CC-2758

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CHEMICAL RESEARCH - RADIATION CHEMISTRY

Milton Burton, Section Chief

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HEALING OF FAST-NEUTRON-INDUCED CHANGES IN GRAPHITE

III. Further Experiments on Effect of Heating During Exposure

Problem Assignment Number 323 MLC 2301

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Abstract:

It has been established that heating samples of graphite during exposure in a pile decreases substantially the observed changes in the elastic modulus and electrical resistance caused by the irradiation. The functional relationship between the percentage changes observed and the temperature of exposure resembles the relationship between the final percentage changes and the temperature of heat treatment after exposure (cf. report CC-1668). Anomalous results reported previously for higher temperatures in CC-1669 are now shown to be attributable to a destructive influence on the graphite, probably oxidation of samples exposed in air. (auth)

1. Introduction: Report CC-1669 gives preliminary results of a series of heating-during-irradiation experiments. Samples of artificial graphite were heated in air in graphite furnaces in hole 20 of the Site X pile and data obtained for neutron bombardment at 55, 83, 125, and 300°. The data at ≤ 125° included no unusual features, but at 300° the modulus change was zero while a small resistance change occurred. This lack of similarity between results at 125° and at 300° and the possibility of oxidation of the sample during the long irradiation at 300° made necessary a second more elaborate series of experiments with some of the higher-temperature samples exposed in vacuo.

2. Experimental details: In these experiments ten furnaces covered the range from pile temperature to 300°C in small steps. To heat each furnace separately, as in the earlier work, demanded a volume of power leads too large to fit in the stringer slots leading into the pile. Consequently, the ten units were wired in series and run from a single Variac through only one pair of power leads. Each furnace was wound with a particular kind, size, or length of wire adjusted to give the power dissipation required for maintenance of the unit at the desired temperature. Windings were chosen for a current of 1 ampere and an overall drop across the string of about 100 volts A.C. With the exception of this alteration, these furnaces were in every way identical with those described earlier (CC-1669 Appendix A). Two special furnaces were run at 300°C and at 500°C with the samples in vacuo. These were somewhat larger units built on a foundation of thin walled alundum extraction thimbles which accomodated six graphite samples sealed in evacuated quartz ampoules. Iron-constantan thermocouples in each furnace were used for temperature determination.

In the pile, the two alundum furnaces containing the samples sealed in vacuo, were put nearest the center in experimental hole 20. After these, were placed the ten series-connected furnaces, terminating in two unheated units containing control samples. A smooth temperature gradient was thus established from the 500°C heater nearest the center of the pile down to the pile temperature control samples nearest the face of the shield. The equilibrium temperatures, averaged from readings taken on the last five days of the run, are given in Table 1.

Table 1. Equilibrium temperatures for furnaces used in the high temperature irradiations in the Clinton pile

Unit	Temperature °C av. of last five days	Temperature °C last 24 hr.	Unit	Temperature °C av. of last five days	Temperature °C last 24 hr.
Control 4A[a]	110	110[b]	Furnace 6	225	226
Control 3A[c]	124	126	" 7	244	244
Furnace 1	130	131	" 8	310	311
" 2	142	143	" 9	333	334
" 3	159	160	" 10	343	344
" 4	178	180	Vac. furnace A	336	338
" 5	208	209	" " B	---	490

(a) This set was not directly heated.
(b) Average pile temperature in hole 20, during operation.
(c) Not directly heated; the excess above pile temperature is due to heat from the adjacent unit.

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The bombardment lasted 32 days, during which time the pile developed 46.8 Mw-d power (~3.5 L irradiation). There were no serious mishaps in the course of the experiments so far as temperatures were concerned. On discharging the furnaces, however, it was found that the vacuum furnace which was to have run at 500°C had burst and the samples were burned away. The 300° vacuum samples were in good condition; but even here, it was found on opening the quartz ampoules that there was no vacuum. Apparently there were gases driven from the graphite or other materials in the furnace (aluminum foil and asbestos) at high temperatures which developed pressures high enough to break a quartz ampoule at 500°C.

3. Results: Figures 1, 2, and 3 show the neutron-induced changes in the elastic modulus and electrical resistivity of the samples of the three types of graphite plotted against the temperature of irradiation. This temperature of irradiation was the temperature of the samples during the last 24 hours of irradiation and agreed, within the limits of fluctuation set by variation of pile temperature (~ $\pm$ 3 °C), with the averaged temperature for the last five days of running.

