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THE DYNAMIC MECHANICAL BEHAVIOR OF GRAPHITES*

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Abstract—The stress–amplitude independent internal friction and dynamic elastic modulus of pitch-bonded natural graphite crystals and various grades of commercial graphites were measured from 4 to 750°K at frequencies in the range of 0.6 to 10 kcps. For these materials, the internal friction, which was an order of magnitude larger than that previously reported for as-deposited pyrolytic carbon and vitreous carbons, is primarily characterised by a broad peak (designated as the α peak) centered near room temperature, accompanied by an elastic modulus relaxation. The peak characteristics, including a reduction in peak height by annealing or low-dose reactor irradiation (4×10^{16} nvt), closely corresponded to that previously observed for the Bordoni peak in fcc metals. Similar to the suggested mechanism in metals, the α peak may be associated with the motion of basal plane dislocations. The investigation also revealed the presence of a small relaxation below 60°K in some graphites, and, in one case, a very sharp peak above room temperature. It is assumed that the former may be associated with impurities. The latter peak, which anneals out, is similar in some respects to a few cited cases in metals.

1. INTRODUCTION

Tsuzuku and co-workers have published several reports(1–4) and a review paper(5) dealing primarily with the strain–amplitude dependence of the internal friction (Q^{-1}) and dynamic modulus (E) for certain graphites and carbons. In general, they found a linear relation when $\ln (Q_H^{-1} \epsilon_o)$ was plotted against $1/\epsilon_o$ where ϵ_o is the maximum strain amplitude and Q_H^{-1} is the amplitude-dependent part of the internal friction. This linearity is predicted by the Granato-Lücke theory,(6, 7) which is based on the stress-induced unpinning of dislocation loops at intermediate points while the ends of the dislocation remain fixed. However, in addition to the above, linear relations were also observed for glassy carbon and as-deposited pyrolytic carbons, although these materials are relatively disordered.

Tsuzuku and co-workers(5) have also measured the amplitude-independent values of Q^{-1} and E as a function of temperature for several samples of reactor grade graphite, brominated reactor grade graphite and boronated as-deposited pyrolytic carbon. Currie *et al.*(8) reported room-temperature damping factors for several grades of graphite, but they did not indicate the strain amplitudes employed. Davidson *et al.*(9) measured the damping of several graphites at elevated temperatures. Since they used relatively large strain amplitudes, it is assumed that they were probably in the amplitude-dependent region.

Investigations by the present authors and co-workers represent the first reported attempt to systematically investigate the strain-amplitude independent behavior of the dynamic mechanical properties (DMP) of a variety of graphites and carbons. The present paper, which is concerned with the DMP results for various commercial graphites and pitch-bonded natural graphite crystals, is one of a series reporting the results of these studies. Previous papers reported behavior of the internal friction and dynamic modulus of as-deposited pyrolytic carbon(10) and of vitreous carbon.(11) Subsequent papers will

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deal with the changes in the DMP of pyrolytic carbon caused by stress-annealing and boronation and with the effect of low-dose reactor irradiation on the DMP of various graphites and carbons.

2. EXPERIMENTAL

2.1 *Apparatus*

Two types of apparatus were used in conjunction with the DMP studies. The longitudinal apparatus was a modified version of one described by CRISSMAN and McCAMMON.(12) The method consists of driving the vertically suspended sample in either its fundamental longitudinal mode or a higher mode and measuring the resonant frequency and internal friction. A magnetostrictive transducer is used to excite the sample. One end of the sample is attached to the transducer by means of a small diameter tube or rod. Iron filings are glued to the other end of the sample, and then this end is positioned within a pickup coil to detect sample vibrations. The signal induced in the coil resulting from the movement of the iron filings in a divergent magnetic field is amplified, filtered and recorded. Provisions are incorporated for varying the sample temperature from 4 to 570°K and for operating from a vacuum of about 10^{-4} torr to atmospheric pressure.

