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Neutron Irradiation Effect in Glassy Carbon[+]

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The effects of neutron irradiation up to dose 1.15×10^{20}nvt on the physical properties were studied for three kinds of glassy carbons heat treated at different temperatures. The change of thermal resistivity, Young's modulus and electrical resistivity in glassy carbon were a few tenths of those in reactor graphite. The thermoelectric power of glassy carbon was almost independent of the irradiation dose. The dependence of electrical resistivity of glassy carbons on the heat treatment temperature was opposite to that of graphite. The structure of irradiated glassy carbon was observed, and recovery process of the electrical resistivity was also studied. Discussion about the irradiation effects in the glassy carbon was attempted, taking into consideration the network structure of it.

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ガラスカーボンの中性子照射効果[+]

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種々の温度で熱処理された3種類のガラスカーボンの物理的性質に対する中性子照射効果（照射量，1.5×10^{20} nvt まで）が研究された。熱抵抗，ヤング率，電気抵抗の照射に伴う変化の割合は，原子炉用黒鉛の場合に比べて数分の1程度であった。熱起電能は照射量にほとんど依存せず，また電気抵抗変化の熱処理温度に対する依存性は黒鉛の場合と逆の傾向を示した。照射後の組織観察，および電気抵抗の回復過程の研究も行なわれた。これらの結果から，ガラスカーボンの照射効果に関する議論が，その網目構造を考慮に入れて試みられた。

[+] 本報告の主な部分は，第7回カーボン国際会議（Cleveland，1965年6月）において発表された。

[*] 東海電極株式会社から外来研究員として派遣

目次なし

Introduction

Glassy carbon has been known as one of the most typical hard carbon having vitreous properties. Its unique properties are of much interest for nuclear reactor material such as a fuel sheath and a fuel matrix, if it is confirmed to be stable under irradiation. While several works have been done on the physical properties of this carbon,1) its irradiation behaviors have not been well known2).

A number of works has been done on irradiation effects of artificial graphites. Crystal lattice defects created by fast energetic neutrons and recoil carbon atoms cause appreciable changes of physical properties in graphite. These effects induced by irradiation are more severe in the highly crystallized material than the less crystallized one. Because of noncrystalline structure of glassy carbon,3) its properties are expected to be less affected by irradiation than those of graphite.

In the present work the effects of neutron irradiation on glassy carbons were examined by measuring the changes of dimensions, Young's modulii, thermal resistivities, electrical resistivities and thermoelectric powers. Besides these, microscopic observations of specimens' surfaces were done.

Experimental

Specimens of glassy carbons used in this work were obtained from

Tokai Electrode Mfg. Co. Ltd. They were specified into three grades, which were heat treated at 1300, 2000 and 3000°C, being designated as GC-A, B and C in this paper respectively. Dimensions of specimens in each grade were of two types; 5 × 5 × 50 mm and 5 × 5 × 100 mm corresponding to measurements of various physical properties. Fifteen test pieces were prepared for each grade as well as size; that is ninety specimens in total. In addition to these, reactor graphites were used together as reference material in the similar experimental conditions for glassy carbons. They were of two types, axes of test pieces being parallel and perpendicular to their extrustion axes. (RG-$\parallel$ and RG-$\perp$)

Irradiations were wholly conducted in a vertical test hole in JRR-2 which is of similar type as CP-5 in ANL with heavy water as moderator. Twenty test piecies including each grade and dimension of glassy carbons as well as graphites were enclosed in one capsule made of aluminum. Two or three sets of the specimens were irradiated at the same time and one or two sets of them were reirradiated for added exposure. Integrated neutron fluxes were estimated by means of activation of cobalt wire. Maximum total neutron dose up to 1.15×10^{20} nvt, including slow neutrons was attained after intermittent irradiations. Irradiation temperature was confirmed to be in the range between 150 and 200°C through the fusion tests of some material such as sulfur, tin and solders.

Dimensions of specimens were measured with ocular microscope possible to be read to 0.01 mm on vernier scale. Apparent crystalline lattice parameter c_0 and crystalline size L_c were estimated by means of X ray diffraction using diffractometer.

Young's modulus was obtained from measurement of duration in which 100 kcps ultrasonic wave travels in a specimen.

Thermal conductivity was measured by the Kohlrausch method. A specimen rod which was held at both ends with copper blocks cooled by water was heated by supplying electrical power and temperature difference between a center of rod and a point near its end was measured, using copper constantan thermocouples.

Electrical resistivity was measured by conventional four probes method. Thermoelectric power was obtained through the measurements of electromotive force between two points of a specimen rod having temperature gradient along the axis of it which contacted with copper blocks, one of which was cooled with water and the other heated with electrical resistance. At first thermoelectric power of a specimen was obtained against copper, being a lead of thermocouple, and thereafter that was obtained against lead by exchanging a specimen by a lead rod which has a small value of thermoelectric force as well as of its temperature coefficient.

Results and discussion

Physical properties of the specimens were measured at room temperature before and after irradiations which were conducted intermittently. The average values of the physical properties of unirradiayed glassy carbons used in the experiments are shown in Fig.1 as functions of their heat treatment temperatures. In these, c_0-spacing and L_c-dimension mean an apparent lattice parameter and an apparent crystalline size respectively which were obtained from a broard peak at bout $2\theta \simeq 25^o$ in X-ray analysis, assuming as if the glassy carbon had an crystalline structure such as graphite, while it should be noticed that glassy carbon has non-crystalline structure as was found by T. Noda and M. Inagaki.3) In Fig.1, apparent density, electrical resistivity, Young's modulus and c_0-spacing are decreased with the elevation of heat treatment temperature, wheras thermal conductivity and L_c-dimension were increased.