Data reported in CC-1669 and other observations, show that in the region below 130°C, neutron induced changes in the elastic modulus are much less temperature sensitive than the electrical resistivity. The extrapolations to lower temperatures were made in such a way that values obtained for expected changes at 35°C were consistent with existing $\Delta E/E_o$ versus $\Delta R/R_o$ plots prepared from other data for irradiations at 35°C. (See CC-2233 Figures 1, 2, and 3.)

The high temperature ends of the curves in Figures 1, 2, and 3 have two different forms, depending upon the presence or absence of air during the irradiation. This oxygen effect certainly is important for temperature of irradiation above 250°C and may be important at even lower temperatures. For samples irradiated in air at high temperature, there is apparently some degrading process which causes the resistance changes observed to be higher than those for vacuum exposed samples. The modulus changes for samples irradiated in air are lower, however, than those observed for vacuum irradiated specimens. The changes in weight observed on several of the samples used in these experiments, irradiated both in air and in vacuo, are given in Table 2.

At the same time the samples were under irradiation a similar set was heated in a graphite furnace identical with those used in the pile experiments and described earlier. The temperature of the furnace was maintained at 300°C and a slow stream of ozonized air (from an Electronaire ozonizer) was passed over it for 30 days. Table 3 gives the effects. In general, the electrical resistivity increased about 4%, and the elastic modulus decreased about 7%. Changes in weight were -0.6 to -0.8%. The interpretation is that the bending at the high-temperature ends of the neutron effect versus temperature curves in Figures 1, 2, and 3, is an oxidative degradation. The description of the phenomenon as a degradation is consistent with some observations on several samples of irradiated and unirradiated graphite purposely maltreated by placing the samples on a smooth steel surface and gently pounding them with a hammer. This treatment was found to decrease the elastic modulus by as much as 30% and to increase the resistivity by ~12%, depending upon the extent and severity of the treatment.

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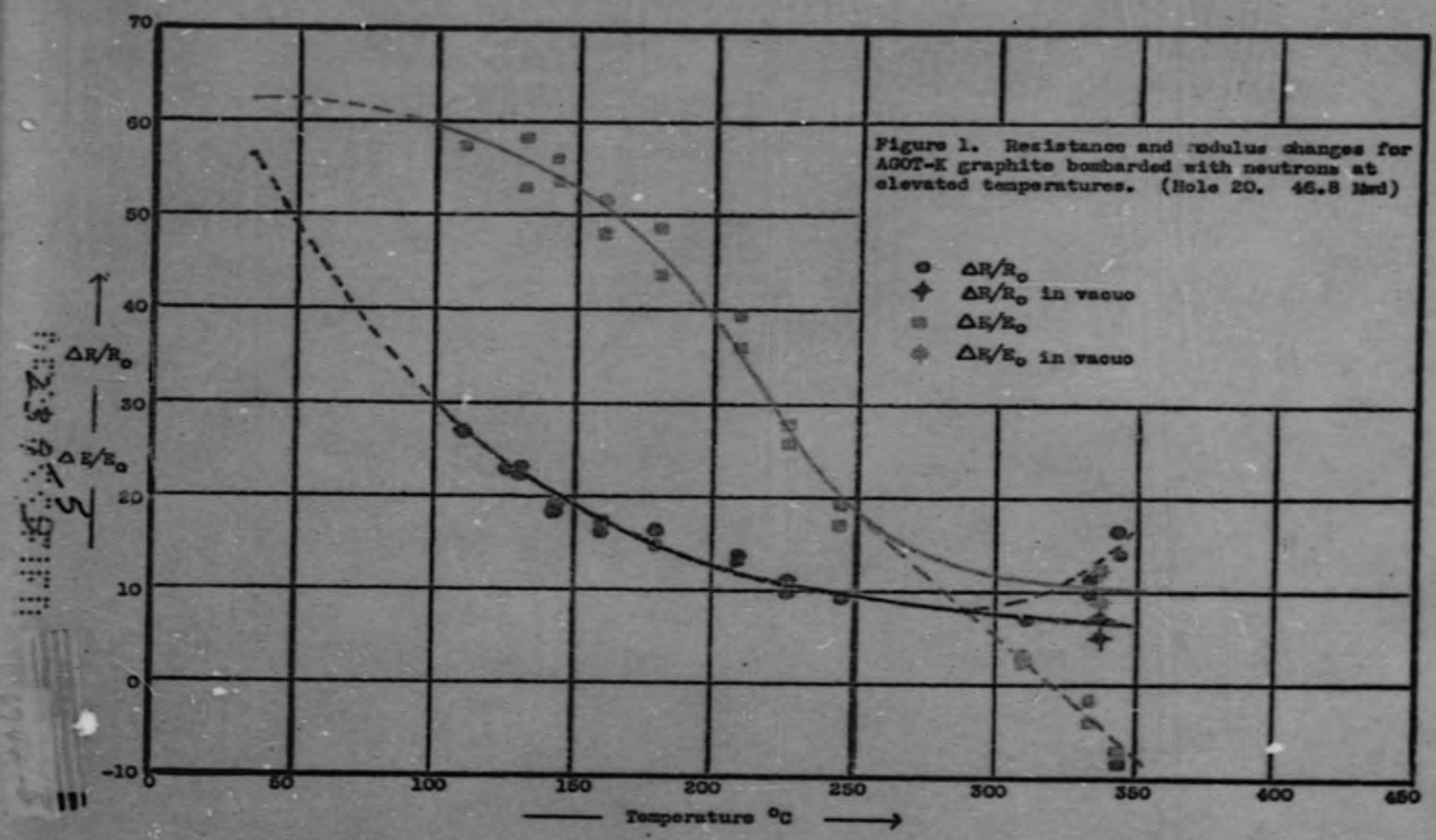

