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The effect of high fluence neutron irradiation on the properties of a fine-grained isotropic nuclear graphite

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Abstract

A fine-grained isotropic nuclear graphite (IG-110), manufactured from a petroleum coke, was irradiated to a total neutron dose of 3.8×10^{26} n/m^2 or 25 displacements per atom (dpa) at 600°C in the high flux isotope reactor (HFIR) at Oak Ridge National Laboratory (ORNL). The effect of irradiation and the influence of post-irradiation thermal annealing on the properties of the graphite were evaluated. Volume change turnaround was clearly observed at 15–20 dpa and the return to original volume ($\Delta V/V_0 = 0$) can be estimated to occur at ~ 30 dpa. Strength and elastic moduli of the irradiated graphite increased by a factor of 2–3, and maximums in the σ/σ_0, and E/E_0 curves were at ~ 20 dpa at 600°C. Recovery of volume, fracture strength and thermal conductivity by thermal annealing were found, and thermal conductivity returned to better than about 30% of the unirradiated value after 1200°C thermal annealing.

1. Introduction

Japan Atomic Energy Research Institute's (JAERI) graphite moderated, gas-cooled reactor, the High Temperature Engineering Test Reactor (HTTR) has been under construction since 1990. The HTGR has a core consisting of an array of stacked graphite fuel blocks and replaceable reflector blocks. These blocks are machined from IG-110, a high-strength, fine-grained isotropic graphite. JAERI has been conducting graphite research and development for over 10 years and has built a database to support reactor design [1]. Moreover, many studies of mechanical, thermal, and chemical properties were carried out in collaboration with other research institutes and universities [2,3]. Notable among these activities are studies of irradiation effects on the properties of graphites. These studies have been performed in the research reactor (JRR) and material testing reactor (JMTR) at JAERI. Irradiation temperatures of up to 1200°C and neutron fluences of the order of 10^{25} n/m^2 ($E > 50$ keV) have been attained [4,5]. However, very high fluence irradiation experiments are required to predict the 'lifetime' of the graphite components. Graphite lifetime is defined as the dose at which the graphite irradiation induced volume change returns to zero [6]. The lifetime of a particular graphite is a function of the irradiation temperature and its structure.

The thermal recovery of the properties of graphite is an important phenomena offering the potential extension of the lifetime of graphite components. Recently, Burchell and co-workers [7,8] presented data for the recovery of thermal conductivity of irradiated carbon–carbon (C/C) composite materials after thermal annealing. However, the data are limited and it is not clear if thermal recovery can occur in graphites irradiated to a very high fluence.

The purpose of this paper is to elucidate the effect of very high fluence irradiation, and of the recovery

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after thermal annealing on the properties of a fine-grained nuclear graphite.

2. Experimental

2.1. Material and specimens

IG-110 graphite is a nuclear-grade, fine-grained, isotropic petroleum coke-based graphite manufactured by Toyo Tanso Co. Ltd. Typical properties of this graphite are listed in Table 1. Three blocks of this graphite (50 × 50 × 500 mm) were prepared for the pre- and post-irradiation experiments. They were cut into several different specimens, ring and small disk specimen geometries: three types of ring specimens, i.e., 38.1 mm outside diameter (OD) × 27.9 mm inside diameter (ID) × 6.4 mm thickness; 19.1 mm OD × 8.9 mm ID × 6.4 mm thick, and 6.4 mm OD × 3.1 mm ID × 6.4 mm thick and a 2 mm thick disc with 6.4 mm diameter. The smallest ring and the small disk specimens were chosen for irradiation.

2.2. Measurement of the properties

Pre- and post-irradiation brittle ring specimens were evaluated using the eddy-current technique to measure the electrical resistivity [9], and an ultrasonic technique to measure the elastic constant [10]. For all of the pre- and post-irradiation specimens their ultrasonic velocity and electrical resistivity were measured by connecting the eddy-current or ultra-sonic detectors to the specimen side surface. All the specimens were weighted so that individual density and elastic moduli calculations could be made. Thermal diffusivity of the smallest ring specimens (6.4 mm OD × 3.1 mm ID × 6.4 mm thick) was measured at elevated temperatures ranging from room temperature to 1200°C using the thermal-pulse technique [11]. From the diffusivity data the thermal conductivity (K) was calculated using the following formula [12]:

$$K = \alpha \rho C_p \quad (\mathrm{W/(m\,K)}),$$

where α is the thermal diffusivity in m^2/s, ρ is the specimen density in kg/m^3, and C_p is the heat capacity (J/(kg K)). Values for the specific heat of unirradiated graphite published in the literature [11] are used here.

