NB 31, except for the final treatment. For NS 31 the final step is injection of liquid silicon. CFC NS 31 contains about 8–10 at.% of silicon, partly in the form of SiC. The density of this material is ~2150 kg/m^3, porosity is ~5%, average room temperature thermal conductivity (in *x* direction) is ~320 W/mK.

Recrystallized graphite RGTi-91, produced by the Russian Federation [6]. This material is produced by mixing graphite and titanium powders that are finally treated at high temperature (2500–3000 °C) and high pressure. The density of this material is ~2180 kg/m^3, average room temperature thermal conductivity (in direction perpendicular to the moulding pressure) is ~410 W/mK.

CFC UAM 92, produced by the Russian Federation, [6]. This is a 5D CFC constituted of PAN fibres, with cell size ~ 1.5 × 1.5 × 0.75 mm. The 5D woven preform is densified by chemical vapour deposition at 900–1000 °C, impregnated by pitch and heat treated at 2500–2800 °C. The density of this material is ~1720 kg/m^3, porosity is ~10%, and average room temperature thermal conductivity is ~70 W/mK.

The samples are discs with diameter −10 mm, thickness −5 mm. The higher thermal conductivity was oriented through their thickness (5 mm).

2.2. Neutron irradiation and measurements

The samples were irradiated in the RBT-6 nuclear reactor, Dimitrovgrad, Russia. The experimental channels in this reactor are located in cells of reactor core, the section size of each cell is 70 × 70 mm^2, and length ~350 mm. Experimental capsules were cooled by water from the main cooling system. The fast neutron flux in the active zone is $(4.1\text{–}6.7)\times10^{13}$ n/cm^2 s ($E > 0.1$ MeV). The disc samples were placed in a stainless steel cylindrical capsule (diameter 12 mm, thickness of wall 0.8 mm). The gap between disks and the inner surface of the capsule wall was 0.2 mm that provides the required irradiation temperature. Before the irradiation, the samples in capsules were annealed for 2 h at 300 °C in a He atmosphere to remove the impurities adsorbed at the surface. Nine capsules were irradiated. For continuous control of the irradiation temperature, three thermocouples were installed in one of the capsules. Other capsules were identical, but were not supplied with thermocouples. The position of all capsules in the reactor core was absolutely symmetrical and the irradiation temperature was expected to be the same. Irradiation temperature during the experiment was measured as 90 ± 10 °C.

Neutron fluences (at 6 reference points) were in the range of $2.9 \times 10^{18}\text{–}1.78 \times 10^{20}$ n/cm^2 ($E > 0.1$ MeV). The calculated displacement damage values were ~0.0021, 0.007, 0.014, 0.025, 0.067 and 0.13 dpa.

The thermal conductivity of the materials before and after irradiation was evaluated by the following equation:

$$K = \alpha\rho C_\mathrm{p}, \tag{1}$$

where K is the thermal conductivity, ρ is measured density (kg/m^3), C_p is the specific heat (J/kgK) and α is the measured thermal diffusivity (m^2/s). The thermal diffusivity was measured by a flash (Parker) method: a short (lasting about 1.3 ms) high intensity light pulse was applied to the surface of a disk and a temperature response on the disk back surface was measured by thermocouples. The measured signal depends whether the thermocouple head is in contact with the fibres or with the binder. To reduce this effect, for each sample, 12 measurements with different thermocouple position have been performed. The thermal diffusivity was measured at room temperature (~20 °C). The specific heat for these materials has not been measured. The typical value of ~720 J/kgK was used also for calculation of thermal conductivity of the studied materials.

