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THERMOELECTRIC POWER AND INTERNAL FRICTION OF SOME GRAPHITIC CARBONS

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The authors and co-workers have recently prepared a series of articles[1-5] concerned with the dynamic mechanical properties (DMP) of various graphitic and turbostratic carbons and the effects of heat-treatment and irradiation on these properties. It was shown[3] that an internal friction peak (α peak) was usually present near room temperature in samples possessing appreciable three-dimensional ordering (graphitic carbons) and that the height of this peak was markedly reduced by low temperature (~500°K) annealing or low dose reactor irradiation ($<10^{16}$ nvt fast).[5] It was concluded that the α peak had nearly all the characteristics of a Bordoni peak in metals.[3] It was also shown[4] that stress-graphitizing as-deposited pyrolytic carbon (PC) typically increased the internal friction by an order of magnitude, sometimes resulting in the appearance of an α peak, and often greatly increasing the dynamic modulus. Irradiation effects on the internal friction and dynamic modulus of the stress-graphitized PC were observed to be much greater[5] than for the as-deposited material.[1]

It is probable that the α peak in graphite is determined primarily by the density of basal dislocations and their mobility. The mobility, in turn, is primarily determined by the number of point defects in the graphite, a fraction of which act to effectively pin the dislocations. With increased pinning, the internal friction decreases. The thermoelectric power (TEP) of graphitized carbons is also markedly dependent upon the concentration of point defects.[6,7] Some of the point defects act as trapping states for negative carriers, resulting in the TEP changing in the positive direction. Thus it is of interest, for a variety of graphitic carbons, to see if there is any relation between their internal friction (α peak) and TEP, and to observe the changes which occur in these properties with annealing and neutron irradiation.

A previously described apparatus[6,7] was used for the TEP measurements. A check of the apparatus was made using Chromel-P alloy; the results were within four percent of published values.[8] All values reported are absolute TEP. Results for commercial grades of artificial graphite, hot-pressed artificial graphite (UHD), and pitch-bonded natural graphite flakes (SP-1 plus binder) are summarized in Fig. 1. The grades are characterized in Table 1. Duplicate samples of each grade were measured. At least one sample of each grade was removed from the apparatus and then was reinserted and remeasured.

From the data of Fig. 1 and the previous DMP results,[3] it appears that there is no simple relationship between TEP and internal friction. For example, the α peak was very pronounced for the SP-1 plus binder and UHD samples, but it was much smaller for the reactor grade material; whereas the TEP of the reactor grade material generally falls between that for the SP-1 plus binder and UHD samples. Also, the α peak was about the same height for the 791, 787S and reactor grade sample, while the TEP level of the reactor grade sample was appreciably more negative than those for the 791 and 787S grades.

Samples of SP-1 plus binder and grade 791 were irradiated to a fast flux of 1.4×10^{17} nvt. Their TEP was shifted in a positive direction as a result of the irradiation (Fig. 2). Heating the irradiated sample to 490°K produced no measurable change in TEP. Also non-irradiated but machined samples of SP-1 plus binder and grade 791 were heated to 1800°C without measurably changing their TEP. In contrast, marked changes occurred in the DMP after these treatments.[3,5]

The TEP results for the as-deposited PC

TABLE 1 CHARACTERIZATION OF GRAPHITES

Grade	Density, g/cc H_2O	 C_2H_5OH	Interlayer Spacing A	TEP* $\mu v/^{o}K$	Internal Friction x 10^4 (α peak)
791	1.56	2.01	3.360	-1.4	54
787S	1.71	2.12	3.360	-0.13	47
Reactor	1.68	1.99	3.360	-3.8	42
UHD	2.00	2.08	3.358	-2.9	76
MI	1.77	1.99	3.360	+0.62	35
SP-1	——	——	3.354	-4.6	80
PC**	2.21	2.21	3.44	+9.8	6
PC***	2.24	2.24	3.354	-6.1	50