Irradiated specimens are annealed at 600, 800, 1000 and 1200°C for 8 h in vacuum to measure the thermal recovery of the properties, that is, the dimensional change, fracture strength and thermal conductivity of irradiated specimens [7,8].

2.3. Strength test

Brittle ring tests were performed according to ASTM Standard C608 using the pre- and post-irradiation brittle specimens. Brittle ring fracture load was measured and fracture strength, S, was calculated using the following formula [13]:

$$S = 6K_t P(D_2 + D_1)/\pi h(D_2 - D_1)^2,$$

where K_t is the stress intensity factor [13], P is the peak load at failure (N), D_2 is the outside diameter (m), D_1 is the inner diameter (m), and h is the ring thickness (m).

2.4. Irradiation experiments

Irradiation was performed in a capsule placed in the target region of the HFIR at ORNL [14]. IG-110 graphite specimens were accommodated in the capsule along with several other grades of graphite [14]. Irradiation continued until a peak fluence of 3.8×10^{26} n/m^2 ($E > 50$ keV), or 25 dpa was attained. Irradiation temperature was controlled at 600°C by adjusting the gas composition in the annular gap between the specimens and the capsule inner wall.

3. Result and discussion

3.1. Irradiation induced volume change

It is well known that neutron irradiation initially produces significant volume shrinkage and densification of nuclear graphite materials [14–17]. The volume change, $\Delta V/V_0$ (%), of IG-110 graphite after irradiation is presented in Fig. 1 as a function of neutron fluence. In the figure, additional data from previous experiments in JMTR at low dose and in the temperature range of 600–1000°C are also shown [18]. The solid line in this figure was derived by fitting a second

Table 1
Mechanical properties of IG-110 graphite

	Bulk density (g/cm^3)	Tensile strength (MPa)	Compressive strength (MPa)	Bending strength (MPa)	Young's modulus (GPa)
IG-110	1.78	25.3	76.8	37.2	10.2

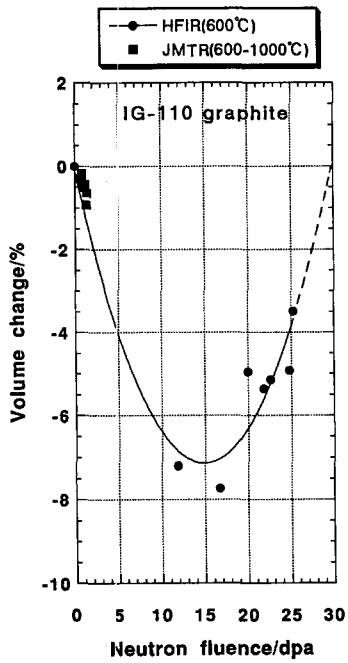

Fig. 1. Volume change for IG-110 graphite as a function of neutron fluence.

order polynomial to the data as Burchel et al. did [14]. From these data, it is clear that the volume of irradiated specimens decreases with increasing fluence until a minimum volume (maximum density) is attained. With increasing fluence further, the graphite commences volume expansion and eventually returns to its original volume. This phenomenon is called 'turnaround'. The turnaround of IG-110 graphite (at $T_{irr} = 600°C$) occurs at a fluence of about 2.3×10^{26} n/m^2 [$E > 50$ keV] (15 dpa), and $\Delta V/V_0$ is estimated to return to zero at approximately 4×10^{26} n/m^2 [$E >$ 50 keV], or 30 dpa. The volume shrinkage at turnaround

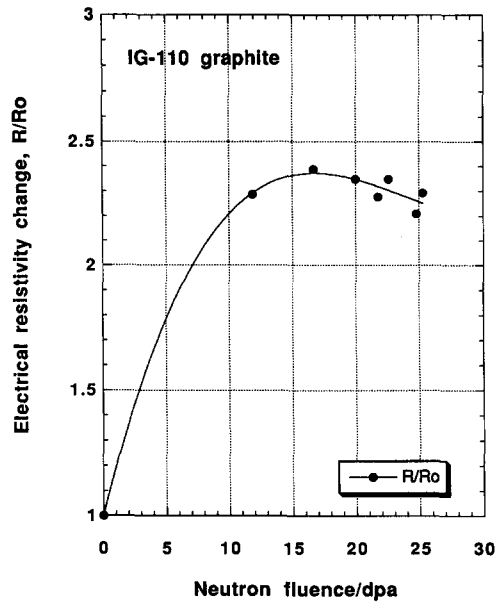

Fig. 3. Change in electrical resistivity modulus as a function of neutron fluence.

