On the Thermal Conductivity Change of Matrix Graphite Materials after Neutron Irradiation

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1. Introduction

In developing the matrix graphite material to be used for the HTGR fuel element which should contain fuel kernel coated with various pyrolytic carbon and silicon carbide layers, it is essential to understand the behavior of the selected graphite matrix material during neutron irradiation, not only in the integral form of fuel element with coated fuel particles but the material without fuel materials in order to analyze the response of the material against the neutron irradiation.

The fuel element for an HTGR is in general fabricated by mixing coated fuel particles with matrix graphite powder and forming them into either pebble type or cylindrical type compacts depending on their use in different HTGR cores. The selected graphite matrix by Korean HTGR Program is based on the so-called A3-3, which has been developed within German and Chinese HTGR development programs and utilized for their reactor operations, and the fabrication processes relevant to the fuel pebbles and compacts are described in detail in a number of literatures. [1]

KAERI has performed its first HTR fuel irradiation test utilizing its Hanaro research reactor from August 2013 to March 2014 for 132 EFPD. A detailed description of the irradiation test has been presented. [2] In this test, together with the fuel compact specimens, 4 sets of graphite specimens were irradiated. 2 test rods were encapsulated in the test capsule, of which one rod was loaded with 9 fuel compact specimens and the other rod with 5 fuel compacts and 4 sets of graphite specimens. One set of graphite specimen consists of a pair of 1 matrix graphite disc and 1 IG-110 structural graphite disc.

After the irradiation test, a series of post irradiation examinations (PIEs) were carried out, in order to understand the irradiation behavior and performance of the coated particle fuel as well as the variation of the properties of A3-3 matrix graphite and IG-110 structural graphite. In this study, the change of thermal conductivity of A3-3 matrix graphite material due to the neutron irradiation was investigated and evaluated and compared with that of IG-110 structural graphite material.

2. Experimental

2.1 Materials used and preparation of matrix graphite compact samples for irradiation

Natural graphite powder and electro-graphite powder, supplied by Graphit Kropfmühl AG, and SGL, Germany, respectively, were used. A phenolic resin was used for a binder material. The mixing ratio of the raw materials is; natural graphite powder : artificial graphite powder : phenolic resin = 64 : 16 : 20 (in wt%).

In order to prepare the graphite powder mixture incorporating the phenolic resin, mixing of the natural graphite and artificial graphite powders was first carried out using a V-mixer for 1 hr at 100 rpm. And then, kneading of the powder mixture and binder solution, pre-prepared by dissolving phenolic resin in methanol to get an appropriate viscosity of the binder solution, was conducted for 30 min using a laboratory kneader, followed by the forced sieving of the kneaded bulk to make matrix graphite cakes and drying for a total of 15 hrs at 373K. Finally, milling of the prepared matrix graphite cake was carried out using an attrition mill at 280 rpm for 8 hrs to obtain the matrix graphite powder. To prepare the green matrix graphite disc samples, the matrix powder prepared was compacted in a steel mold of 8.05mm in diameter using a uni-axial single-acting laboratory hand press. The compacting pressure applied was 1.0 ton/cm^2 and the compacting temperatures was 373K (±2K). The pressure holding time was 2 min. 30 secs. Compact samples were carbonized at 1173K for 38 hrs in a nitrogen atmosphere and finally heat-treated at 2073K for 2 hrs in vacuum. The dimension of the prepared matrix graphite disc of the irradiation test specimens was 7.98 (±0.01) mm in diameter, 5.06 (±0.01) mm in thickness. The weight was 0,449 (±0.005) g and the bulk density measured by dimension was 1.77 (±0.01) g/cm^3.

The IG-110 graphite specimens were machined from a small block to the same dimension as that of matrix graphite specimens. The IG-110 blocks were purchased from ToyoTanso Co., Japan. The dimension of the machined IG-110 graphite disc was 7.97 (±0.01) mm in diameter, 5.00 (±0.02) mm in thickness. The average

weight was 0,441 (±0.003)g and the bulk density measured by dimension was 1.77 (±0.01) g/cm^3.

2.2. Irradiation conditions in Hanaro reactor [2]

Fig. 1 shows a schematic construction layout of encapsulated two fuel test rods in the irradiation capsule, which was a non-instrumented device. The fuel compact and graphite specimens were loaded in graphite sleeves, clad in the stainless steel 316L tubes and end-cap welded. The cladding tubes are approximately 16 mm in diameter and 150 mm in height including the plenum space. The temperature of the fuel test rod specimens was controlled by filling mixtures of He and Ne gases when fabricating fuel test rods: a mixture of 30% He and 70% Ne for the fuel rod 1 and a mixture of 10% He and 90% Ne for the fuel rod 2, respectively.