Even after the final irradiation (about 10^{20}nvt) dimensional change was not detected on both glassy carbon and reactor graphite within th accuracy of 0.1 %. Little change in c_0-spacing by irradiation was observed for glassy carbon, while a slight expansion around 1 % was observed for reactor graphite after the maximum exposure about 10^{20}nvt.

The fractional changes of thermal resistivity, $(K_0/K - 1)$, of glassy carbons and reactor graphites as a function of neutron dose are shown in Fig.2. As seen in this figure, the fractional changes for glassy carbons were increased with exposure as well as those for reactor graphites. The rate of increase in glassy carbon is found to be about one third of that for reactor graphite. The difference among the three kinds of glassy carbons obtained from different heat treatment temperatures are too small to be distinguished.

The fractional changes in Young's Modulii, $(E/E_0 - 1)$, of glassy carbon and reactor graphite versus neutron exposure are plotted in Fig.3. The changes are similar to those found in thermal resistivity. The increasing rate for glassy carbon is about a quater smaller than for graphite.

The plots for the electrical resistivity, $(R/R_0 - 1)$, of glassy carbon at room temperature as a function of integrated neutron flux are given in Fig.4, in which results for reactor graphites are also plotted.4) The fractional changes for glassy carbons are far smaller than for graphites. It should be noticed that some correlations exist between the variations of electrical resistivies of glassy carbons and their heat treatment temperatures. In Fig.5 the curves for glassy carbons are plotted in the magnified scale of ordinate. In usual case for graphitizing soft carbon, it is well known that the higher is its heat treatment temperature, the more is the increase of resistivity due to irradiation. On the contrary, in the case of glassy carbon shown here, the fractional change is the largest for the specimen heat treated at 1300°C, and the smallest for the one heat treated at 3000°C. In addition, a specimen heat treated at 3000°C shows a decrease of resistivity in the range of neutron dose of a few times of 10^{19}nvt. These situations seem to be inconsistent to the case of soft carbon.

In Fig.6, thermoelectric powers of glassy carbon and graphite against lead are plotted as a function of exposure. As well known, thermoelectric power of graphite is one of the most sensitive feature for irradiation dose, and this was verified in the present work as seen in Fig.6. It varied with exposure from about $-2\mu v/^{o}C$ to $+8\mu v/^{o}C$. On the other hand, as shown in other three curves, glassy carbons exhibit nearly constant positive values all over the dose range examined. These results obtained in glassy carbons indicate that Fermi level or carrier concentration in glassy carbon is little varied by neutron irradiation.

The fact that Fermi level of glassy carbon is little changed by irradiation seems to suggest that glassy carbon behaves like some amorphous semiconductors which have no discrete level in a forbidden band, even if lattice defects or impurities exist in them.5) Neutron irradiation would not contribute to creations of impurity levels in glassy carbon, but to formations of scattering centers only. In the case of graphite, on the other hand, it has been recognized that neutron irradiation induces both effects, change of carrier concentration and of scattering center density. Neutron irradiation may not only break the bondings of random networks of glassy carbon, which consist of trigonal and tetrahedral bondings,3) but make one type of bonding shift to another one. Competion of these interchanges of bondings would affect the mobility change in irradiated glassy carbon, either a small decrease or possibly even an increase in some case.

Neutron irradiation effects of physical properties in glassy carbon were described in the above paragraphs. Besides these results, some interesting observations were done of irradiated glassy carbons. Photo. 1 shows a surface appearence of unirradiated carbon heat treated at 1300°C, which has no special feature. Appearences of the specimens heat treated at 2000°C and 3000°C were similar as this photograph. After neutron irradiation, some specimens showed marked changes in their surface appearences. Typical examples of the appearences after irradiation are shown in Photo. 2 and 3. Photo. 2 is a microphotograph of the surface of glassy carbon heat treated at 1300°C after irradiation 7.5×10^{19}nvt. Remarkable networks of cracks were observed on the surface of the specimen for the dose beyond 7.5×10^{19}nvt. In the case of the specimen heat treated at 2000°C, similar cracks as above were observed only after an exposure 1.15×10^{20}nvt, the maximum dose in this study. On the other hand, for glassy carbon heat treated at 3000°C no crack was found to take place. As the irradiation was increased, the cracks were extended more and more and at last the region environed by crack networks peeled off from the surface, leaving some conchoidal pits there. Photo. 3 shows such an appearece of the specimen heat treated at 1300°C after the irradiation 1.15×10^{20} nvt. The conchoidal pits with diameter of about 100 μ were observed over the surface. Throughout the series of the irradiations it was only for the specimen heat treated at 1300°C that such a conchoidal pit was observed.

The formations of crack networks or conchoidal structures in glassy carbons heat treated at lower temperatures might be in part responsible to the larger increase rate of electrical resistivity due to irradiation in those carbon. In spite of these considerations, it is to be noted that the increase rates with irradiation of thermal and electrical resistivities in glassy carbons are smaller than in graphites. As discussed in the above paragraphs, these facts suggest that the effects of the competitions of breaks and interchanges of bondings, trigonal and tetrahedral, in random network structures of glassy carbons are important in the variations of physical properties of those due to neutron irradiation.