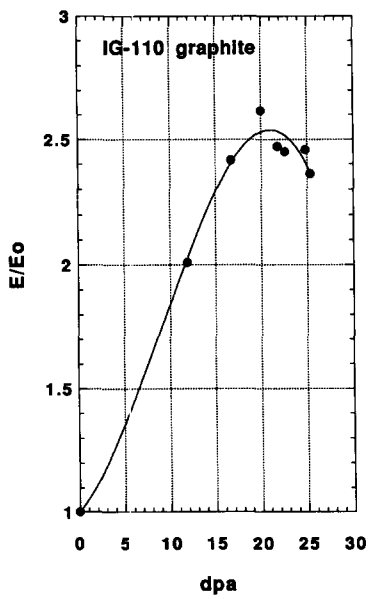

Fig. 2. Change in Young's modulus as a function of neutron fluence.

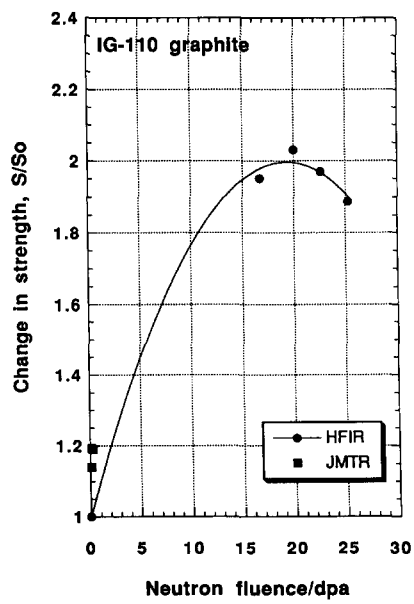

Fig. 4. Change in fracture strength as a function of neutron fluence.

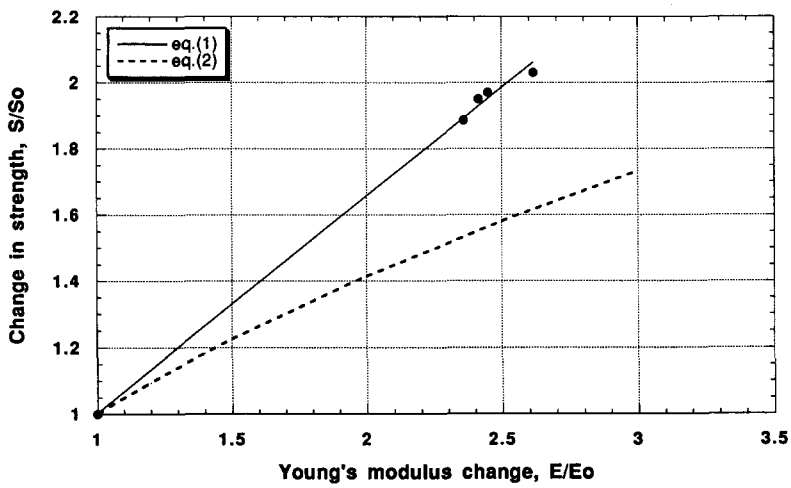

Fig. 5. The relationship between Young's modulus and fracture strength.

for IG-110 was about 7%. Recently, Burchell and Eatherly [12] reported high dose irradiation damage data for the high strength isotropic graphite, GraphNOL N3M, developed at ORNL for aerospace applications. They showed that GraphNOL irradiated at 600°C had a volume turnaround point at 21 dpa, and returned to original volume at 33 dpa. The volume shrinkage at turnaround for GraphNOL N3M was about 7.5%. Therefore, the lifetime of GraphNOL N3M graphite is longer than that of IG-110 graphite.