The transverse apparatus, which was described in a previous paper(10) has been used by a number of researchers to measure the DMP of a variety of materials. Each specimen, in the shape of a rod, is suspended horizontally by two strings near its primary nodes of transverse vibration. One string is attached to a magnetostrictive transducer used to drive the sample, and the other string is attached to the stylus of a piezoelectric crystal pickup cartridge used as a detector. The oscillator and power amplifier used to supply driving power for the sample, as well as the amplifiers, filters, oscilloscope and recorder used to measure the sample response, are identical to that used with the longitudinal apparatus. The sample is supported within a chamber whose temperature can be varied from 80 to 800°K.

The longitudinal apparatus can be used down to 4°K and operates in a vacuum. The results are relatively independent of the cross-sectional sample geometry. However, for some investigations, the transverse apparatus has several distinct advantages. The present upper temperature limit for the transverse apparatus is about 800°K compared to about 570°K for the longitudinal apparatus; and because of the higher detector sensitivity, the strain amplitudes are several orders of magnitude less. The fundamental resonant frequency for the flexural mode is one to two orders of magnitude less than for the longitudinal mode. Usual frequencies for the flexural mode are in a convenient range for linear operation of the presently employed magnetostrictive transducer and associated electronics.

2.2 *Materials*

A series of polycrystalline graphites with widely varying densities were used in the present study. Commercial grades included Speer Carbon Company's grades 791, 787S and UHD, the reactor grade graphite used in the Pennsylvania State University sub-critical reactor facility, and an unspecified grade which is arbitrarily designated as MI. The UHD grade was obtained by hot-pressing the 787S grade at 3200°C and 10,000 psi by the Speer Carbon Company. This grade is similar to the National Carbon Company's grade ZTA which has been extensively studied by BUSHONG and NEEL.(13)

Highly purified natural graphite crystals (grade SP-1 from Union Carbide Corporation) were also used. Some properties of SP-1 crystals were described previously.(14) Microscopic investigation revealed the powder to be composed of flake-like particles having a mean diameter of about 30μ; it is thought that their average thickness is about 0.5μ. Formed bodies were produced from 87 parts SP-1 and 13 parts of a medium melting point coal tar pitch; these bodies were heated to 2900°C.(15)

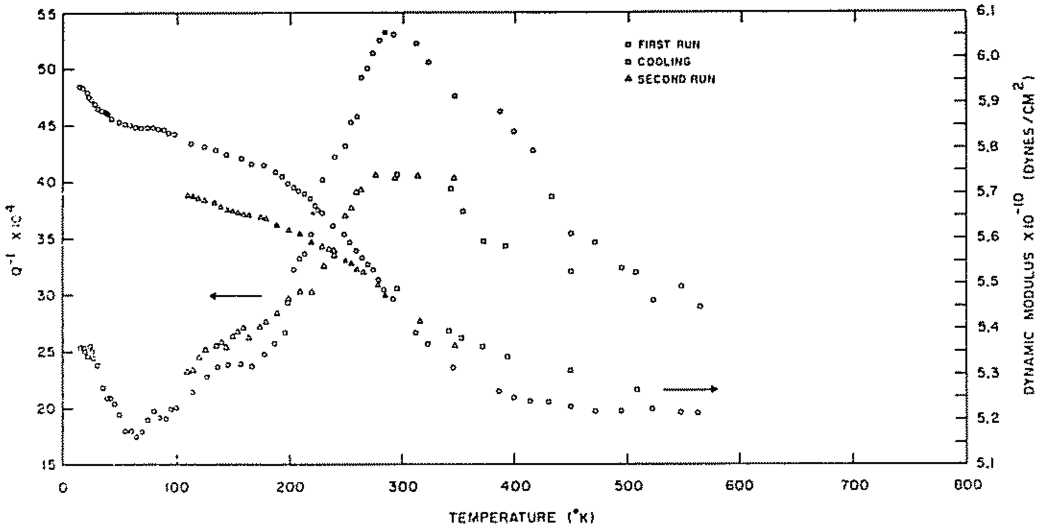

FIG. 1. Internal friction and dynamic elastic modulus (longitudinal method) of artificial graphite (Speer Grade 791, Sample 791-G-3).