The average peak temperature before irradiation test was estimated about 1045 K under a mixed gas atmosphere of 10% He and 90% Ne in the fuel test rod 2 which contained the graphite specimens, and axial temperature distribution as shown in Fig. 2.

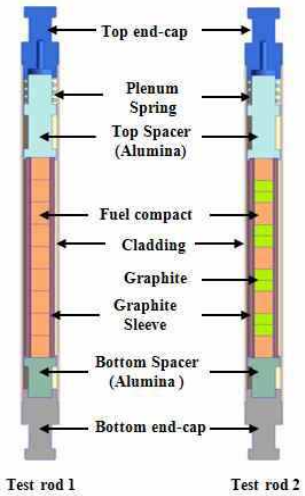

Fig. 1. Schematic construction layout of the 2 fuel rod specimens in the test capsule [2]

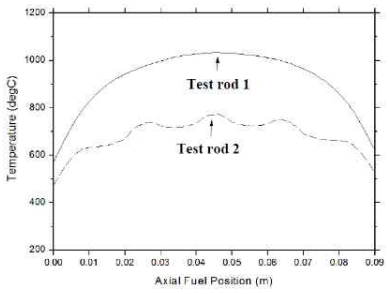

Fig. 2. The estimated axial temperature distribution of the fuel test rod 1 and 2 before irradiation test. Fuel test rod 2 contained graphite specimens which were sandwiched between the fuel compact specimens, visible in the temperature curve [2].

The maximum power of fuel compact in the fuel test rod 2 was 50 W, and the maximum power of particle is 197.5 mW. The maximum discharged burn-up was about 35,698 MWd/MtU (3.81 FIMA (Fissions per Initial Metal Atom)). The maximum fluence of graphite specimen was estimated to be 2.99×10^{24} n/m^2 (E > 0.18 MeV). The temperatures calculated for the 4 sets of the graphite specimens ranged, along the different axial position, from 783 to 853 K on re-analyses of the filled gas of the fuel test rods after the irradiation test. [3]

2.3. Graphite specimen measurement methods

The dimensions of graphite specimens were measured using digimatic micrometers to obtain the bulk volume and dimensional variations. The thermal diffusivity of the graphite specimens before and after irradiation test was measured by the laser-flash method using Netzsch LFA 427, Germany, and the thermal conductivity (λ) of the compact samples was calculated using the following equation:

$$\lambda = \alpha \text{ x } \rho \text{ x } C_p \qquad (1)$$

where, α is the thermal diffusivity, ρ the density, and C_p the specific heat of graphite specimens. The specific heat of the un-irradiated matrix graphite specimens was determined by use of a DSC apparatus Netzsch DSC 200 F3, Germany. For the specific heat of the irradiated graphite specimens, various literature data were reviewed for the evaluation (see 3.1.) and data were appropriately selected to be used in this study.

3. Results and Discussions

3.1. Evaluation of the heat capacity of the irradiated graphite specimens

In the determination of thermal conductivity derived from the thermal diffusivity measurement of a specimen by use of the laser flash method, it is inevitable to measure or at least to know the specific heat of the specimens as well as its density as can be shown in Eqn. (1). In this study, the specific heat of the un-irradiated matrix graphite specimens was determined by use of a DSC apparatus Netzsch DSC 200 F3, Germany. However, due to a matter of radiation protection, the specific heats of the irradiated graphite specimens were not measured. Instead, the selected data on the specific heat of graphite available in the literature were evaluated for use in this study [4,5,6] including the result obtained from the measurement of the un-irradiated matrix graphite specimen prepared by KAERI following the method described in 2.1.

Fig. 3 shows a comparison of the variation of the specific heat as a function of the temperature for the 4 different data: those from POCO for graphite materials

[4] temperatures partly taken (250 ~ 1500 K) and plotted; those from ASTM C781 for graphite materials [5], temperatures partly taken (300 ~ 1500 k) and plotted; data from the work by C.H. Wu et al. [6] and plotted for their un-irradiated S1260 graphite specimen as well as irradiated specimen, including KAERI's own data for matrix graphite specimen. It should be mentioned that the irradiation of the S1260 graphite specimen was carried out at a dose of 14.4 – 30 dpa g and temperature of 693 – 813 K.

