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EFFECT OF THERMAL ANNEALING ON PROPERTY CHANGES OF NEUTRON-IRRADIATED NON-GRAPHITIZED CARBON MATERIALS AND NUCLEAR GRAPHITE

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Effect of Thermal Annealing on Property Changes of Neutron-Irradiated Non-Graphitized Carbon Materials and Nuclear Graphite

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Changes in dimension of non-graphitized carbon materials and nuclear graphite, and the bulk density, electrical resistivity, Young's modulus and thermal expansivity of nuclear graphite were studied after neutron irradiation at 1128-1483 K and the successive thermal annealing up to 2573 K. Carbon materials showed larger and anisotropic dimensional shrinkage than that of nuclear graphite after the irradiation. The irradiation-induced dimensional shrinkage of carbon materials decreased during annealing at temperatures from 1773 to 2023 K, followed by a slight increase at higher temperatures. On the other hand, the irradiated nuclear graphite hardly showed the changes in length, density and thermal expansivity under the thermal annealing, but the electrical resistivity and Young's modulus showed a gradual decrease with ananealing temperature. It has been clarified that there exists significant difference in the effect of thermal annealing on irradiation-induced dimensional shrinkage between graphitized nuclear graphite and non-graphitized carbon materials.

Keywords; Carbon, Nuclear Graphite, Neutron Irradiation, Thermal Annealing, Density, Electrical Resistivity, Young's Modulus, Thermal Expansivity, Dimensional Schrinkage

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中性子照射非晶質炭素及び黒鉛材料の特性変化に及ぼす熱処理の影響

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（1991年5月8日受理）

非晶質炭素及び原子炉用黒鉛材料を1128－1483 Kで中性子照射した後，2573 Kまでの各温度で熱処理して，寸法，密度，電気比抵抗，ヤング率，熱膨張率の変化を調べた。炭素材料は原子炉用黒鉛材料に比較して照射によってより大きくて，また異方的な寸法収縮挙動を示した。この寸法収縮量は，1773 Kから2023 Kまでの熱処理温度で減少したが，それ以上の温度では僅かに増加した。これに対して，照射した原子炉用黒鉛材料を熱処理した場合は，寸法，密度，熱膨張率は殆ど変化しなかったが，電気比抵抗やヤング率は熱処理温度が高くなるにしたがって次第に減少した。これらの実験事実から，非晶質炭素材料と原子炉用黒鉛材料の寸法変化挙動には著しい違いがあることがわかった。

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1. Introduction

The effect of neutron irradiation at high temperatures on the properties of nuclear graphite has been extensively studied because of the development of graphite moderated reactors, since Wigner predicted property changes of nuclear materials by neutron irradiation[1]. A lot of data on nuclear graphites have been published, whereas a few works have been done on carbon materials. The irradiation-induced property changes depend markedly on the kinds of graphite and also on the changes in crystallites depending on the degree of graphitization, porosity and binder. The property changes in crystallites have been studied by using annealed pyrolytic graphite and the effect of irradiation on dimension, thermal expansivity, lattice parameters have become clear[2-6]. Properties of binder are significantly changed due to irradiation as well, and the changes are sensitive to binder coke content[7,8]. Based on the experimental results, a concept for irradiation-induced graphitization of poorly ordered binder coke has been proposed for neutron-irradiated carbon materials[8-10].

The kinds and concentration of irradiation-induced defects which have significant effects on the property changes of crystallites, binder and porosity, depend on irradiation conditions such as temperature and neutron fluence. Irradiation at high temperatures produces more complicated defects than those produced by irradiation at low temperatures. The defects are converted into other forms by thermal annealing at high temperatures. This means that the effect of irradiation on the property changes strongly depend on the usage temperature of the materials in a reactor. Therefore, from the viewpoint of practical use of a graphite material in a reactor it is necessary to obtain information on whether the changes in the properties of irradiated graphite might happen due to variation of irradiation temperature.

In the present report the effect of irradiation and the successive thermal annealing on the property changes of nuclear graphite and non-graphitized carbon materials are described in relation to the evaluation of the changes in the irradiation effects such as dimensional changes, electrical resistivity and Young's modulus of materials for use in a reactor.

2. Experimental procedure

2.1 Sample

Two nuclear graphite materials, IG-110 and H451, and two carbon materials, ASR-ORB and ASR-1RB, were used in the present study. The fine-grained isotropic graphite IG-110, and the near-isotropic graphite H451, were made of petroleum coke. The carbon materials, ASR-ORB and ASR-1RB, were made of coal-tar pitch by means of molding. The impregnation of binder was done once or twice, respectively, therefore, the bulk density of ASR-1RB is larger than that of ASR-ORB. The materials IG-110 and ASR-ORB are the candidate materials for use in the HTTR (High Temperature Engineering Test Reactor). The original properties of the samples are given in Table 1. Although the nominal baking temperature of ASR-ORB and ASR-1RB carbons is 1373 K, the samples were heat-treated at 1373 K for two hours prior to irradiation in order to remove obscurity of the baking temperatures.

Specimens with the sizes, 10×10×25 mm, were machined from logs for the measurements of length, volume and bulk density. Cylindrical specimens with the sizes, 5 mm in diameter and 75 and/or 20 mm in length, were also machined for the measurements of electrical resistivity, Young's modulus and thermal expansivity.