All graphites were characterised by their density, interlayer spacing, absolute thermoelectric power (TEP), and static modulus in addition to their dynamic properties (see Table 1). Densities were obtained by the immersion technique using both water and alcohol. The bulk density obtained by using water was employed in calculating the dynamic moduli. The interlayer spacings were obtained using a GE XRD-5 with an MR5 slit and a copper target. The procedure outlined previously(16) was used. This procedure involved the use of the (222) peak of NaCl as an internal standard to correct the measured position of the (004) peak of graphite for instrumental errors. The interlayer spacings were calculated using the wave length of CuK_{α_1} and were not corrected for thermal expansion or for the various effects mentioned by SHORT and WALKER.(17)

3. RESULTS

3.1 *Grade 791*

The DMP of grade 791 samples designated 791-G-1A, 791-G-2 and 791-G-3 were deter-

TABLE 1. TYPICAL PROPERTIES OF GRAPHITES*

Grade	Density (g/cm³)		Interlayer spacing (Å)	Absolute TEP (μV/C°)	Static modulus (10^{10} dyn/cm²)	Dynamic modulus (10^{10} dyn/cm²)		Internal friction (10^{-4})	
	H_2O	C_2H_5OH				Long.	Trans.	Long.	Trans.
791	1.56	2.01	3.360	−1.4	5.0	5.3	5.3	54	54
787S	1.71	2.12	3.360	−1.3	6.0	6.2	6.1	47	50
Reactor	1.68	1.99	3.360	−3.8	10.4	11.4	11.5	42	45
UHD	2.00	2.08	3.358	−2.9	4.2	4.3	4.3	76	78
MI	1.77	1.99	3.360	+0.6	11.5	12.7	12.7	35	41
SP-1	1.75	2.11	3.354	−4.6	5.1	6.8	3.5–7.7	78	80

* TEP values for 100°C, other values for room temperature.

mined from about 10 to 570°K using the longitudinal apparatus and that of sample 791-G-7 was determined from 90 to 720°K in the transverse apparatus. In addition, several samples were measured over more limited temperature ranges in both pieces of apparatus.

The results obtained on sample 791-G-3 are shown in Fig. 1. The data were obtained during the heating cycle from 12 to 565°K and during the cooling cycle to 293°K. A second run was made from 100 to 345°K. The data from the first run revealed a broad, nonsymmetrical internal friction peak at 290°K which was accompanied by a relaxation in the dynamic modulus. The data obtained during the second run (and during the cooling cycle from the first run) showed that the peak height was substantially reduced and that this reduction was accompanied by a decrease in the magnitude of the modulus relaxation. Further, in the first run Q^{-1} decreased from 25.3×10^{-4} at 13°K to 18.0×10^{-4} at 55°K; this decrease was accompanied by a modulus relaxation. DMP data were not obtained below 13°K, but it is not unreasonable to expect that Q^{-1} again decreases as one approaches absolute zero. Humps in the internal friction curves at about 155°K were also observed during both runs (Fig. 1). There was a small modulus relaxation associated with these humps.

Data for samples 791-G-1A and 791-G-2 were obtained in a different temperature sequence from that used for samples 791-G-3, i.e. the measurements were obtained from liquid-nitrogen to room temperature (*RT*), then liquid-helium to liquid-nitrogen temperature, and finally above *RT*. This latter sequencing was often used during our measurements. The internal friction values obtained in the temperature-overlap regions were almost always in close