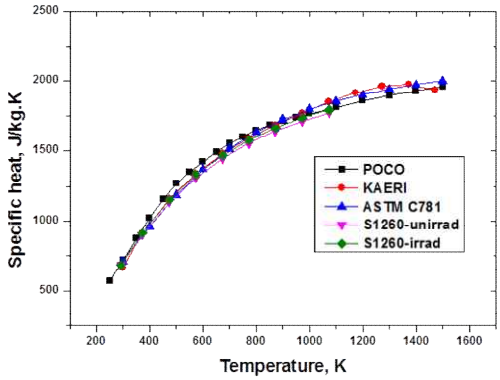

Fig. 3. A comparison of the variations of specific heat as a function of the temperature among POCO [4], ASTM C781 [5], C.H. Wu et al. [6] and KAERI data

As shown in this figure, the variations of the specific heat of all the graphite specimens are well agreed, irrespectively of the difference in specimens (graphite and matrix graphite, and irradiated and un-irradiated). The difference of the values for the un-irradiate and irradiated S1260 graphite is less than 2%. [6] This implies that it should be reasonable that for both structural graphite and fuel matrix graphite, and even for the neuron-irradiated graphite, any of these specific heat data set be used in the calculation of the thermal conductivity. Therefore, in this study, for the comparison of the thermal conductivity, POCO data are used to calculate the thermal conductivity of the IG-110 structural graphite for both un-irradiated and irradiated specimens; and for the calculation of the thermal conductivity of the matrix graphite of both un-irradiated and irradiated specimens, the specific heat data obtained from the un-irradiated matrix graphite specific heat measured by KAERI.

3.2. Variations of thermal conductivity of A3-3 matrix graphite and IG-110

The variation of thermal conductivity of the un-irradiated A3-3 matrix graphite prepared by a un-axial pressing shows an anisotropic behavior; those along the radial direction (perpendicular to the pressing direction) shows fairly high (about 6 to 3 times depending on temperature) compared with those in the axial direction (parallel to the pressing direction) [7]. Fig. 4 is reproduced from [7] to show the variations of thermal conductivities of uni-axially pressed un-irradiated A3-3 matrix graphite compact specimens of different densities along the axial and radial directions to the pressing direction and compared with the published data from NUKEM and that of IG-110 measured by KAERI. In the following, the variation of the thermal conductivities of A3-3 matrix graphite and IG-110 graphite upon neutron irradiation is discussed and compared.

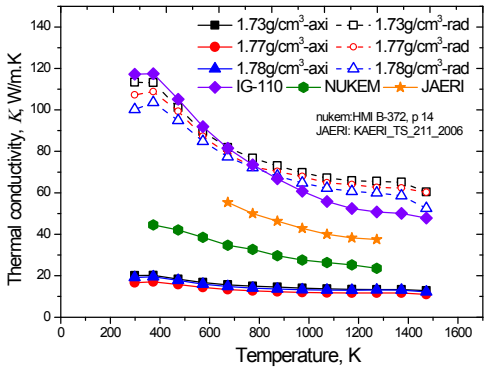

Fig. 4. Variations of thermal conductivities of un-irradiated matrix graphite prepared by uni-axially pressed compact in the axial and radial directions and comparison with other published data [7]

3.2.1. Variation of thermal conductivity of A3-3 matrix graphite

Fig. 5 shows variations of thermal conductivity of A3-3 matrix graphite specimens as a function of temperature up to 1473 K before and after irradiation, on the perpendicular and parallel cross sections to the pressing direction.

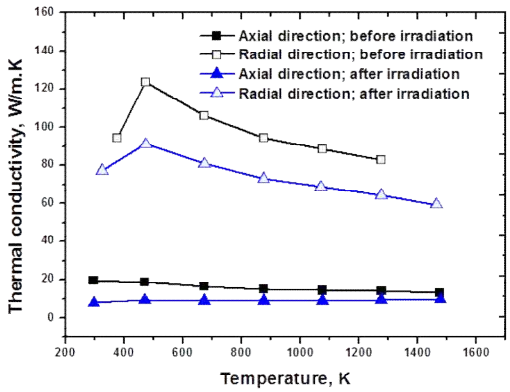

Fig. 5. Variations of thermal conductivity of A3-3 matrix graphite specimens as a function of temperature before and after irradiation

After irradiation, the thermal conductivity decreased on both directions. On the radial direction, the tendency of variation upon temperature is similar to that of un-

irradiated specimen, i.e., decreasing as the temperature increases. Meanwhile, on the axial direction, the thermal conductivity of the un-irradiated specimen shows a slight decrease and that of irradiated specimen is nearly constant as the temperature increases, with a value of 10.2 (±0.4) W/m.K.

In the German irradiation experiments with A3-27 matrix graphite specimens [8], the thermal conductivity of the un-irradiated specimen shows a decrease and that of irradiated specimen is nearly constant as the temperature increases, as shown in Fig. 6. This is a similar observation to that with the variation of thermal conductivity of A3-3 specimen on the axial direction in this study. The German specimens were irradiated at 698 K with a neutron fluence of 1.4 x 10^{25} m^{-2}. The German A3-27 specimens were prepared by use of a special silicon rubber mold during room temperature pressing. Therefore, the specimens would be considered as quasi-isotropic.