3. Results and discussion

3.1. Effect on thermal conductivity

The relation between thermal conductivity and density for the unirradiated samples of the studied materials is shown in Fig. 1. Typically for carbon-based materials, there are some variations in values of these properties. This variation could be attributed to un-homogeneity of the material and experimental errors. The cutting of the samples was made from different positions in the

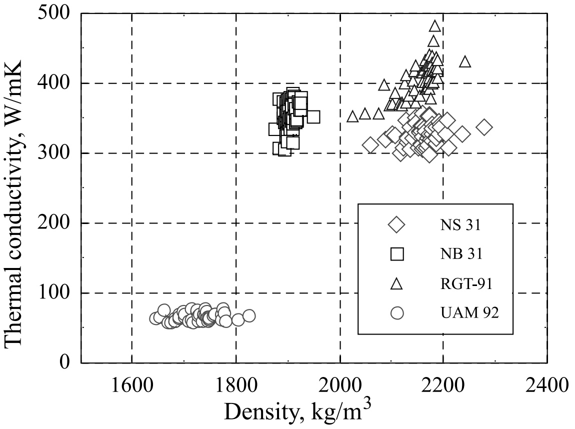

Fig. 1. The relation between thermal conductivity and density of the unirradiated samples for studied materials.

original production batches and the samples could have slightly different properties (different porosity, some loss of binder during sample cutting).

The thermal conductivity and density values in this study for NB 31 and NS 31 are in good agreement with the previous published data [5].

Fig. 2 shows the effect of neutron irradiation on the thermal conductivity of the materials studied. Neutron irradiation leads to a significant decrease of the thermal conductivity even at a damage dose of 0.0021 dpa, particularly after room temperature measurement. A further increase of the neutron fluence leads to a further decrease of the thermal conductivity. However, the highest rate of degradation is observed at low fluence. The saturation effect at damage dose ~0.06 dpa is observed.

It can also be seen that the difference in the thermal conductivity of the irradiated materials is decreasing and after irradiation up to a damage dose ~0.13 dpa the thermal conductivity of these materials is very similar (~4–6 W/mK). The scatter of the data also decrease with increasing damage dose.

The normalized thermal conductivity (ratio K_{irr}/K_o measured at room temperature) is shown in Fig. 3. The lowest value of $(K_{irr}/K_o)_{RT}$ is observed for the RGTi-91 graphite, which has the highest thermal conductivity in the unirradiated state. By contrast, the lowest ratio of $(K_{irr}/K_o)_{RT}$ is observed for UAM-92, which has the lowest original thermal conductivity. A similar effect was reported in [7,8]: materials with high initial thermal conductivity degrade much faster than materials with lower initial thermal conductivity. However, in this work the difference between the value of $(K_{irr}/K_o)_{RT}$ for different materials is much higher. For the studied materials, the difference of $(K_{irr}/K_o)_{RT}$ decreases with increasing neutron fluence.

From this Fig. 3, it seems that a saturation of the thermal conductivity degradation occurs at a damage dose of ~0.06 dpa; and the value of $(K_{irr}/K_o)_{RT}$ is ~0.015–0.02. This saturation effect has been observed in several publications. Burchel reported that at the irradiation temperature of 600 °C the saturation began at 1 dpa and the value of $(K_{irr}/K_o)_{600\,°C}$ is ~0.40 [9]. At lower irradiation temperature (150–200 °C) the saturation is observed at 0.1 dpa and the value of $(K_{irr}/K_o)_{RT}$ is ~0.1, [10]. It can therefore be concluded that a decrease of the irradiation temperature results in a decrease of the dose at which saturation occurs and in a decrease in the value of normalized thermal conductivity.

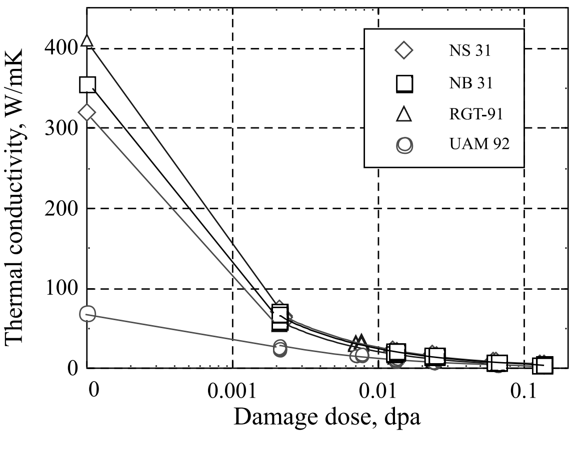

Fig. 2. Degradation of the thermal conductivity as a function of the damage dose, irradiation temperature ~90 °C, temperature of measurement ~20 °C.