3.2. Irradiation induced property changes

Young's modulus and shear modulus of graphite materials increase with increasing neutron fluence due to dislocation pinning and a closure of the fine pores [14,15]. Fig. 2 shows the fractional changes in Young's modulus (E/E_0) as a function of neutron dose for IG-110 graphite. The data show that Young's modulus has a maximum at ~20 dpa, reaching the maximum value of ~2.5 times that of the pre-irradiated modulus. Beyond this maximum value, the Young's modulus decreases with increasing fluence. The deterioration of the mechanical properties can be attributed to the generation of internal porosity at high irradiation fluence, as previously reported for GraphNOL graphite [14].

The electrical resistivity of irradiated graphite materials increases due to electron scattering by interstitial carbon atoms, interstitial clusters and basal plane va-

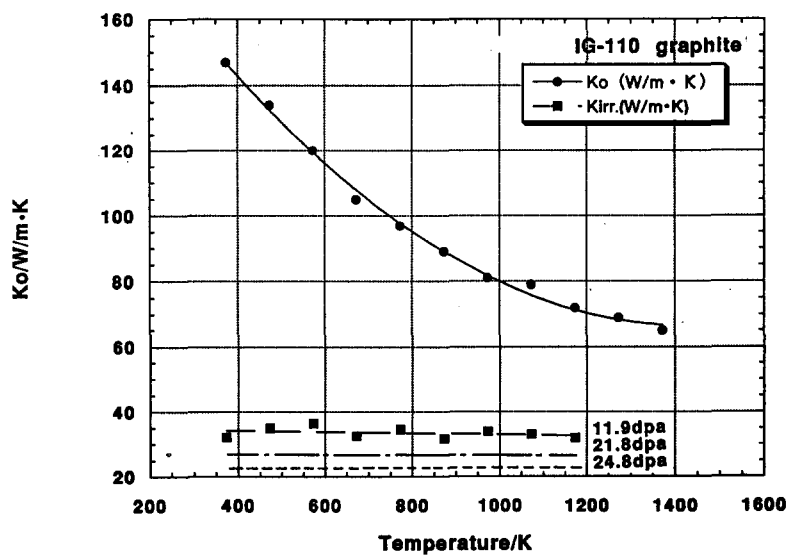

Fig. 6. Thermal conductivity irradiated specimens.

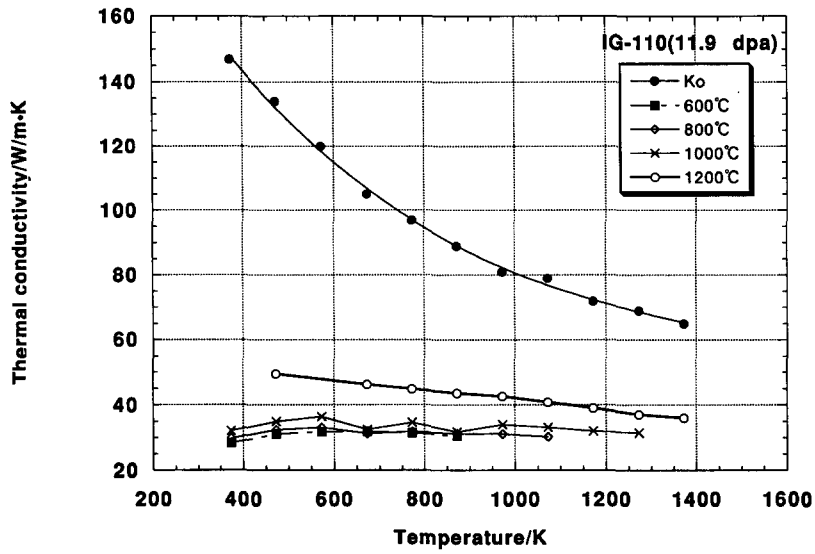

Fig. 7. Thermal conductivity of 11.9 dpa irradiated specimen after thermal annealing.

cancies induced by irradiation [19]. Fig. 3 shows the ratio of electrical resistivity R/R_0 as a function of fluence. Electrical resistivity increased by a factor of 2 over the pre-irradiated value, but only small reduction in electrical resistivity was observed with increasing neutron dose.