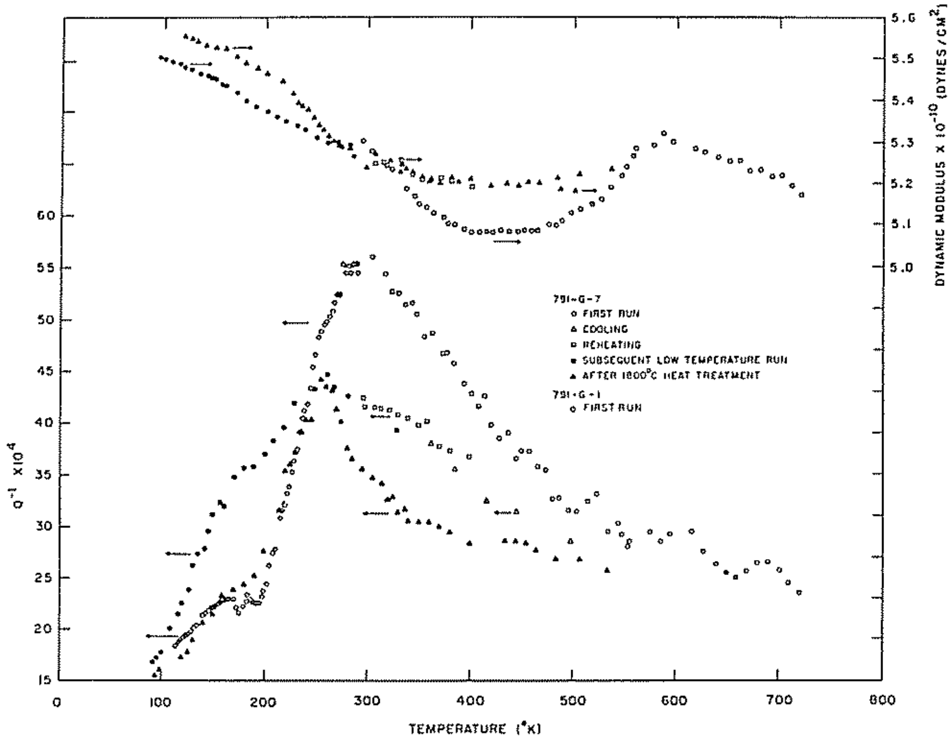

Fig. 2. Internal friction and dynamic elastic modulus (transverse method) of artificial graphite (Speer Grade 791, Samples 791-G-1 and 791-G-7).

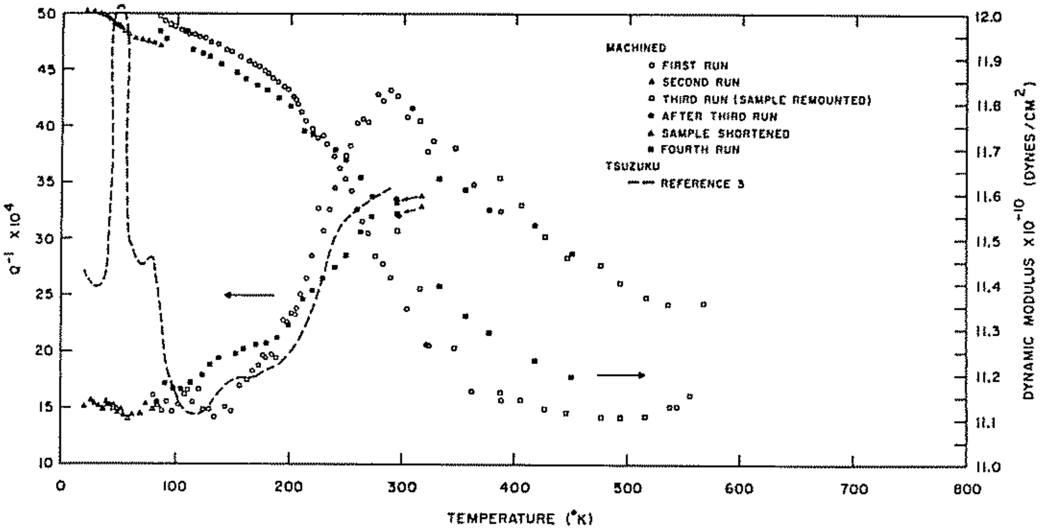

Fig. 3. Internal friction and dynamic elastic modulus of reactor grade graphite.

agreement. However, the overall level of the dynamic moduli curves was often shifted downward a small amount.