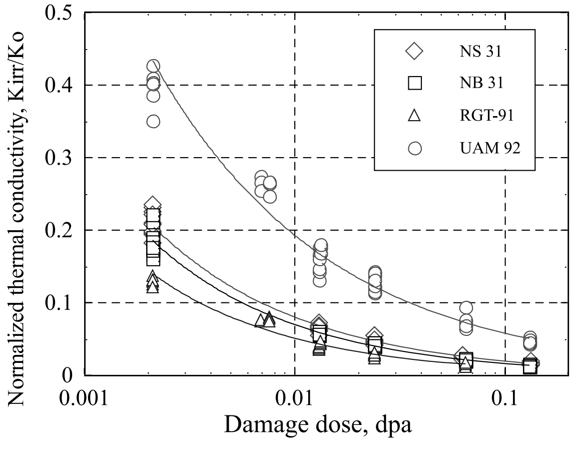

Fig. 3. Normalized thermal conductivity as a function of the damage dose, irradiation temperature ~90 °C, temperature of measurement ~20 °C.

Comparing the behaviour of NB 31 and NS 31, it seems that latter material shows less degradation of thermal conductivity.

The degradation of the thermal conductivity is obviously explained by the formation of radiation defects [10]. The types of defects depend on irradiation temperature. At irradiation temperature less than ~100 °C, most of the defects are vacancies, which are placed in the hexagonal layers, interstitials, and small interstitial clusters, which are placed between the hexagonal layers. The saturation of the density of these defects determines the saturation of the thermal conductivity after irradiation.

3.2. Effect of annealing

Fig. 4 shows the effect of annealing as a function of time on the recovery of the thermal conductivity of NS 31 and NB 31. The samples of these materials were irradiated up to a damage dose of ~0.0021 dpa and annealed at 250 and 350 °C for 6, 12 and 24 h. As it can be seen from this figure, annealing leads to partial recovery of the thermal conductivity: thermal conductivity was increased by 2.5–3 times. Annealing at 350 °C is more effective than annealing at 250 °C. Also for these annealing temperatures, saturation of the thermal conductivity recovery was observed after ~6 h. Annealing at 250–350 °C leads to an annihilation of the vacancies and interstitials and this improves the thermal conductivity. However, the large clusters remain stable at these temperatures and this is a reason why the full recovery of the thermal conductivity was not possible.

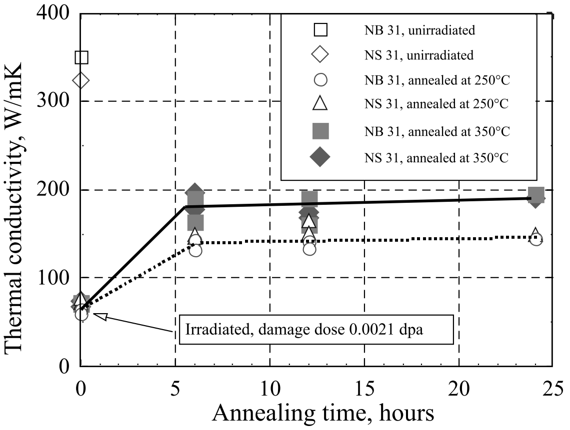

Fig. 4. Effect of annealing on the recovery of the thermal conductivity of NS 31 and NB 31, temperature of measurement ~20 °C.

To check the effect of the neutron irradiation on the thermal conductivity of the annealed materials, two capsules which were irradiated up to damage dose 0.0021 dpa, were taken out of the reactor and annealed at 250 and 350 °C for 24 h. After this annealing, the irradiation was continued up to a damage dose of 0.007–0.008 dpa at ~90 °C.