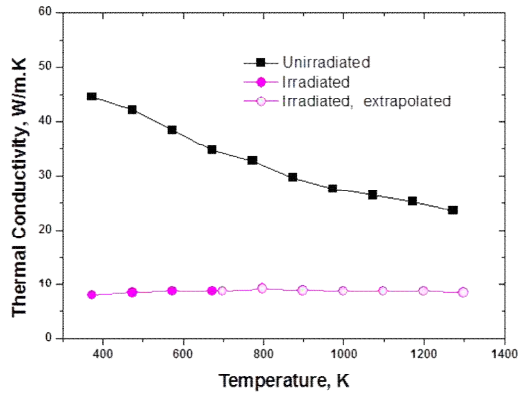

Fig. 6. Variations of thermal conductivity of the German A3-27 matrix graphite specimens as a function of temperature before and after irradiation. Re-plotted from the data partly taken from [8]

3.2.2. Variation of thermal conductivity of IG-110 graphite

Fig. 7 shows variations of thermal conductivity of IG-110 structural graphite specimens as a function of temperature up to 1473 K before and after irradiation. Before irradiation, this graphite specimen was considered as isotropic and the measurement of the thermal diffusivity was carried out on an arbitrary direction and the data is plotted on Fig. 6 [7]. The thermal conductivity of the irradiated IG-110 was considerably decreased compared with that of un-irradiated specimens, as can be seen on the Fig. 7. The difference of the thermal conductivity of un-irradiated and irradiated IG-110 graphite specimens is much larger than that of un-irradiated and irradiated A3-3 matrix graphite specimens, and the variation of the thermal conductivity of the irradiated IG-110 graphite as a function of temperature is nearly constant with a value of about 44.1 (±1.7) W/m.K, showing a similar behavior to that observed with the irradiated A3-3 matrix graphite along the axial direction, though with a different value (10.2 (±0.4) W/m.K).

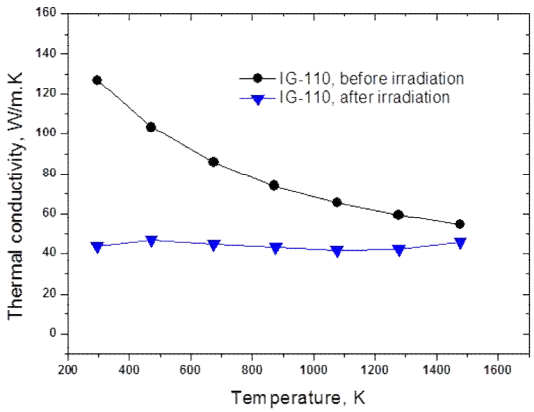

Fig. 7. Variations of thermal conductivity of the IG-110 graphite specimens as a function of temperature before and after irradiation

4. Summary

In this work, the variations of the thermal conductivity of the A3-3 matrix graphite after neutron irradiation is discussed as well as of the IG-110 graphite for comparison. Neutron irradiation of the graphite specimens was carried out as a part of the first irradiation test of KAERI's coated particle fuel specimens by use of Hanaro research reactor. This work can be summarized as follows:

1) In the evaluation of the specific heat of the graphite materials, various literature data were used and the variations of the specific heat data of all the graphite specimens are observed well agreed, irrespectively of the difference in specimens (graphite and matrix graphite and irradiated and un-irradiated). The difference of the values for the un-irradiate and irradiated S1260 graphite is less than 2%.
2) This implies that it should be reasonable that for both structural graphite and fuel matrix graphite, and even for the neuron-irradiated graphite, any of these specific heat data set be used in the calculation of the thermal conductivity.
3) For the irradiated A3-3 matrix graphite specimens, the thermal conductivity decreased on both directions. On the radial direction, the tendency of variation upon temperature is similar to that of un-irradiated specimen, i.e., decreasing as the temperature increases. Meanwhile, on the axial direction, the thermal conductivity of the un-irradiated specimen shows a slight decrease and that of irradiated specimen is nearly constant as the temperature increases, with a value of 10.2 (±0.4) W/m.K.
4) In the German irradiation experiments with A3-27 matrix graphite specimens, the thermal conductivity

of the un-irradiated specimen shows a decrease and that of irradiated specimen is nearly constant as the temperature increases. This is a similar observation to that with the variation of thermal conductivity of A3-3 specimen on the axial direction in this study.

5) The thermal conductivity of the irradiated IG-110 was considerably decreased compared with that of un-irradiated specimens The difference of the thermal conductivity of un-irradiated and irradiated IG-110 graphite specimens is much larger than that of un-irradiated and irradiated A3-3 matrix graphite specimens.
6) The variation of the thermal conductivity of the irradiated IG-110 graphite as a function of temperature is nearly constant with a value of about 44.1 (±1.7) W/m.K, showing a similar behavior to that observed with the irradiated A3-3 matrix graphite along the axial direction, though with a different value (10.2 (±0.4) W/m.K).

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