Recovery of electrical resistivities were studied by pulse annealing. Glassy carbons as well as reactor graphites irradiated up to dose of 1.15×10^{20}nvt were examined. The results are shown in Fig.7, in which the annealing curves for graphites irradiated at about 50°C in a water cooled loop (HWL) are also shown. Graphites showed rapid recovery at about 150°C and above 1200°C. This behavior is similar as the case of Kinchin.6) On the other hand, the glassy carbons showed uniform recovery over the temperature range up to 1230°C without characteristic stages. While some point defects are found to be produced due to irradiation in graphite through recovery experiment of Kinchin, such a definite defect is not considered to be produced in glassy carbon probably because of its random network structure.

Summary

The changes induced by neutron irradiation in thermal resistivity, Young's modulus and electrical resistivity for glassy carbon were smaller than for reactor graphite within the dose range in this study. There is no distinguished relation, regarding the fractional changes of thermal resistivity and Young's modulus, among the glassy carbons heat treated at different temperatures, whereas regarding changes of electrical resistivity some differences were found among them. A small decrease of electrical resistivity in the glassy carbon was found in a dose range of a few times of 10^{19}nvt. Cracks and conchoidal pits were found to be produced by irradiation on a glassy carbon heat treated at 1300°C. While the formations of such cracks and conchoidal pits may be in part responsible to the changes of physical properties in glassy carbons, breaks and shifts of carbon bondings, which form random networks of glassy carbon, induced by irradiation are considered to be important to them. The results of recovery of electrical resistivity in glassy carbon suggest that irradiation produce no definite lattice defect as found in graphite.

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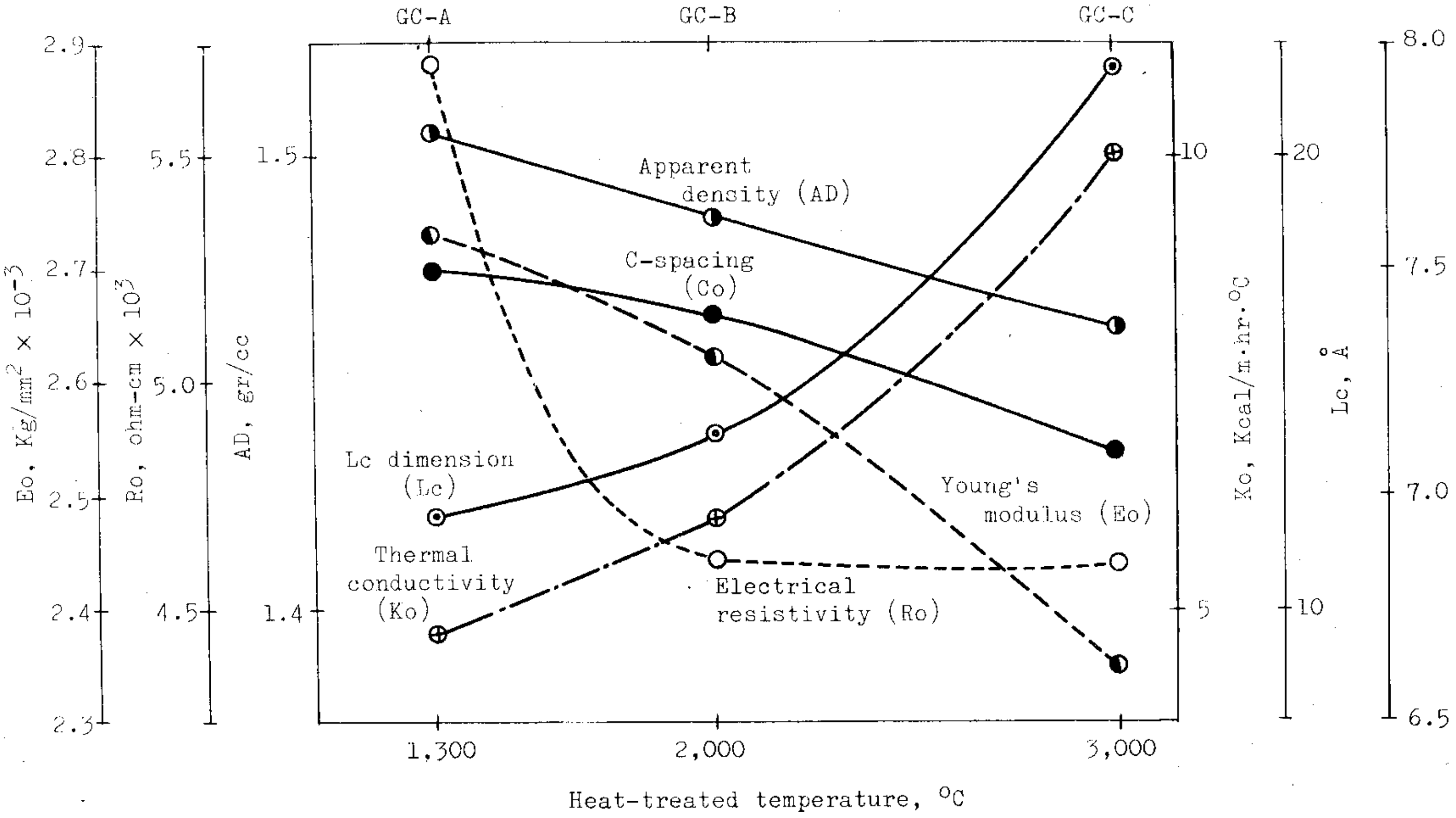