Internal friction and dynamic moduli values obtained on samples 791-G-7 and 791-G-1, using the transverse apparatus, are shown in Fig. 2. In close agreement with the results obtained with the longitudinal apparatus, a broad internal friction peak was observed near *RT*; the peak height was substantially reduced by heating in the 500 to 700°K range. Data for sample 791-G-7 were obtained first from *RT* to 700°K; and since heating over this temperature interval substantially reduced the internal friction peak, a second sample (791-G-1) had to be used to fill in the data from 100 to 295°K. As can be seen in Fig. 2, the data for the two samples agreed near *RT*. The dynamic moduli for sample 791-G-7 exhibited the same large broad relaxation behavior as that shown for sample 791-G-3 (Fig. 1) with one exception. The dynamic moduli obtained during the first run with the flexural apparatus increased above 500°K; whereas, the dynamic moduli measured using longitudinal vibrations were nearly temperature independent between 500 to 560°K.

Following the second run, sample 791-G-7 was heat-treated at 1800°C in a graphite tube furnace prior to remeasuring its dynamic properties. This heat treatment produced a much sharper internal friction peak centered near 255°K. Similar results were obtained with other samples.

3.2 *Reactor grade graphite*

The dynamic mechanical properties of RG-1 were measured from 84 to 388°K during the first run and from 18 to 85°K during the second run. Both the internal friction and dynamic modulus curves are shown in Fig. 3. The mismatch in the dynamic modulus curves for the two runs was 0.8 per cent at 85°K, which was much greater than the usual limit of reproducibility, suggesting that heating to 388°K altered the sample properties. Several months after the second run, the sample was remounted on stainless steel tubing, and data from *RT* to 555°K were obtained (third run, Fig. 3). Room-temperature values following the third run indicated that the internal friction had decreased from 43 to 33×10^{-4}, while the modulus had increased from 11.52 to 11.55×10^{10} dyn/cm^2. Because the bottom of the sample appeared discolored following the third run, about 0.06 in. was machined off the end, and a new iron filing-epoxy layer was applied. Since measurements on the shortened sample agreed quite closely with the results obtained following the third run (see Fig. 3), it was assumed that further experimentation could be carried out on the same sample and a fourth run from 85 to 450°K was made. The results of the four runs showed that the height of the broad internal friction peak at 290°K was substantially reduced by heating to 555°K. There was a hump located on the low-temperature side (130–200°K) of this peak. In addition, the data revealed an inflection in the dynamic modulus in the 30 to 60°K range and a relatively small decrease in Q^{-1} around 50°K.

The internal friction curve obtained by TSUZUKU[2] for reactor grade graphite is also shown in Fig. 3. Since TSUZUKU reported frequencies rather than dynamic moduli and did not include sample geometries in his report, dynamic modulus values for his sample are not included in Fig. 3.

3.3 *Grades 787S and MI*

The DMP of samples of grades 787S and MI were also investigated. A broad internal friction peak centered near *RT* was observed during the initial run for each of these samples. This peak was decreased by annealing above 500°K in the manner indicated for the 791 and reactor grade material. The height of the internal friction peak was 50×10^{-4} for the 787S material and about 40×10^{-4} for the MI material. The dynamic modulus behavior of the 787S and MI samples was also similar to that described for the 791 and reactor grade materials.

3.4 *Speer Grade UHD*

The DMP of a sample designated UHD-A-6, obtained from 6 to 338°K during the first run using the longitudinal apparatus, are shown in Fig. 4. The data between 338 and 340°K indicated an extremely sharp Q^{-1} peak. The internal friction increased from 70×10^{-4} at 338°K to 154×10^{-4} at 340°K and decreased to 90×10^{-4} at 343°K. The sample was then allowed to cool from 342°K, and this sharp peak was also observed during the cooling cycle. About 0.03 in. was machined off the lower end of the sample, and the DMP were measured from 295 to 350°K. These data (designated in Fig. 4 as second run—sample shortened) indicated that the sharp peak was no longer present. Sample UHD-A-6A, whose RT DMP values were very close to those of UHD-A-6, was used to obtain data from 295 to 562°K presented in Fig. 4. No sharp peak was observed with sample UHD-A-6A.

The Q^{-1} peak near *RT* for the UHD material was about twice as high as that observed with the 791, 787S and reactor grade graphites, and the modulus relaxation was correspondingly greater. However, the hump observed on the low-temperature side of the Q^{-1} peak for UHD-A-6 was less pronounced than for the other graphites. There was also some evidence of minor-sized Q^{-1} peaks below 80°K for sample UHD-A-6. For instance, a small peak and an inflection in the dynamic modulus were discernible near 10°K.