Fig. 4 shows the fracture strength of irradiated brittle ring specimen as a function of fluence. In this figure, irradiated ring strength data (irradiated at the temperature of 575–650°C with the dose of 0.13–0.25 dpa) obtained previously were also plotted [18]. These results also show a turnaround of fracture strength approximately at 20 dpa, which correspond to the value for the elastic modulus. The relationship between Young's modulus and fracture strength of irradiated ring specimens is shown in Fig. 5. The results demonstrated good linear correlation between Young's modulus and fracture strength, and these relation can be expressed as the following formula:

$$(S/S_0)/(E/E_0) = \text{Const.}, \quad (1)$$

where S_0, S are fracture strength of unirradiated and irradiated specimens and E_0, E are Young's modulus of unirradiated and irradiated specimens, respectively. At lower dose, strength of irradiated graphite is normally believed to be estimated by the formula [1]

$$(S/S_0)^2/(E/D_0) = \text{Const.} \quad (2)$$

However, the strength of the graphite irradiated at higher doses, such as 10–25 dpa is underestimated by Eq. (2), as shown in the figure.

Thermal conductivity of graphites [17–21] and carbon–carbon composites [7] is degraded by environmental temperature and neutron irradiation due to the scattering of phonons by thermally induced lattice vibrations and the formation of neutron irradiation induced interstitials and vacancies. Fig. 6 shows the thermal conductivity of unirradiated and irradiated IG-110 graphite ring specimens as a function of temperature for different doses. The thermal conductivity of unirradiated and irradiated graphite decreases monotonically with increasing measurement temperature and dose. The large reduction, at a dose of 11.9 dpa, from

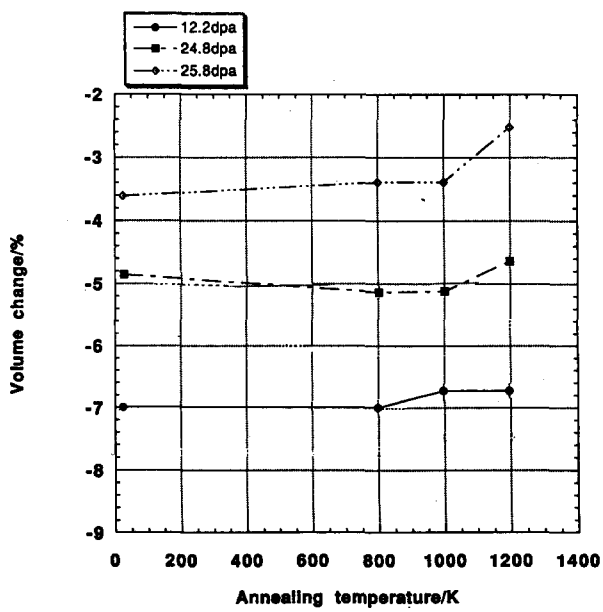

Fig. 8. Change in volume of irradiated specimens after thermal annealing.

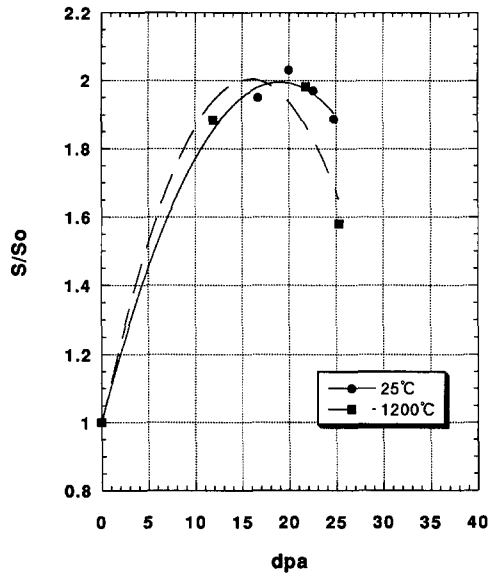

Fig. 9. Change in fracture strength of irradiated specimens after thermal annealing.

its unirradiated value of ~160 W/m K to ~30 W/m K at room temperature can be attributed to the introduction of neutron damage which acts as phonon scattering sites.