Fig.1 Changes in properties of glassy carbon with heat-treated temperature

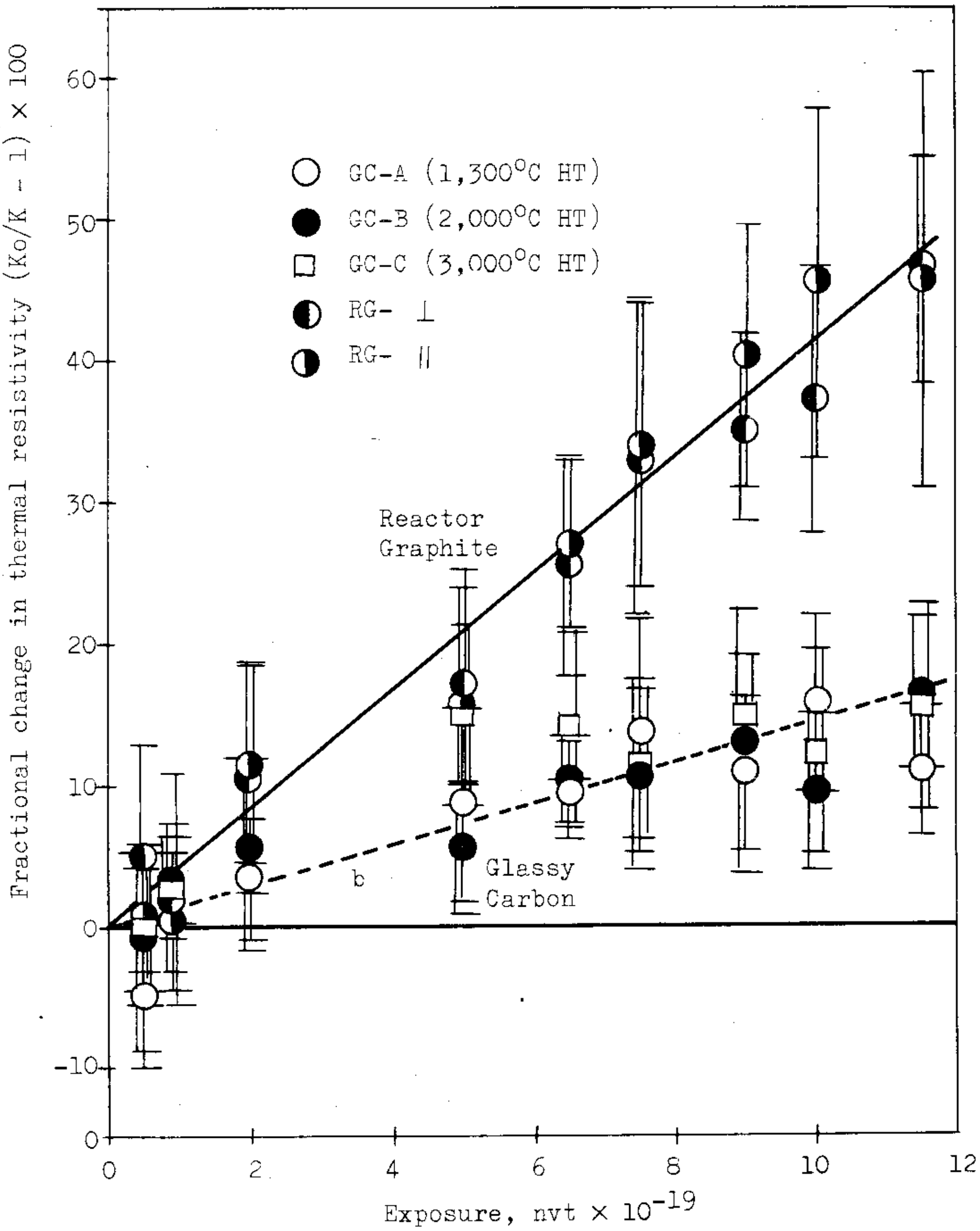

Fig.2 The fractional change in the room temperature thermal resistivity due to irradiation at 150-200°C