Figure 1. Resistance and modulus changes for AGOT-K graphite bombarded with neutrons at elevated temperatures. (Hole 20. 46.8 Mwd)

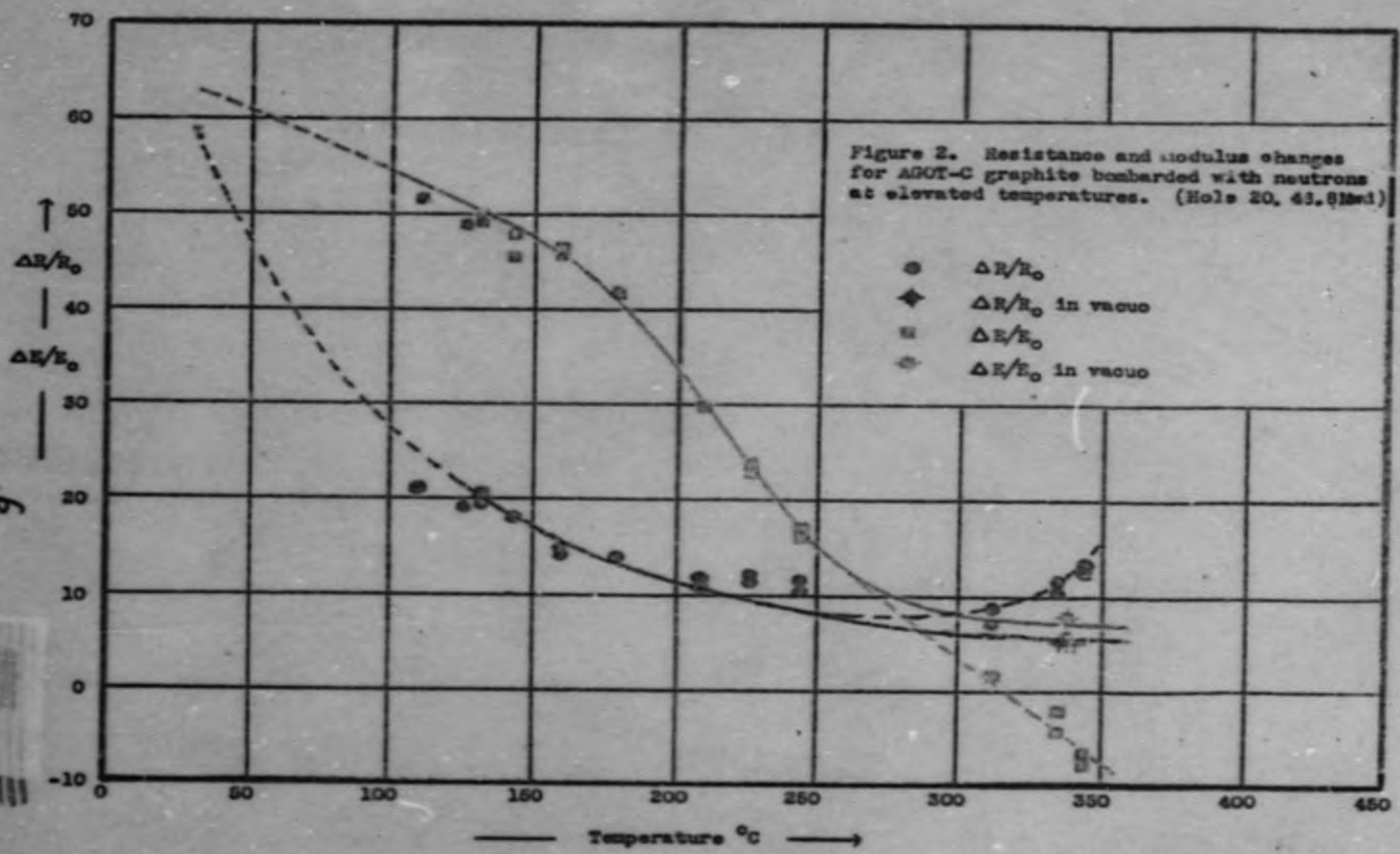

Figure 2. Resistance and modulus changes for AGOT-C graphite bombarded with neutrons at elevated temperatures. (Hole 20, 43.8 Mwd)