2.2 Irradiation

Specimens were irradiated at 1128-1483 K in the JMTR (Japan Materials Testing Reactor) up to a neutron fluence of about 4×10^{25} n/m^2 (E > 29fJ). The neutron fluence was obtained from the reaction ^{54}Fe (n,p) ^{56}Mn, and the irradiation temperatures were monitored and controlled by using WRe/5-26 thermocouples during irradiation.

2.3 Thermal annealing and property measurements

Measurements of length, volume, bulk density, electrical resistivity and Young's modulus were carried out at room temperature. A high accuracy micrometer was used for measuring the lengths of the specimens, and the bulk density was obtained from the measured dimensions and weight of the specimens. Electrical resistivity was

measured by a potential-drop method. Young's modulus was obtained by combining measurements of the transmission time of a 100 kHz ultrasonic wave propagated through the specimen with the data for bulk density. Measurement on thermal expansivity was done in a vacuum of about 0.13 Pa from room temperature to 1173 K by using a dilatometer with a fuzed quartz as a standard sample.

First, the properties were measured before and after irradiation, and then the irradiated specimens were thermally annealed at elevated temperatures up to 2573 K, where the specimens were kept at each annealing temperature for one hour in an atmosphere of flowing nitrogen gas. The thermal annealing at each temperature and the measurements were repeated up to 2573 K.

3. Results and discussion

3.1 Irradiation effects

In Fig. 1 the irradiation-induced dimensional changes of the samples IG-110, H451, ASR-ORB, and ASR-1RB are shown as a function of neutron fluence. The data are plotted for the samples irradiated at 1128-1413 K. After irradiation length shrinkages were observed for all samples. The carbon materials, ASR-ORB and ASR-1RB, showed higher shrinkage rate in the perpendicular direction to the molding direction, hereafter called with-grain (W.G.), than the shrinkage rate of the nuclear graphites, IG-110 and H451. However, there was not so much difference in the other direction. The samples irradiated at higher temperatures showed much larger dimensional shrinkage rates as well.

Maximum irradiation temperature of the samples, ASR-ORB and ASR-1RB, was almost the same as the baking temperature 1373 K. It is, therefore, considered that the length shrinkage might be caused only by irradiation, though it is known that carbon material mostly shrinks at an early stage of heat-treament and its saturation is observed in the following heat-treatment for the samples heat-treated at the temperatures being close to the present irradiation temperature[11].

Regarding with the effect of binder contents, the sample ASR-1RB containing more binder showed larger anisotropic shrinkage rate than that of ASR-ORB carbon. This suggests that the irradiation induced

shrinkage rate depends on the amount of non-graphitized materials contained, and the irradiation effect is similar to the results reported in the literature[8].

In Fig. 2 irradiation-induced volume changes are shown for the four materials. The carbon materials showed a little larger volume contration than those of the nuclear graphites.

The experimental results indicate that non-graphitized carbon material shows marked anisotropic dimensional shrinkage due to irradiation, however volume changes seem to be not dependent on whether the materials are graphitized or not.

3.2 Thermal annealing effects

Changes in the lengths of irradiated and as-received ASR-ORB and ASR-1RB carbons are shown in Fig. 3 and Fig. 4 as a function of annealing temperature. The irradiation temperatures were 1243-1413 K. The irradiation-induced dimensional shrinkage decreased in the range of annealing temperature 1773-2023 K, followed by a slight increase up to 2573 K. On the other hand, the lengths of the as-received samples expanded with annealing temperature, showing the similar tendency for both the directions, with-grain (W.G.) and against-grain (A.G.) directions.

The expansions in the temperature range 1773-2023 K were smaller than those of the irradiated samples. The marked difference between the length changes of the irradiated and unirradiated samples was observed above the annealing temperature of 2023 K; the irradiation-induced length shrinkage hardly recovered above the temperature, however the length of the as-received samples gradually expanded. The length change of the irradiated samples at the high annealing temperatures suggests that stable defects were formed by annealing up to 2023 K and no subsequent structural change occurred by the successive thermal annealing at higher temperatures.

Figure 5 shows the effect of thermal annealing on the irradiation-induced length shrinkage for the nuclear graphites irraadiated at 1403-1483 K[12]. Dimensional shrinkage keeps almost constant over the whole range of annealing temperatures up to 2573 K. The results are very different from those of the carbon materials described above.

Henson et al.[13] analyzed the changes in lattice parameter and

dimensional changes of graphite materials irradiated between 573 and 1623 K. Their results show that interstitials in dislocation loops, vacancy loops and vacancy lines play an important role at higher irradiation temperatures. However, the concentration of free vacancies fall off with increasing irradiation temperature. Based on their analysis, the present experimental results lead to suggestion that the three kinds of defects such as interstitial loops, vacancy loops and vacancy lines except for free vacancy hardly recovered by thermal annealing up to 2573 K. However, as shown in Fig. 6 and Fig. 7, the electrical resistivity and Young's modulus showed a gradual decrease with annealing temperature. The results indicate that free vacancy plays an important role on the changes in electricla resistivity and Young's modulus by thermal annealing. Also their results suggest that the large defects such as interstitial loops, vacancy loops and vacancy lines intrinsically do not cause the change in lattice parameter of crystallites, though the height of crystallites might be changed. This is related to the results on thermal expansivity shown in Fig. 8, showing a slight change with annealing temperature to about 2273 K. This is very similar to the previous results on the effect of thermal annealing on neutron-irradiated pyrolytic graphite[14], except for the decrease at higher annealing temperatures.