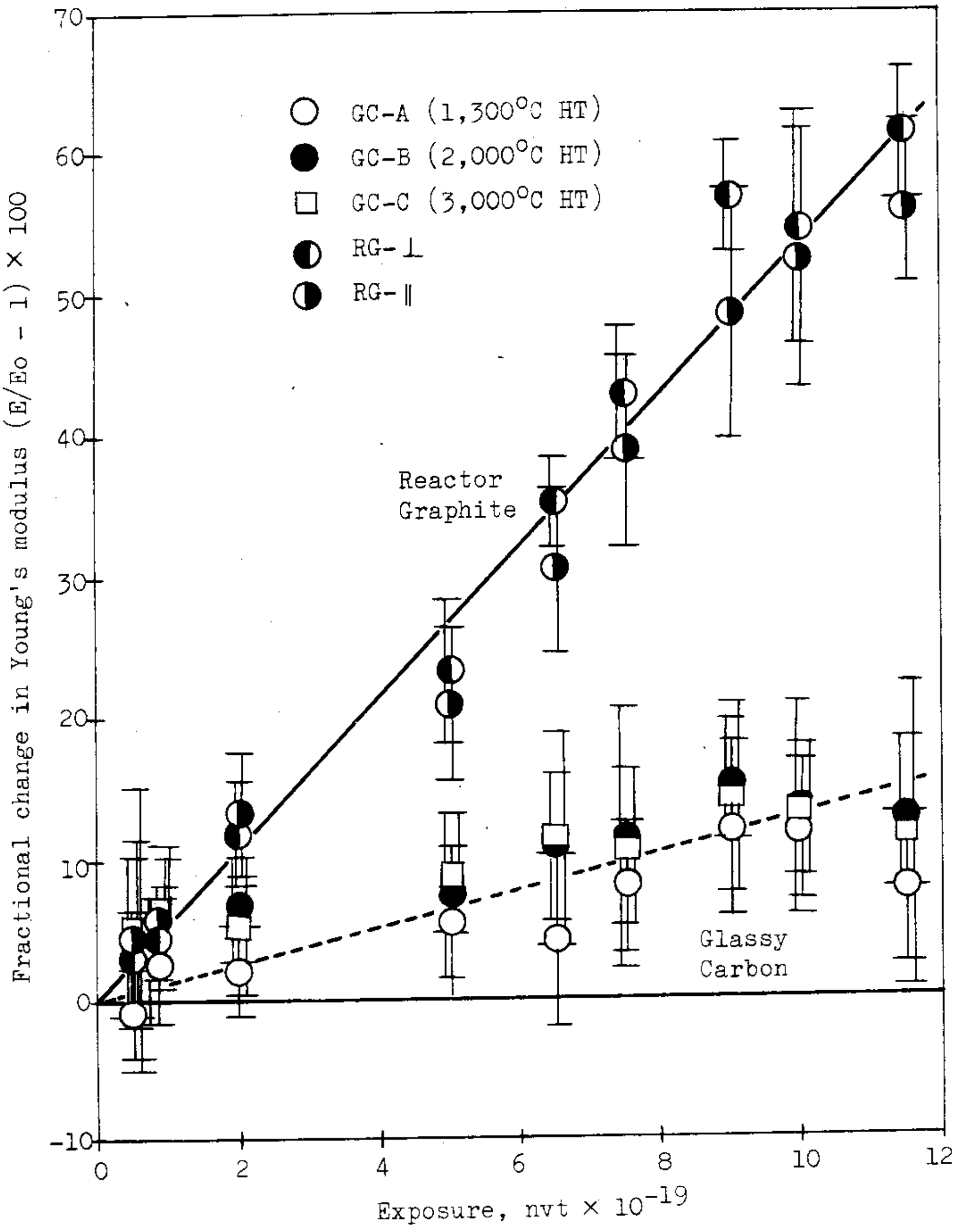

Fig.3 The fractional change in the room temperature Young's modulus due to irradiation at 150-200°C