* at 100°C
** as-deposited
*** stress-graphitized

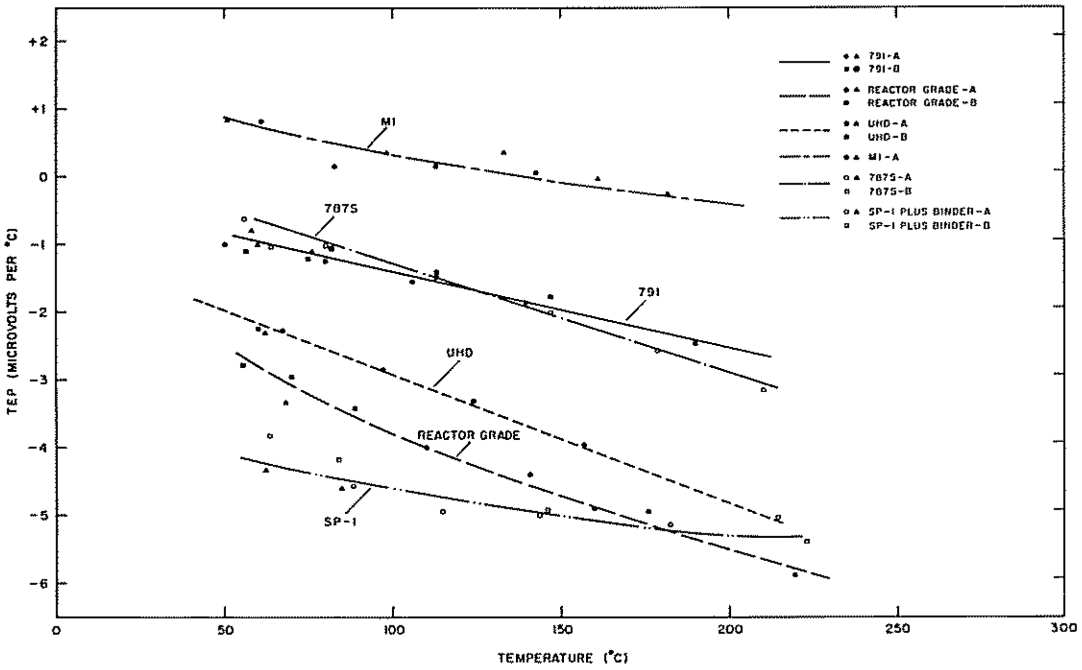

FIG. 1, TEP OF VARIOUS GRAPHITIC CARBONS

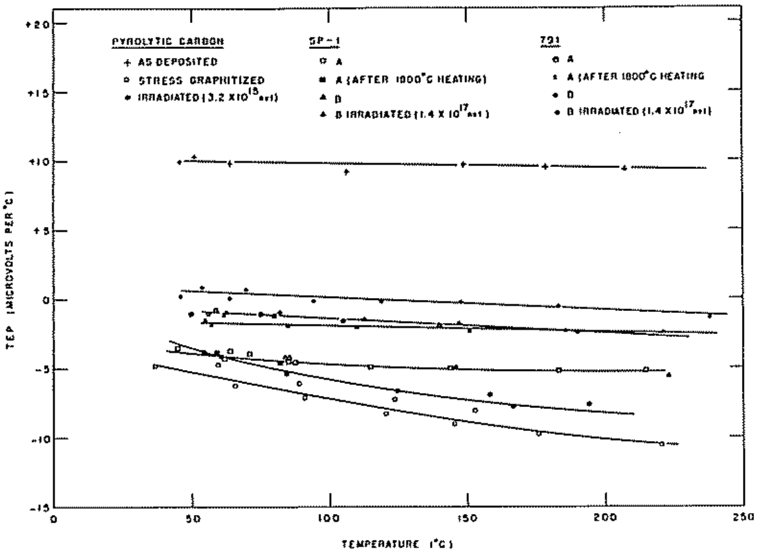

FIG. 2, EFFECT OF HEAT TREATMENT AND IRRADIATION ON TEP OF SELECTED GRAPHITIC CARBONS

and for the same samples after stress-graphitizing[4] are shown in Fig. 2. The TEP changed from +9.8 to -6.1 volts/°C (at 100°C) as a result of stress-graphitizing. Internal friction of samples stress-graphitized under the same conditions[4] increased from $6x10^{-4}$ to $50x10^{-4}$. Thus stress-graphitizing as-deposited PC (resulting in removal of point defects) markedly affects both the TEP and internal friction, in the direction expected.

Reactor irradiation of the stress-graphitized sample to an integrated fast neutron flux of $3.2x10^{15}$ nvt changed the TEP to somewhat more positive values. This level of dose produced the appearance of strong internal friction peaks at 165, 340 and 440°K.[5] Thus both the TEP and the DMP of stress-graphitized PC are quite sensitive to the radiation-induced production of point defects.

In summary, there appears to be no simple overall correlation between the internal friction and TEP of graphitic carbons. Low temperature annealing of machined samples significantly reduced internal friction but did not detectably change the TEP. Low-dose irradiation caused complex changes in internal friction-temperature plots while only the general level of the TEP was changed somewhat in the positive direction. Stress-graphitizing as-deposited PC markedly changed both internal friction and TEP.

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REFERENCES

1. Brennan, J. J. and D. E. Kline, Carbon 5, 181 (1967).
2. Taylor, R. E. and D. E. Kline, Carbon, in press.
3. Taylor, R. E., D. E. Kline and P. L. Walker, Jr., Carbon, in press.
4. Taylor, R. E. and D. E. Kline, Carbon, accepted for publication.
5. Taylor, R. E. and D. E. Kline, Chemistry and Physics of Carbon, P. L. Walker, Jr., Editor, M. Dekker, New York, Vol. 5, in preparation.
6. Walker, P. L. Jr., L. G. Austin and J. J. Tietjen, Chemistry and Physics of Carbon, Vol. 1, 1966, pp. 327-365.
7. Walker, P. L. Jr. and Y. Sasaki, Carbon 4, 536 (1966).
8. Grosewald, P. S. Ph. D. Thesis, The Pennsylvania State University, 1966.