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Properties of Irradiated and Periodically Annealed Graphite*

S. Aronson, D. G. Schweitzer, and R. M. Singer
Brookhaven National Laboratory
Upton, New York

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Send Proofs To:

Seymour Aronson
Metallurgy Division, Bldg. 480
Brookhaven National Laboratory
Upton, New York

ABSTRACT

The effects of annealing frequency on the physical, electrical, and thermal properties of irradiated graphite have been investigated. AGOT nuclear graphite was irradiated in the Brookhaven Graphite Research Reactor at 30° to 40°C for approximately 200 MWD (~1.5×10^{19} nvt for neutrons above 0.6 Mev). At regular intervals, samples were temporarily removed from the reactor and were annealed at 350°C. From one to seventeen anneals were performed on the samples. The amount of radiation damage determined from the property changes decreased with increasing annealing frequency. During the final 100 MWD of exposure, the most frequently annealed samples showed no net dimensional growth. The results are discussed qualitatively in terms of the types of defects formed during irradiation.

The properties of neutron-irradiated graphite have been studied by a number of investigators (1,2). The recovery of radiation damage during thermal annealing has also been investigated in some detail (1,2). Studies of the thermal annealing of graphite have, however, generally been confined to one annealing treatment after an irradiation. Little information is available on the effects of a number of irradiation and annealing cycles. Such information is of value from a practical point of view. Rates of accumulation of radiation damage in graphite employed as a moderator and structural material in nuclear reactors can be drastically altered by changes in annealing frequency (3). In addition, basic information about the nature of the damage incurred during irradiation can be obtained from an investigation of the properties of irradiated and periodically annealed graphite (4).

In the present study, the effects of annealing frequency on the properties of irradiated graphite have been investigated. Samples of synthetic graphite were irradiated in the Brookhaven Graphite Research Reactor at 30 to 40°C for about 200 megawatt days per adjacent ton of uranium. The samples were temporarily removed from the reactor and were annealed at 350°C at regular intervals during the 200-MWD exposure. The number of anneals ranged from one to seventeen. Changes in sample dimensions, C-axis parameter, Hall coefficient, electrical resistivity, thermal conductivity, and stored energy were measured. The results of these measurements indicate that periodic annealing greatly reduces the amount of damage caused by neutron irradiation.

Experimental

AGOT nuclear grade synthetic graphite obtained from the National Carbon Company was used in these experiments. For the dimensional studies, cylindrical samples (2-in. long and 0.75-in. in diameter) cut with their long axes perpendicular to the extrusion axis of the graphite bar were measured with a Sheffield Optical Comparator. Electrical conductivity and Hall coefficient measurements were made using standard D.C. potential-probe techniques (5). Magnetic fields of 2 to 13 kilogauss were employed. Samples for the electrical measurements were parallelpipeds, 1.20-in. by 0.20-in. by 0.04-in. These were also cut perpendicular to the extrusion axis. Thermal conductivity specimens, 1.5-in. long cylinders, 0.5-in. diameter, were measured according to the procedure of Meyer and Schweitzer (6). C-axis parameters were measured on powder samples scraped from the specimens used for the dimensional measurements.

X-ray powder patterns were obtained using a copper target and a nickel filter. Stored energy values were obtained from heat of combustion measurements performed by the thermochemistry section at the National Bureau of Standards on selected samples sent to the Bureau.

The graphite was irradiated in the Brookhaven Graphite Research Reactor (BGRR). A megawatt day per adjacent ton of uranium, one MWD, corresponds approximately to 7×10^{16} nvt for neutrons above 0.6 Mev.

Results and Discussion

Seven groups of graphite samples were irradiated in the Brookhaven Graphite Research Reactor for 200 to 240 MWD at temperatures of 30 to 40°C. Two of the groups, F′ and H′, were irradiated continuously for the entire exposure. Samples in group F′ were annealed at 350°C for one to four hours after the total exposure. The other groups, A to E, were annealed at approximately equal intervals between irradiation periods and also after the last irradiation.

Table I shows the dimensional changes observed in these samples. The average growth measured on eight samples in each group is listed in the fourth column together with the average deviation of the values. The average growth per MWD during irradiation is given in the final column of Table I.

Samples in each group were irradiated in two reactor locations. The two exposure values shown in Table I result from the slightly different fluxes in each location. The differences in growth between groups F′ and H′ are an example of the variations in properties which are frequently observed in synthetic graphite samples.