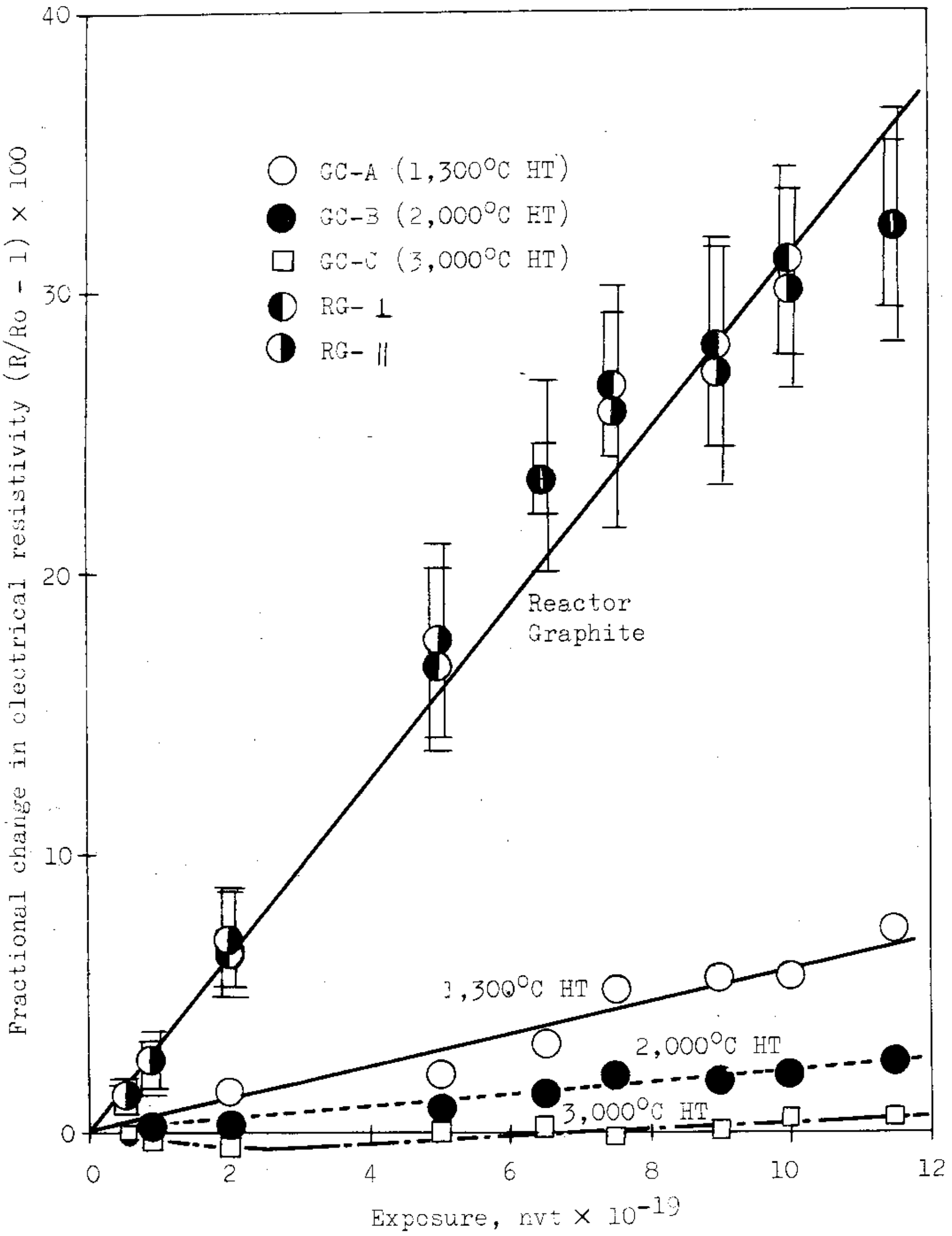

Fig.4 The fractional change in the room temperature electrical resistivity due to irradiation at 150-200°C

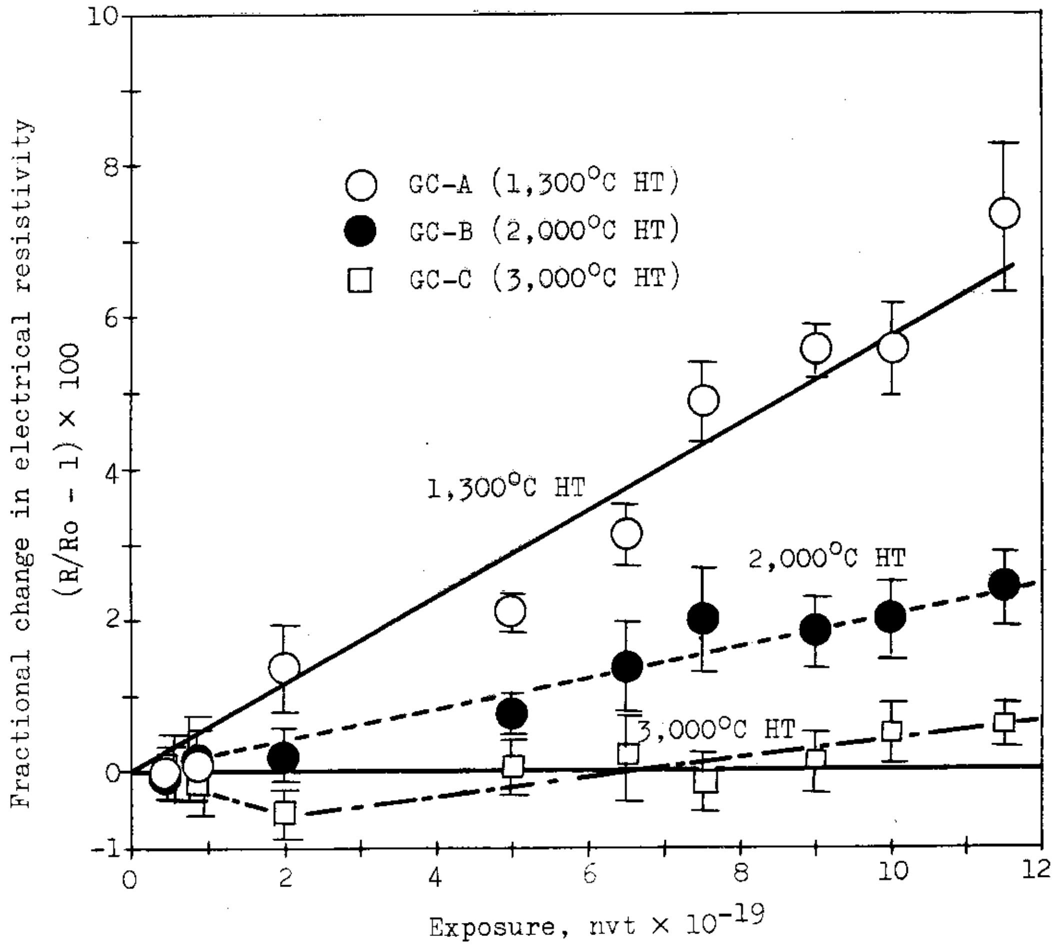

Fig.5 The fractional change in the room temperature electrical resistivity of glassy carbon due to irradiation at 150-200°C