In Fig. 9 and Fig. 10 the volume and bulk density changes of ASR-ORB and ASR-1RB carbons are shown as a function of annealing temperature. The volume changes did not occur up to 1773 K, followed by an increase at the successive thermal annealing at higher temperatures. The volume of the as-received samples showed a slight increase with temperature, however the irradiated sample showed a rapid increase in the temperature range 1773-2023 K, showing almost constant in the successive higher annealing temperature range. The density change of the as-received ASR-1RB was a little larger than that of ASR-ORB, showing the dependence on the fraction of non-graphitized component contained in the material.

Figure 11 shows the changes in volume and bulk density of the nuclear graphites as a function of annealing temperature, where a slight recovery was observed for both samples.

As shown in Fig. 3, Fig. 4, Fig. 9 and Fig. 10, the changes in length, volume and bulk density of the irradiated carbon materials with annealing temperature were observed. However the irradiated

nuclear graphites hardly showed the changes in length, volume and density as in Fig. 5 and Fig. 11. And the as-received carbon materials showed different changes with annealing temperature compared with irradiated ones as shown in Fig. 3 and Fig. 4. It is known that the three-dimensional structure of crystallites is gradually developed with heat-treatment at elevated temperatures in the case of non-irradiated graphitizable carbon material such as ASR-ORB and ASR-1RB in the present experiment. And lattice parameters in the c- and a-axes of crystallites become smaller together with the expansion of crystallites in the c- and a- directions.

As shown in Fig. 1 the irradiation-induced dimensional shrinkage of the as-received carbon materials are larger than those of the graphitized nuclear graphites. This is considered to be owing to the improvement of orientation of crystallite, namely irradiation-induced graphitization[8-10]. As shown in Fig. 3 and Fig. 4 the length of the as-received carbon materials expand monotonously with heat-treatment above 1773 K. It is, therefore, considered that for non-irradiated carbon materials the three-dimensional strcture is gradually formed in the process of graphitization with the progressive improvement of the initially defective structure and also crystallites are preferentially orientated by thermal annealing. On the other hand, in the case of the irradiated carbon materials the formation of the three-dimensional structure and preferential orientation of crystallites might be supressed owing to the shrinkage of crystallites and subsequent graphitization due to irradiation, and the three-dimensional structure is hardly developed furthermore by thermal annealing. These results also suggest that non-graphitized binder contained in the materials together with graphitized component play an important role on the irradiation-induced changes in length, volume and bulk density of the carbon materials.

One of the most useful results in the present experiment for a graphite-moderated reactor is that there exists no marked annealing effects on the changes in dimension, volume, bulk density and thermal expansivity, and the irradiation-induced property changes are stable under an unexpected rapid temperature rise of graphite material.

Although the carbon materials showed a significant different recovery stage on dimensional changes compared with those of the nuclear graphite, it might happen that some irradiation-induced

structural changes were caused for the non-graphitized carbon materials. This is one of the subjects to be studied in the future.

4. Summary

The experimental results and discussion on the present study are summarized as follows:

(1) The carbon materials showed larger length shrinkage and anisotropic change than those of the nuclear graphite after the irradiation. However, the changes in volume and bulk density were not so much different between the carbon materials and the nuclear graphite.

(2) Irradiation-induced dimensional shrinkage of the carbon materials decreased in the annealing temperature range 1773-2023 K, followed by a slight incrrase up to 2573 K. However the length of the as-received carbon materials expanded monotonically with annealing temperature.

(3) Irradiated nuclear graphites hardly showed the changes in length and density by thermal annealing up to 2573 K. However, thermal expansivity decreased at higher annealing temperatures.

(4) Changes in the bulk density of the irradiated carbon materials were not observed up to 1773 K, followed by a decrease at the successive higher annealing temperatures. On the other hand, the as-received carbon materials showed a gradual decrease in bulk density with annealing temperature.

(5) Electrical resistivity and Young's modulus of the nuclear graphite showed a gradual decrease with annealing temperature. The changes are significantly different from those for dimensional changes and thermal expansivity, showing generation of permanent structural changes in crystallites which has no influence on the changes in electrical resistivity and Young's modulus.