It is evident from Table I that frequent annealing of irradiated graphite significantly reduces growth. The two exceptions to this generalization observed in Table I, in groups B and C and groups D and E, probably are due to slight differences in the properties of the samples introduced furing manufacture of the graphite such as impurity content, density, and pore structure and to experimental error.

An interesting observation concerning the A and B groups is that dimensional stability was achieved after several irradiation and annealing cycles. Growth and recovery data on a few samples are shown in Figure 1. The vertical lines result from anneals at 350°C. The samples were annealed at regular intervals during the entire exposure period. Complete growth and recovery records were kept only above 100 MWD. It is observed that samples A-10 and A-16 do not show net growth in the exposure range plotted. The other A group samples also showed no net growth in the same exposure range. Less data are available on the B group samples because fewer anneals were performed. Although some net growth is observed on sample B-13 in Figure 1, examination of all the B samples indicates that dimensional stability has been approximately achieved in this group also. The behavior of the A and B group is similar to that observed by Woodruff (7) on graphite irradiated for longer exposures and periodically annealed at 500°C.

A number of properties were measured on selected samples from the various groups. These measurements are shown in Table II. The data shown on virgin AGOT graphite are values obtained on single samples. The values for the various properties may vary slightly from sample to sample. Hall coefficient and electrical resistivity measurements were made at 27°C and -194°C. The Hall values are averages obtained for several fields between 2 and 13 kilogauss. The thermal conductivity measurements were made at 350°C. The data, with a few exceptions, show decreasing damage with increasing annealing frequency. Thus, the C-axis parameter, electrical resistivity, and stored energy decrease with increasing annealing frequency. The thermal conductivity and the absolute value of the Hall coefficient at -194°C increase with the number of anneals. The values of the electrical resistivity and the Hall coefficient at 27°C and -194°C converge as the frequency of annealing decreases. Such convergence is expected as the radiation damage increases (8).

In order to obtain a physical picture of the damage incurred in the various samples, the assumption was made that specific properties reflect specific types of damage in the graphite lattice. It was assumed that macroscopic growth and C-axis expansion are directly proportional to the number of interstitial carbon atoms trapped between the graphite planes. Such an assumption appears to be valid for continuously irradiated graphite (1,2). An indication that this may be only approximately correct for the periodically annealed samples is that the average rates of growth during irradiation are somewhat lower than for the continuously irradiated samples (see Table I). An approximate theory of the electrical properties of irradiated graphite (8) indicates that changes in the Hall coefficient reflect changes in the number of electrons transferred from the band structure of graphite to localized traps such as vacancies and interstitial atoms. The Hall coefficient at 27°C and -194°C is plotted as a function of continuous irradiation in Figure 2. The Hall data on the periodically annealed samples seems to correspond approximately to the curves for continuously irradiated graphite shown in Figure 2 for exposures above 10 MWD. In addition, changes in the Hall coefficients of the A and B groups samples resultings from one irradiation period without an anneal are similar to changes obtained on continuously irradiated samples having the same initial Hall coefficients and irradiated for the same exposure intervals. These data indicate that the electronic changes in the periodically annealed samples and the continuously irradiated samples result from the same types of damage. The stored energy accumulation in continuously irradiated graphite appears to be closely related to the C-axis and dimensional expansion (9,10). Its magnitude may, therefore, primarily depend on the concentration of interstitial carbon atoms which are probably present in the form of small molecular clusters (11). In annealed graphite, larger clusters are formed and the stored energy dependence may change.

A comparison of the properties of the various groups of graphite is shown in Table III. For continuously irradiated samples, the reasonable assumption was made that growth, C-axis expansion, and stored energy vary linearly with exposure for the relatively low exposures considered here. Figure 2 was used for comparing the Hall coefficient data. The exposures corresponding to the various Hall values obtained were compared. The Hall coefficient at 27°C and the electrical resistivity are not very sensitive to exposure and were not used in the comparison. The thermal conductivity data were felt to be insufficient for comparison.

In Table III values are presented for the ratio of the change in a property of a periodically annealed sample to the change in a continuously irradiated sample having the same total exposure. Average values were used in the cases where more than one value was obtained. A comparison of the data on the samples annealed seventeen times (Group A) and the samples annealed once (Groups F and H) indicates that the amount of damage is five to ten times as great in the latter samples. The small amounts of growth and stored energy in the frequently annealed samples are especially interesting from the standpoint of nuclear reactor application. The relatively low ratios of damage obtained in the case of the Hall coefficient data compared to the other properties indicate that the anneals are more efficient in returning electrons from localized traps to the band structure of graphite than in removing carbon atoms from interstitial sites. Considering the relatively poor precision of the data and the variability often observed in graphite properties, the growth and C-axis values are probably sufficiently similar to qualitatively support the conclusion that they are measures of the same microscopic phenomenon, the accumulation of interstitial carbon atoms. The data in Table III are not sufficiently accurate to warrant a quantitative comparison of the values.