Table 1 includes the summarised data on the influence of irradiation, annealing and subsequent irradiation on the thermal conductivity of the studied materials. Annealing increases thermal conductivity by ~2.5–3 times (at least for NB 31 and NS 31). However, after additional irradiation up to a total damage dose ~0.007–0.008 dpa, the thermal conductivity is only ~5–40% higher, than the thermal conductivity without annealing.

The possible reasons for this are schematically presented in Fig. 5. The key point is that the maximum decrease of the thermal conductivity at low irradiation temperature occurs at very low damage dose.

In the real design (such as divertor in ITER) it is possible to anneal the irradiated CFCs at moderate temperatures, e.g. as 250 or 350 °C. These annealing temperatures allow to recover a part of the initial thermal conductivity (Fig. 5). However, after a damage dose of ~0.0021 dpa (~100 pulses of operation of ITER), such annealing does not seem to be so effective to recover the thermal conductivity. It seems that in the case of more frequent annealing, the effect could be significantly higher, but this should be checked further. All these data presented have been measured at room temperature, to confirm this results, measurements at

Table 1
The results of the annealing and subsequent neutron irradiation

Material	First irradiation (dpa)	$K_{0.0021}$ (W/mK)	Annealing for 24 h (°C)	$K_{0.0021}$ after annealing (W/mK)	Final dose (dpa)	K final with annealing (W/mK)	K final without annealing (W/mK)	K_{irr} annealed/ K_{irr} not annealed
NB 31	0.0021	65.7	250	150	0.007	37.1	35	1.06
NS 31	0.0021	68	250	145	0.007	39.35	36	1.09
NB 31	0.0021	65.7	350	195	0.008	34.7	32	1.08
NS 31	0.0021	68	350	190	0.008	36.3	33	1.1

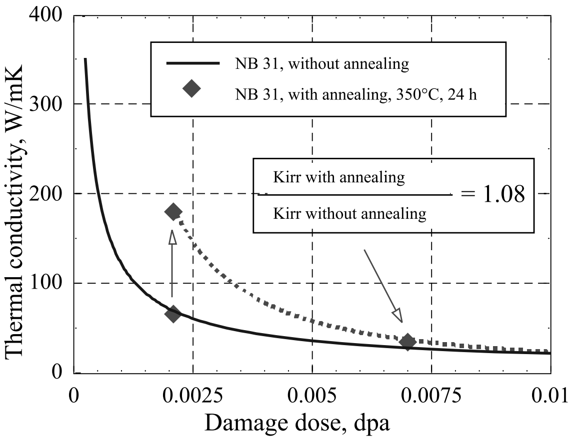

Fig. 5. The scheme of the thermal conductivity behaviour after annealing and further irradiation.

irradiation temperature are required and will be performed.

4. Conclusions

The following main conclusions can be made:

- The thermal conductivity of the materials studied decreases significantly after irradiation at 90 °C and the highest rate of degradation is observed at very low damage dose (less than 0.002 dpa).
- The normalised thermal conductivity $(K_{\mathrm{irr}}/K_{\mathrm{o}})_{\mathrm{RT}}$ is lower for materials with high initial thermal conductivity. With increasing damage dose, the difference in $(K_{\mathrm{irr}}/K_{\mathrm{o}})_{\mathrm{RT}}$ value is decreased.
- Saturation in the degradation of the thermal conductivity for all materials at a fluence ~0.06 dpa and irradiation temperature ~90 °C was observed. Based on this result and the results of previous studies it could be concluded that a decrease of the irradiation temperature decreases the saturation dose and the value of the normalized thermal conductivity.
- CFCs NB 31 and NS 31 behave very similarly. However, it seems that Si doped NS31 has less degradation in thermal conductivity.
- Annealing at 250 and 350 °C of the irradiated samples (NS 31 and NB 31) up to a damage dose ~0.0021 dpa can partially recover the thermal conductivity (up to ~55–60% of initial value). However, subsequent irradiation leads to a further significant decrease of the thermal conductivity. More frequent annealing (or annealing after lower fluence) seems to be required to preserve the high thermal conductivity of carbon-based material.

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