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Table 1 Samples used in the present experiment

Sample	Coke	Forming method	Baking temperature(K)	Bulk density (Mg/m^3)
ASR-ORB	Coal tar pitch	Vibration molding	1373	1.67
ASR-1RB	Coal tar pitch	Vibration molding	1373	1.72
IG-110	Petroleum	Isostatic molding		1.76
H451	Petroleum	Extrusion		1,72

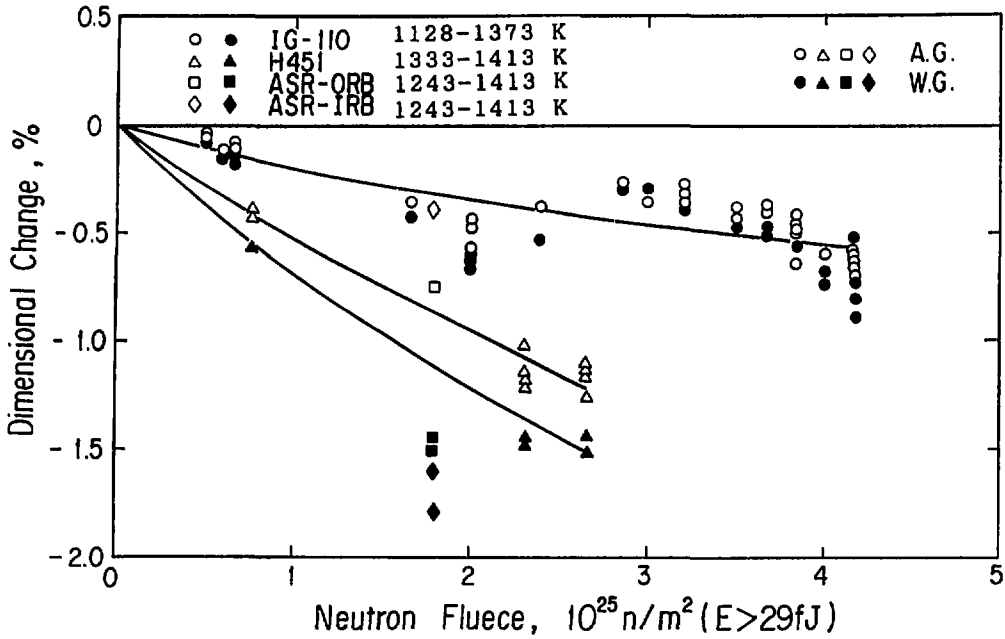

Fig. 1 Dimensional changes of IG-110, H451, ASR-ORB and ASR-1RB

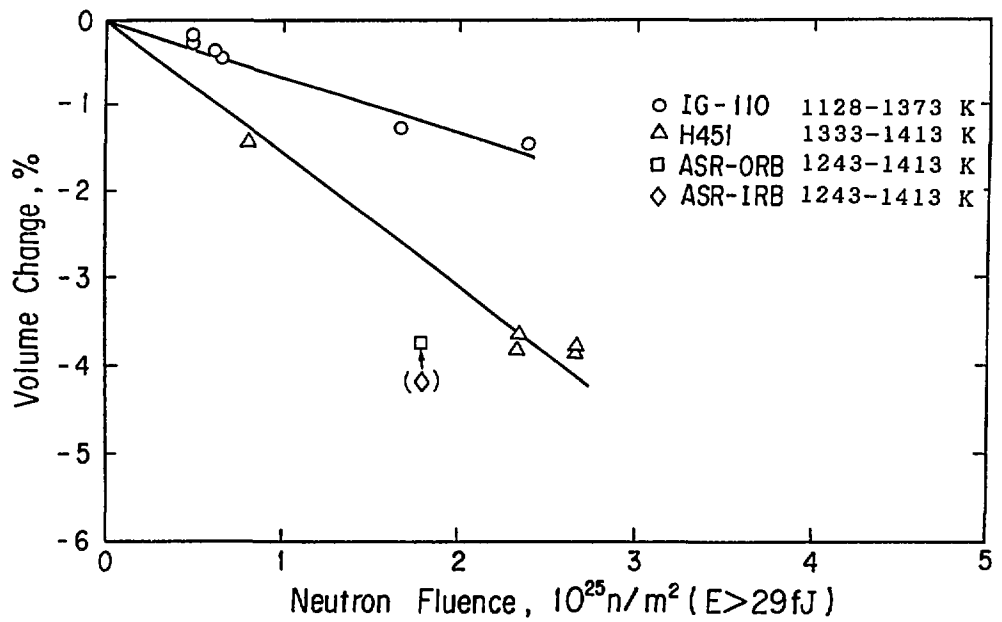

Fig. 2 Volume changes of IG-110, H451, ASR-ORB and ASR-1RB

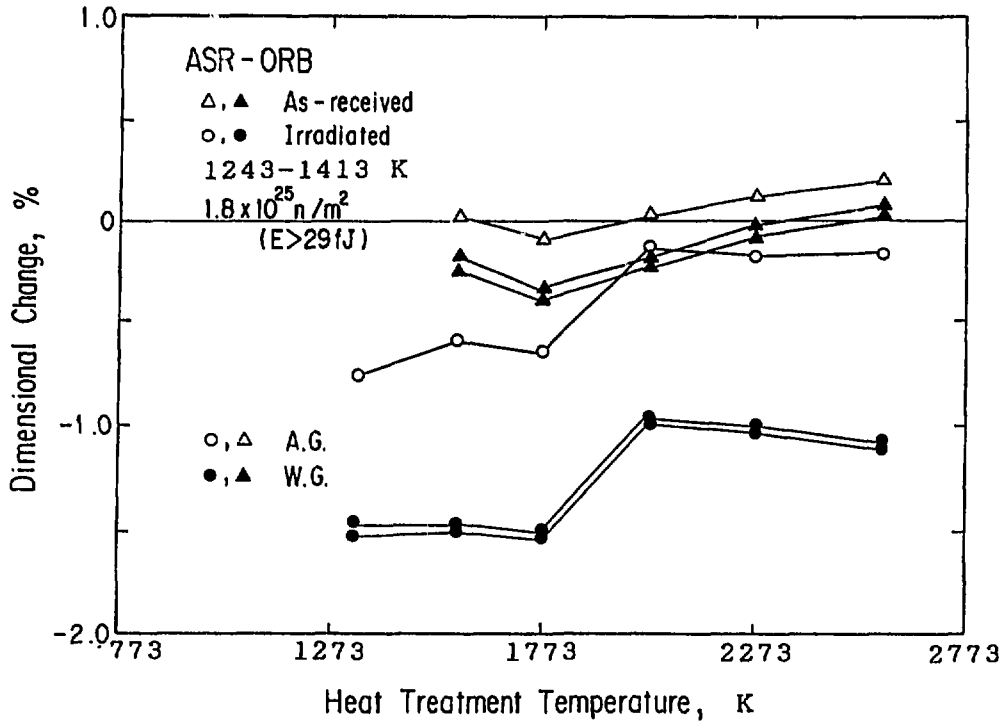

Fig. 3 Annealing of dimensional changes of ASR-ORB carbon

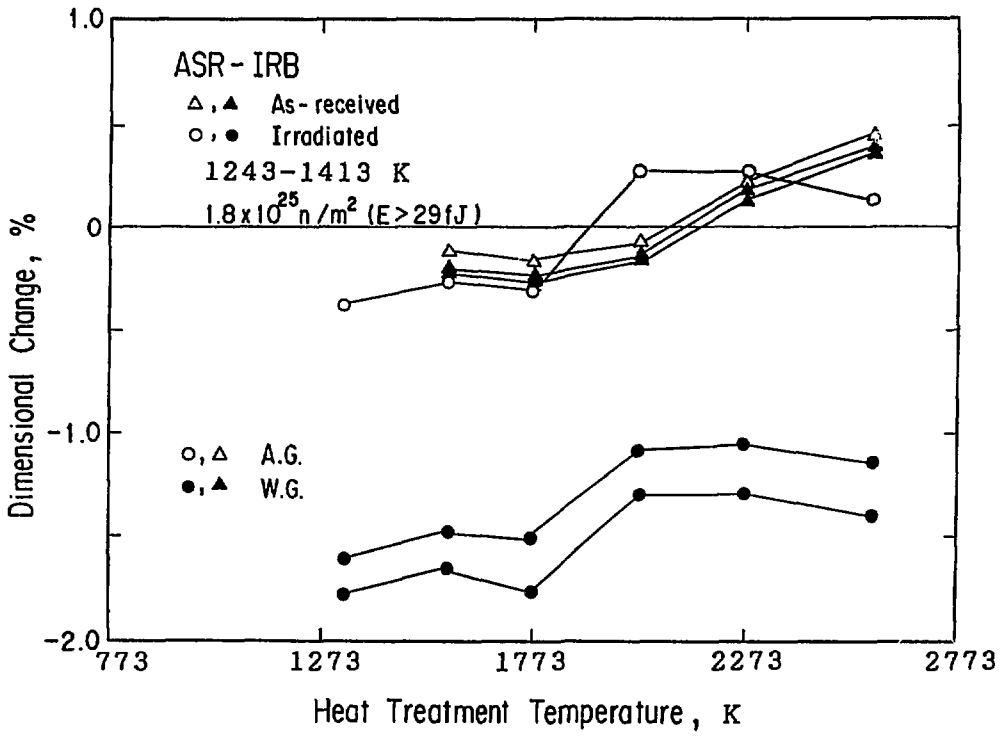