A complete explanation of the effects of annealing frequency on the properties of irradiated graphite is not available. It is likely that during the first irradiation period, the interstitial atoms accumulate in the form of small molecular clusters (11). During thermal annealing, a fraction of the interstitial atoms are removed by combination with vacancies and other trapping centers (grain boundaries, dislocations, etc.). There is also an agglomeration of the small clusters into larger, more stable and less mobile clusters. A partial explanation for the reduced rate of damage accumulation in the frequently annealed samples can be given. The fraction of interstitial carbon atoms which agglomerate into large clusters during annealing probably increases with increasing exposure period. Samples annealed once after about 235 MWD exposure recover about 30% of their growth (see Table III). Dimensional recoveries during an anneal after exposures of 15 to 30 MWD are greater than 60%.[1] The lower concentrations of small interstitial clusters result in decreased fractions of large agglomerates being formed during annealing. Larger fractions of interstitials atoms are annealed out. Frequent anneals, therefore, reduce the accumulation of defects. However, there is no good explanation for the dimensional stability achieved by the A and B group samples. One would expect net growth after each irradiation and annealing cycle. It is of interest to note that graphite samples which were strongly irradiated and then subjected to the same treatments as the A and B groups recovered during each anneal more than 100% of the growth incurred during the previous irradiation.[2] This large recovery in the highly damaged samples and the approximately 100% recovery observed in the A and B groups may be related. These data may indicate that some of the interstitial clusters present after an anneal may decompose during the subsequent irradiation and annealing cycle.

Acknowledgments

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Footnotes

[1] Unpublished data.

[2] Unpublished data.

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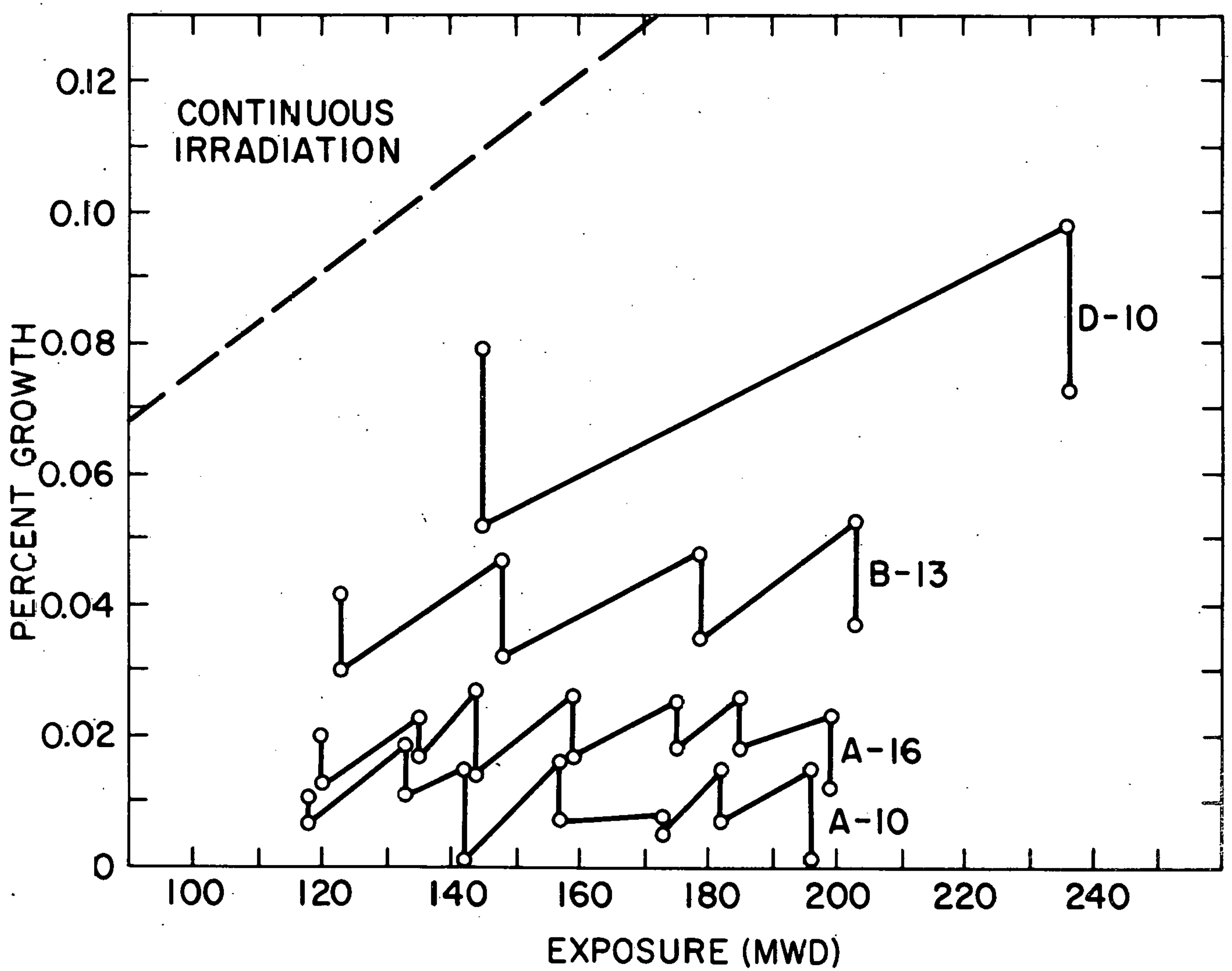
Figure Captions