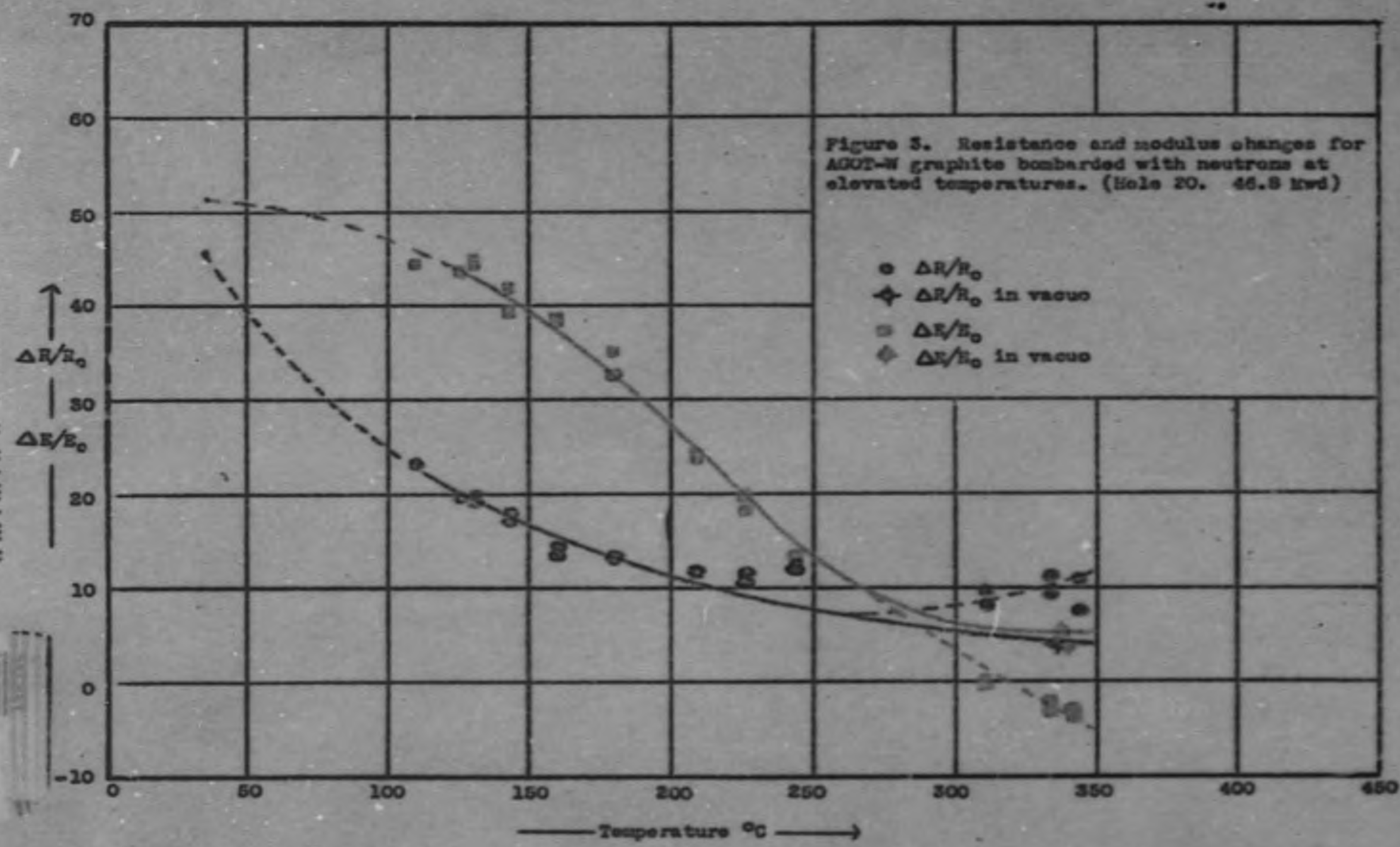

Figure 3. Resistance and modulus changes for AGOT-W graphite bombarded with neutrons at elevated temperatures. (Hole 20. 46.8 Mwd)

Table 2. Weight changes for samples heated and irradiated in air and in vacuo

Sample	Furnace temperature	W_o (g)	W_x (g)	$\frac{\Delta W}{W_o}$
CP95 CP96	244°C	.7176 .6687	.7162 .6705	+.001 +.003
WP115 WP116	244°C	.6847 .6807	.6857 .6819	+.002 +.002
CP97 CP98	311°C	.7125 .7306	.7129 .7292	+.001 -.002
WP117 WP118	311°C	.6854 .6813	.6835 .6796	-.003 -.003
CP99 CP100	334°C	.7118 .7265	.7081 .7224	-.005 -.006
WP106 WP107	334°C	.6872 .6850	.6838 .6798	-.005 -.008
CP101 CP102	344°C	.7125 .7187	.7065 .7143	-.009 -.006
WP97 WP105	344°C	.6822 .6775	.6783 .6719	-.006 -.008
CP120 CP119 CP121	338°C in vacuo	.7146 .7224 .7167	.7163 .7224 .7169	+.002 0 0
WP95 WP96	338°C in vacuo	.6866 .6821	.6873 .6825	+.001 +.001

4. Discussion: The uncertainties raised by the zero modulus change at 300°C reported in CC-1669 have been very satisfactorily explained by the data obtained in the present work. There is apparently an oxidation occurring at high temperatures which has the effect of lowering the elastic modulus. At 300°C this decrease resulting from oxidation and the increase caused by irradiation so counterbalance that no net change is observed. These details emphasize the importance of conducting future experiments in vacuo even at much lower temperatures than 300°C, for at present there is no way of knowing at what temperature the oxidizing phenomena begin to be important.

Table 3. Data obtained for four unirradiated graphite samples heated at 300°C for 30 days in a stream of "ozone"

Type of graphite	$\Delta R/R_o$	$\Delta E/E_o$	W_o (g)	W_f (g)	$\Delta W/W_o$
AGOT-K	+.044	-.070	.8382	.8334	-.0057
	+.037	-.056	.8302	.8251	-.0061
AGOT-N	+.037	-.065	.6793	.6743	-.0080
	+.042	-.080	.6757	.6703	-.0080

The shape of the neutron effect versus temperature of irradiation curves, Figures 1,2, and 3, are very dependent upon the method of extrapolation back to low temperatures. Every effort has been made to keep these extrapolations consistent with all our knowledge of the behavior of graphite. However, additional irradiations will be necessary in parts of the pile where the lowest temperature of the string of furnaces can be much closer to 35°C. This procedure will eliminate the difficulties of extrapolation to low temperatures.

A third incomplete detail is the dependence of the neutron-induced changes at various elevated temperatures upon the extent of irradiation. This topic is under active investigation.