Fig. 4 Annealing of dimensional changes of ASR-1RB carbon

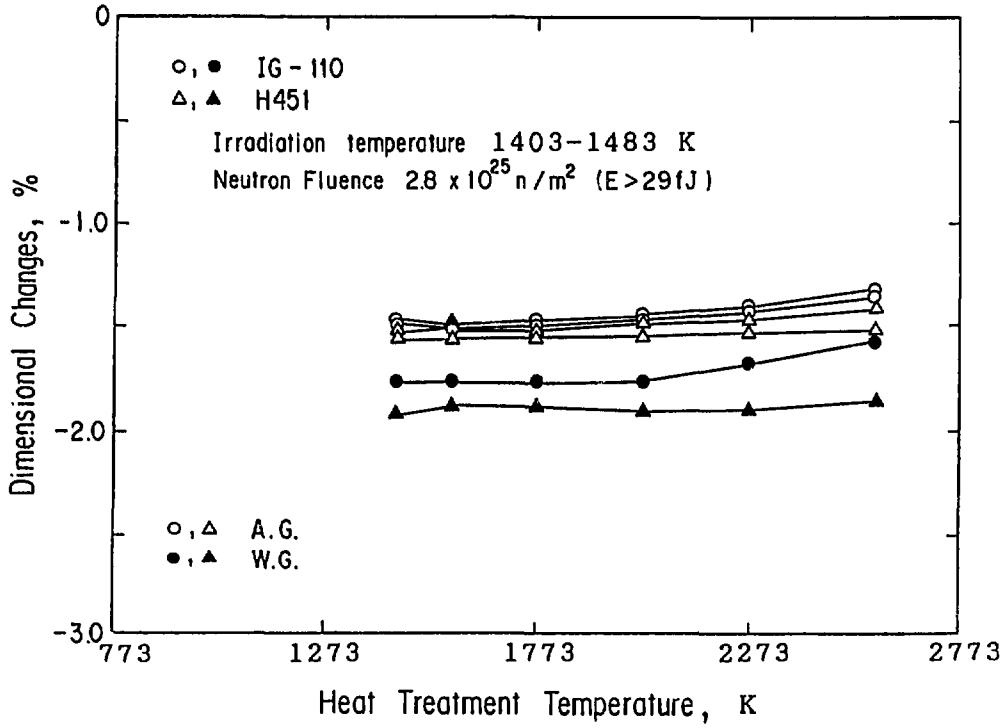

Fig. 5 Annealing of dimensional changes of IG-110 and H451 nuclear graphite

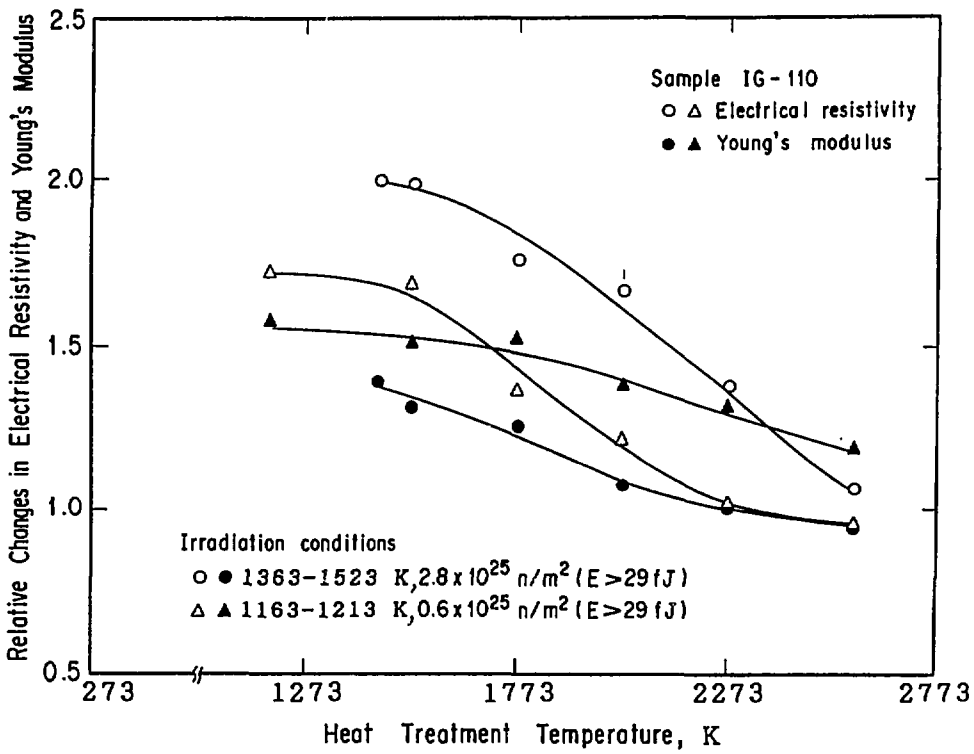

Fig. 6 Changes in electrical resistivity and Young's modulus of IG-110 nuclear graphite as a function of annealing temperature