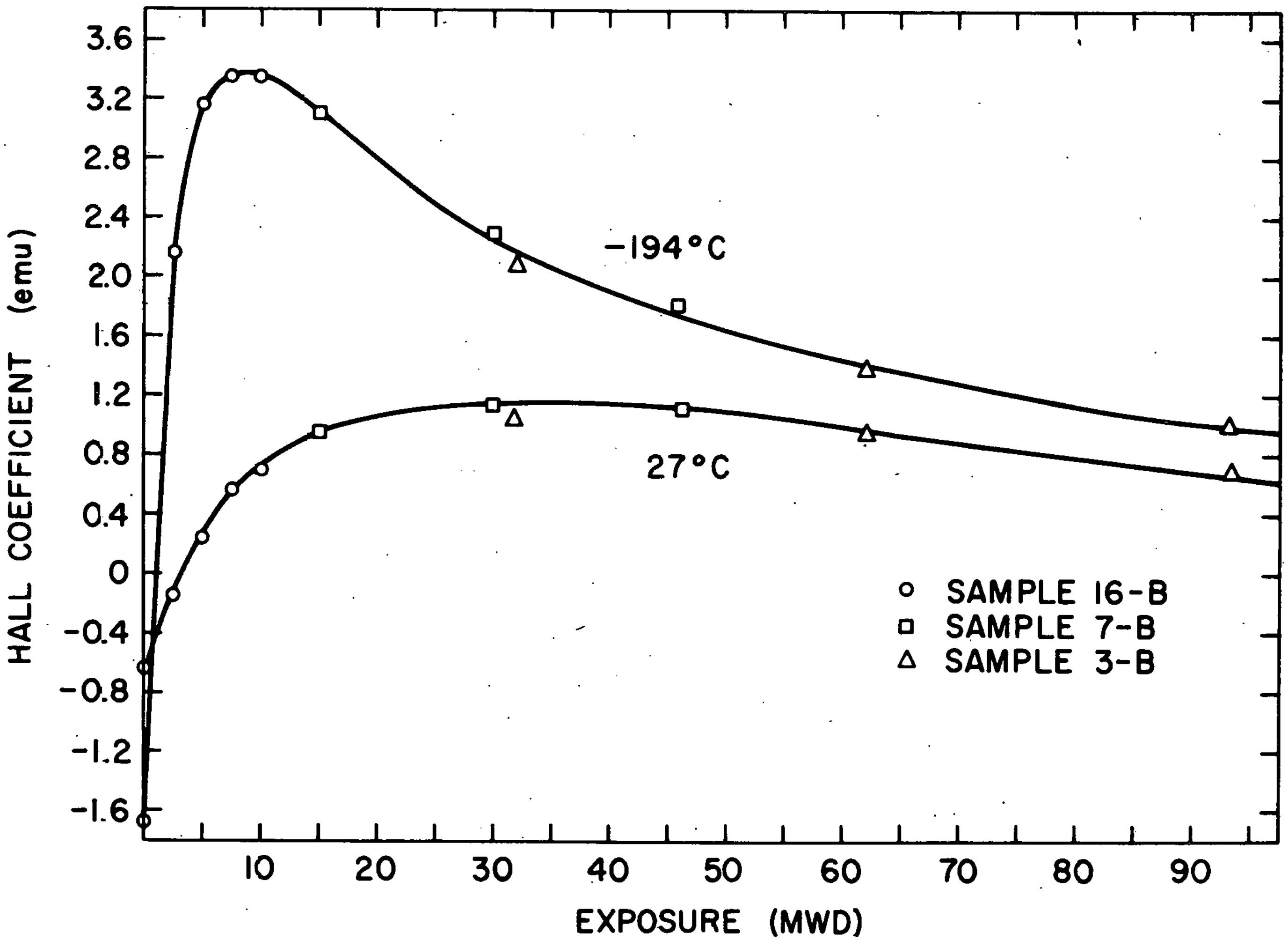
Figure 1. Dimensional changes in irradiated and periodically annealed graphite.