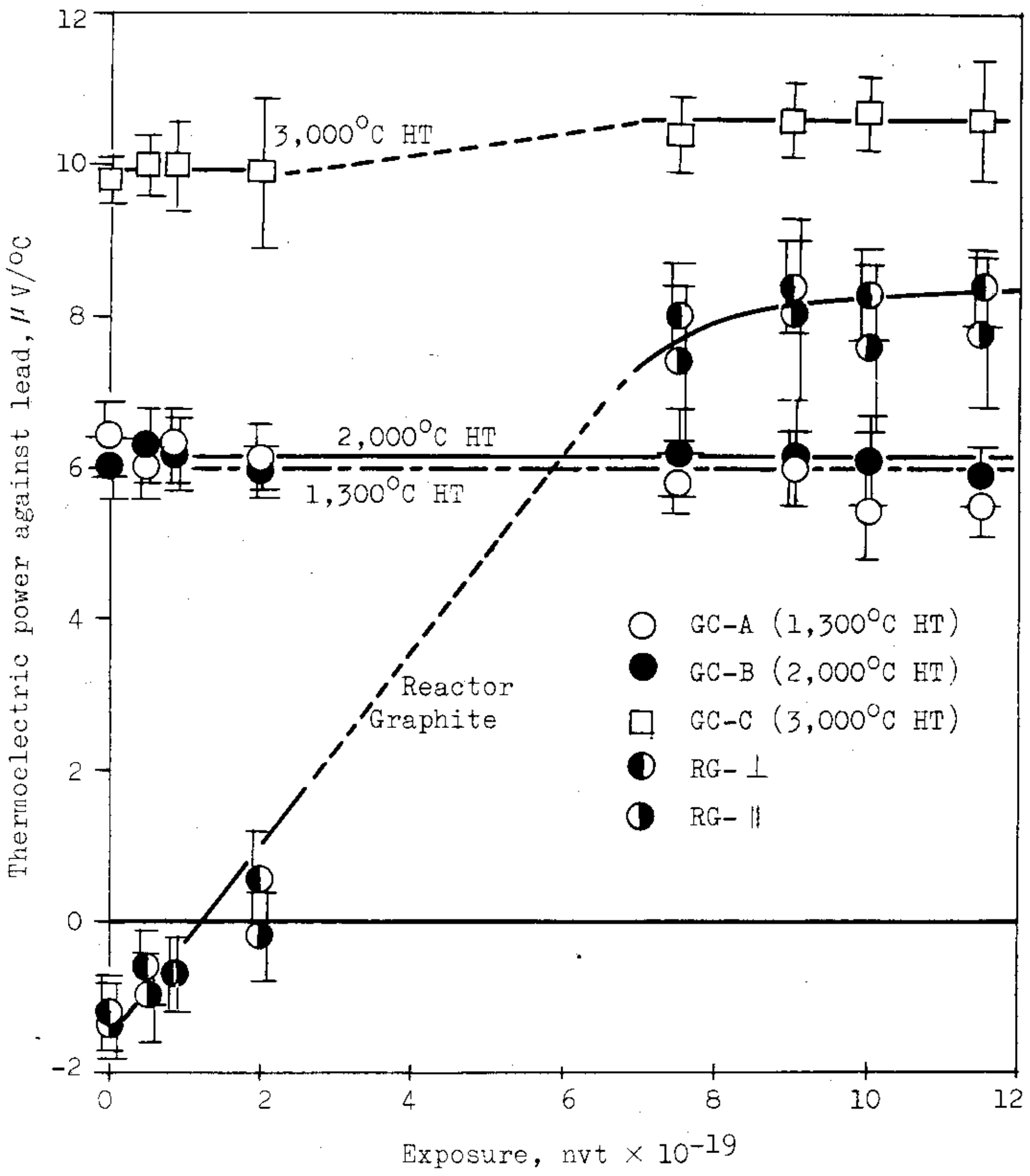

Fig.6 The thermoelectric power of irradiated glassy carbon and reactor graphite at room temperature

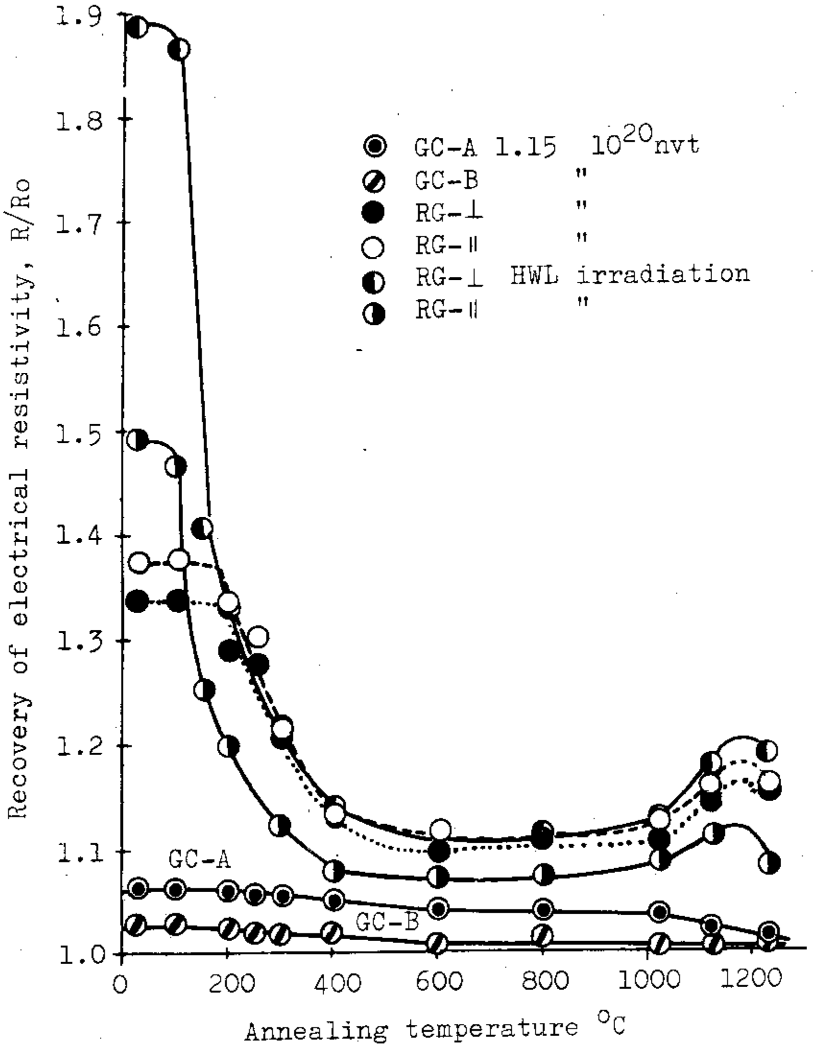

Fig.7 Thermal recovery of electrical resistivity in irradiated reactor graphite and glassy carbon during pulse annealing (one hour at each temperature)