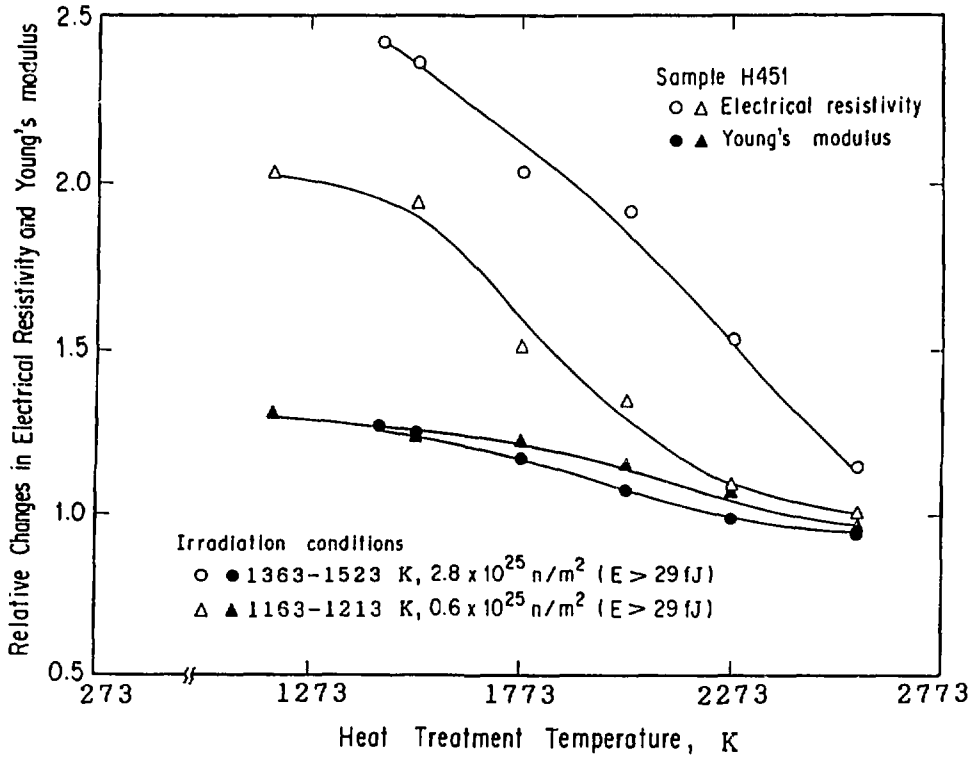

Fig. 7 Changes in electrical resistivity and Young's modulus of H451 nuclear graphite as a function of annealing temperature

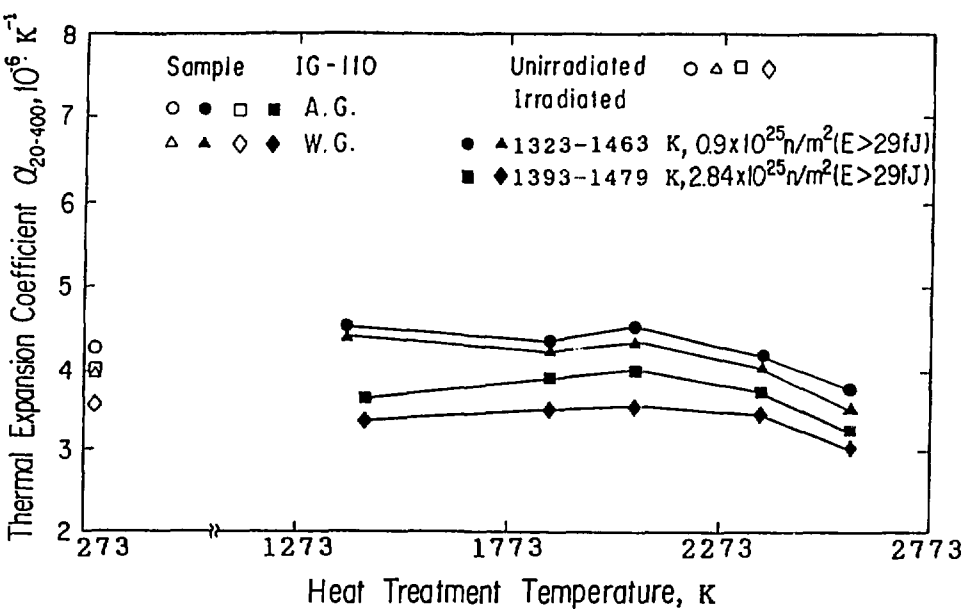

Fig. 8 Changes in thermal expansion coefficient of IG-110 nuclear graphite as a function of annealing temperature