Figure 2. Changes in the Hall coefficient during irradiation.



0.12
0.10
0.08
0.06
0.04
0.02
0
PERCENT GROWTH
CONTINUOUS
IRRADIATION
D-10
B-13
A-16
A-10
100
120
140
160
180
200
220
240
EXPOSURE (MWD)

Fig 1.



HALL COEFFICIENT (emu)
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0
-0.4
-0.8
-1.2
-1.6
-194°C
27°C
SAMPLE 16-B
SAMPLE 7-B
SAMPLE 3-B
10
20
30
40
50
60
70
80
90
EXPOSURE (MWD)

Fig. 2

Table I

Dimensional Changes in Irradiated and Periodically Annealed Graphite

Group	Total exposure (MWD)	Number of anneals	Average total growth (%)	Average growth per MWD during irradiation (%)
A	196-199	17	0.010±0.005	0.00063
B	199-203	9	0.031±0.009	0.00060
C	230-235	6	0.028±0.012	0.00056
D	236-240	3	0.074±0.002	0.00049
E	228-232	2	0.072±0.013	data not available
F	233-237	1	0.117±0.003	0.00069
F′	233-237	0	0.163±0.007	same as F
H′	232-234	0	0.187±0.009	0.00080

Table II

Property Changes in Irradiated and Periodically Annealed Graphite

Sample designation	Number of anneals	C-axis values (A)	Hall coefficient (emu)		Electrical resistivity (ohm-cm)		Thermal conductivity at 350°C (Btu/hr-°F-ft)	Total stored energy (cal/g)
			-194°C	27°C	-194°C	27°C		
Virgin AGOT	Unirradiated	6.735	-1.71	-0.67	0.00217	0.00127	60.9	none
A-16	17	6.755	3.31	1.21	0.00393	0.00319	—	—
A-12	17	6.741	—	—	—	—	—	—
A-11	17	—	—	—	—	—	—	7
A-K2	17	—	—	—	—	—	30.4	—
B-16	9	6.761	2.74	1.31	0.00390	0.00341	—	—
B-13	9	6.755	—	—	—	—	—	—
C-13	6	6.772	2.56	1.35	0.00347	0.00316	—	—
C-K2	6	—	—	—	—	—	18.4	—
D-10	3	6.792	1.97	1.23	0.00406	0.00369	—	—
E-11	2	6.790	2.05	1.20	0.00403	0.00376	—	—
H-10	1	6.835	1.23	0.91	0.00414	0.00392	—	—
H-9	1	—	—	—	—	—	—	79*
F-K2	1	—	—	—	—	—	13.4	—
H-10′	0	6.900	0.52	0.45	0.00447	0.00416	—	—
H-9′	0	—	—	—	—	—	—	160*

*Samples H-9 and H-9′ were irradiated for 265 MWD.

Table III

Property Changes in Periodically Annealed Graphite
Compared to Changes in Continuously Irradiated Graphite

Group	Number of anneals	Growth	C-axis	Hall coefficient (-194°C)	Stored energy
A	17	0.07	0.09	0.06	0.06
B	9	0.22	0.16	0.10	
C	6	0.17	0.22	0.10	
D	3	0.45	0.34	0.16	
E	2	0.44	0.33	0.15	
F,H	1	0.72	0.60	0.30	0.49
F′,H′	0	1	1	1	1