3.3. Recovery of the properties after thermal treatment

Fig. 7 shows the change of thermal conductivity after annealing at the elevated temperatures (600, 800, 1000 and 1200°C for 8 h). It is clear that the thermal conductivity has not recovered after thermal annealing at 600°C or below, but after annealing at a temperature higher than 800°C it progressively recovered as the annealing temperature increases. This type of recovery may be attributed to thermal recombination of vacancies and interstitials.

Figs. 8 and 9 show the change of volume and strength as a function of annealing temperature for the specimens irradiated to 12.2, 24.8 and 25.8 dpa. The volume and strength of irradiated specimens can be slightly recovered at 1200°C. Moreover, the fraction of volume and fracture strength recovered for the irradiated specimens was greater for the specimens irradiated to a higher dose.

4. Conclusions

A fine-grained, isotropic nuclear graphite (IG-110), manufactured from a petroleum coke, was irradiated to a peak fluence of 3.8×10^{26} n/m^2 ($E > 50$ keV), or 25 dpa at 600°C. Irradiation damage and thermal recovery of the properties of this graphite were evaluated.

Turnaround of volume change and other properties was clearly observed at ~15 to 20 dpa, with the return to original volume estimated as being ~30 dpa.

Thermal conductivity for heavily irradiated specimens decreased from an unirradiated value of ~160 W/m K to approximately 30 W/m K at room temperature. The dependence of the change in thermal conductivity on fluence was also observed.

Recovery of volume, fracture strength and thermal conductivity occurred due to thermal annealing. The recovery of thermal conductivity was greatly enhanced with increasing annealing temperature above the irradiated temperature. The recoverable fractions of volume and of fracture strength are larger for the specimens irradiated a higher dose.

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References

[1] S. Sato, T. Arai, H. Airai et al., Japan Atomic Energy Research Institute Report, JAERI Memo 02-135 (1990).
[2] S. Sato, H. Awaji et al., Nucl. Eng. Des. 61 (1980) 383.
[3] T. Tsuzuki and M.H. Saito, Chemistry and Physics of Carbon, Vol. 4 (Marcel Dekker, New York, 1968) p. 185.
[4] T. Oku, M. Eto and S. Ishiyama, J. Nucl. Mater. 172 (1990) 77.
[5] H. Ugachi, T. Oku S. Ishiyama and M. Eto, Nihon Kikai Gakkai Ronbunshu, in Japanese, to be published.
[6] B.T. Kelly, Prog. Nucl. Energy 2 (1978) 219.
[7] T.D. Burchell, W.P. Eatherly and J.P. Strazak, Effects of Radiation on Materials, ASTM-STP 1175 (1994) 1266.
[8] T.D. Burchell and W.P. Eatherly, Proc. Int. Conf. on Carbon, Buffalo, 1993 p. 135.
[9] C.R. Kennedy, DOE/ORNL Report DOE-HTGR-88511, ORNL/TM-11666 (1990).
[10] C.R. Kennedy, Elastic constants of graphite, Proc. 13th Biennial Conf. on Carbon Extended Abstracts and Program, 1977, Irvine, California, p. 437.
[11] H. Mazuo, Netsu Sokutei 17 (1) (1990) 2, in Japanese.
[12] ASTM Standard C608 (ASTM, Philadelphia, 1992).
[13] S.P. Timoshenko and J.N. Goodier, Theory of Elasticity (McGraw–Hill, New York, 1970) p. 97.

[14] T.D. Burchell and W.P. Eatherly, J. Nucl. Mater. 179–181 (1991) 205.
[15] W.N. Reynolds, Chemistry and Physics of Carbon, Vol. 2 (Marcel Dekker, New York, 1966) p. 121.
[16] J.W.H. Simmons, Radiation damage in Graphite (Pergamon, Oxford, 1965) p. 1064.
[17] G.B. Engle and W.P. Eatherly, High Temp.–High Press. 4 (1972) 119.
[18] S. Ishiyama, T. Oku, K. Fujisaki and M. Eto, J. At. Energy Soc. Jpn. 29 (1987) 1014, in Japanese.
[19] B.T. Kelly, Physics of Graphite (Applied Science, London, 1981) p. 167.
[20] B.T. Kelly, The thermal Conductivity of Graphite, in: Chemistry and Physics of Carbon, Vol. 5 (Marcel Dekker, New York, 1969) p. 119.
[21] T. Maruyama and H. Herayama, J. Nucl. Mater. 195 (1992) 44.