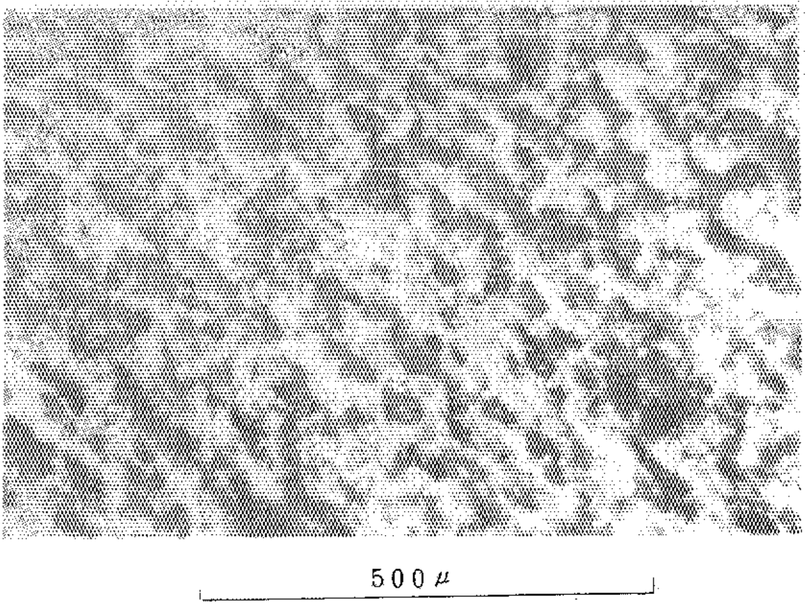

Photo.1. Appearance of surface on unirradiated glassy carbon heat treated at 1,300°C.

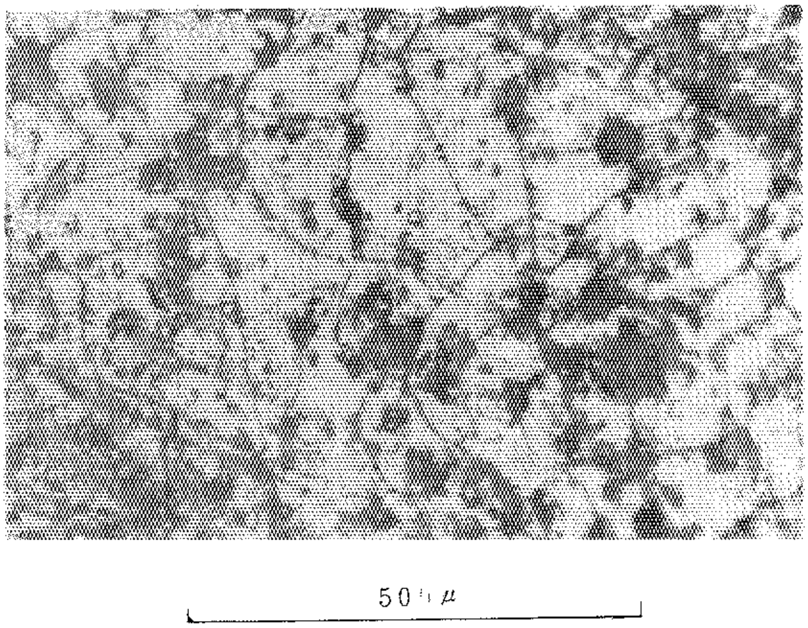

Photo.2. Appearance of surface on 1,300°C HT glassy carbon after exposure of 7.5×10^{19}nvt.

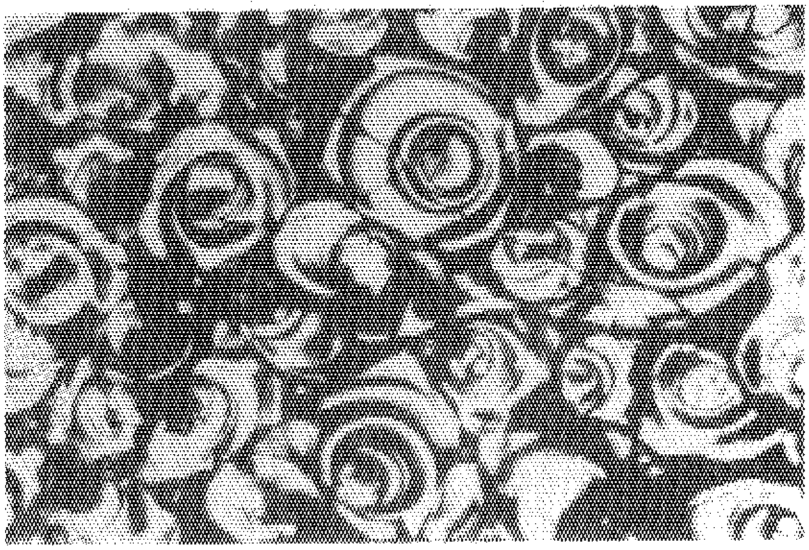

Photo.3. Appearance of surface on 1,300°C HT glassy carbon after exposure of 1.15×10^{20}nvt.