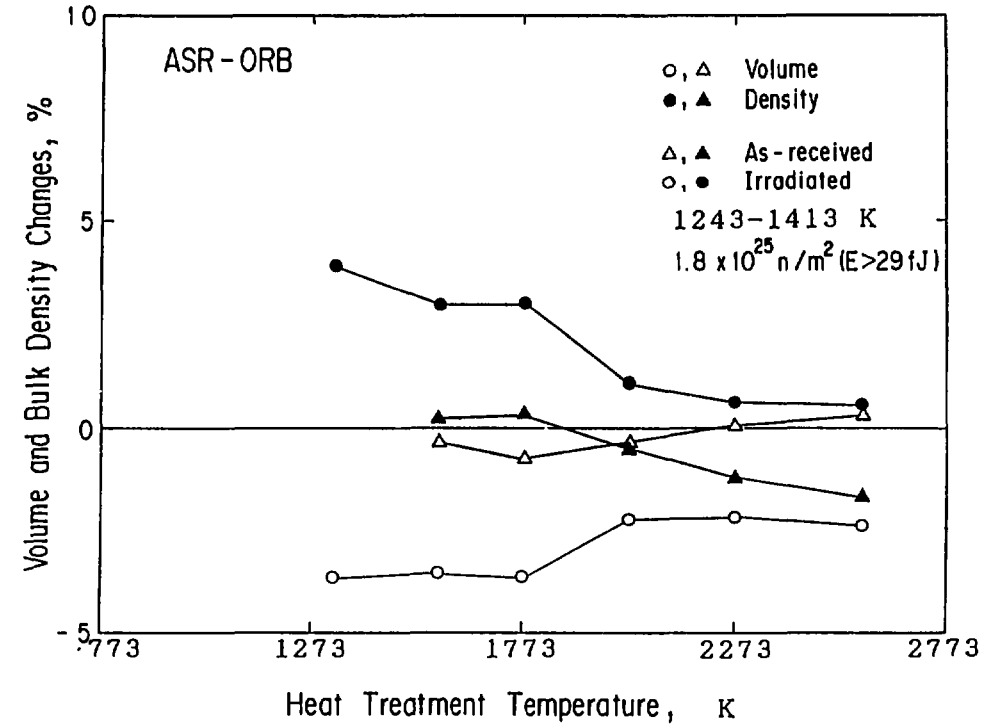

Fig. 9 Annealing of volume and density changes of ASR-ORB carbon

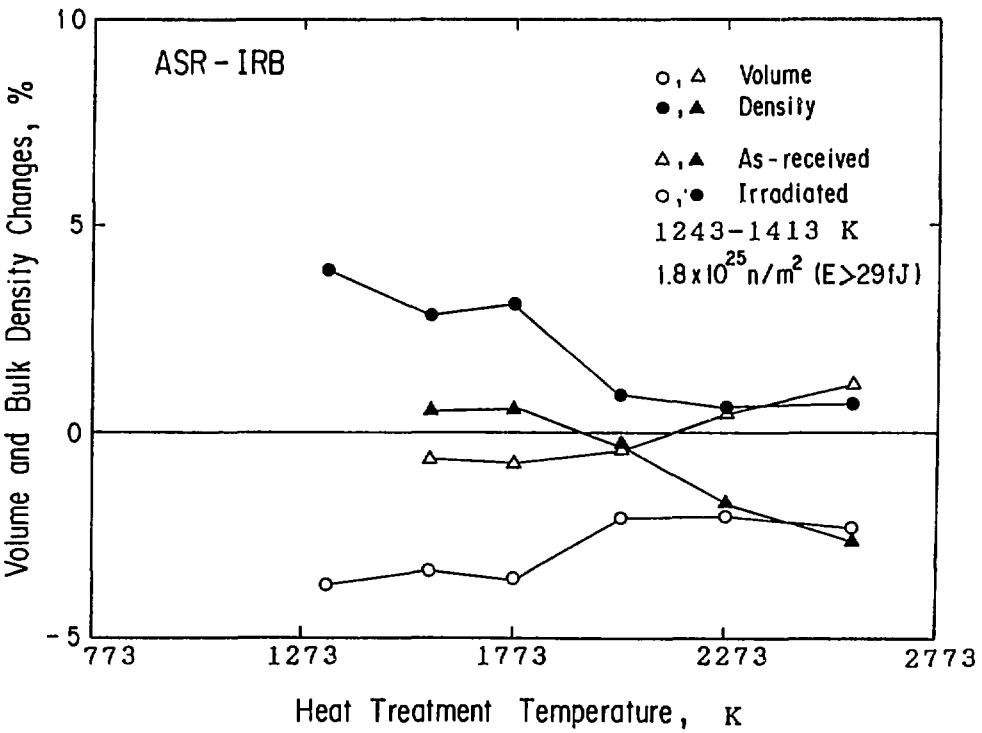

Fig. 10 Annealing of volume and density changes of ASR-1RB carbon

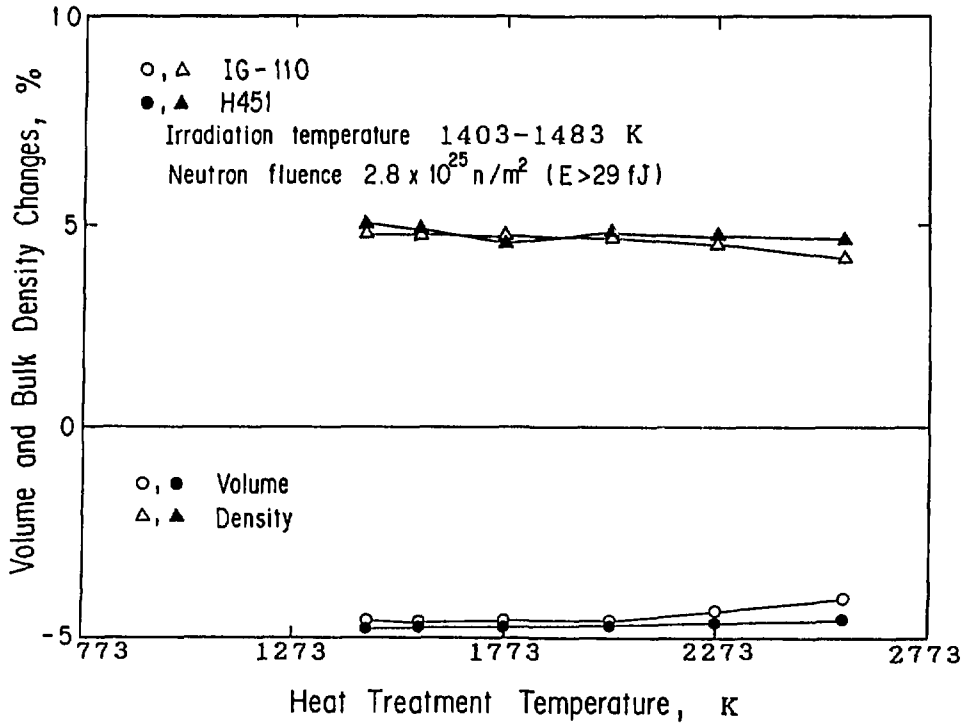

Fig. 11 Annealing of volume and density changes of IG-110 and H451 nuclear graphite