As a result of heating UHD-A-6A to 562°K, its *RT* Q^{-1} value decreased from 85.4 to 55.8×10^{-4} while its dynamic modulus increased from 4.197 to 4.204×10^{10} dyn/cm². The large change in Q^{-1} caused by heating and the relatively high mechanical strength of the UHD material indicated that this would be a good material for investigating the effects of cold working and annealing. Consequently, sample UHD-A-6A was subjected to a sequence of non-uniform compressive forces followed by annealing. The compressive forces were applied by compressing the round sample between flat plates in a vise. The results (all measured at room temperature) are presented in Table 2.

The DMP of sample UHD-A-9A were measured with the transverse apparatus. DMP data were obtained from 120 to 650°K during the first run, and the sample was then cooled and remeasured from 109 to 392°K. The Q^{-1} data were in very close agreement with that obtained using the longitudinal apparatus. How-

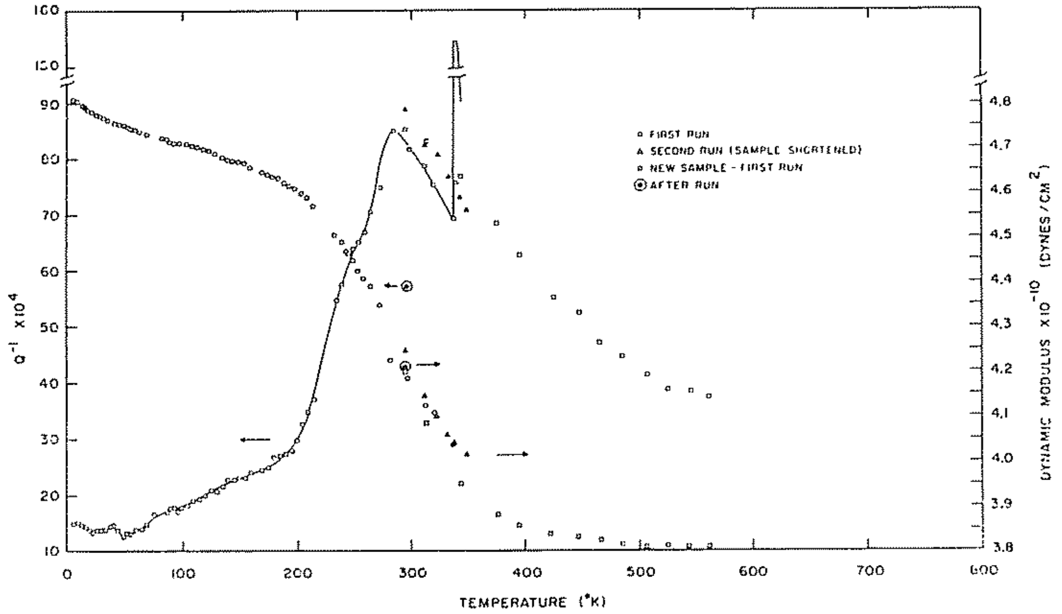

FIG. 4. Internal friction and dynamic elastic modulus of hot-pressed artificial graphite (Speer Grade UHD, Samples UHD-A-6 and UHD-A-6A).

ever, the indicated dynamic modulus obtained in flexure increased with temperature between 500 to 600°K, while the longitudinal measurements showed the modulus to be essentially temperature independent between 500 and 562°K. A comparison of the first and second runs further showed that the DMP values were markedly altered as a result of heating to 650°K.

3.5 *Pitch-bonded natural graphite crystals*

The DMP data for a typical sample of pitch-bonded SP-1 crystals (sample SP-1V) are shown in Fig. 5. The first run revealed the presence of a large Q^{-1} peak at 255°K. The second run (185–580°K) showed that although heating to 350°K had reduced the Q^{-1} peak height from 110 to 100 × 10^{-4}, the peak was

TABLE 2. EFFECT OF COMPRESSION AND ANNEALING ON SAMPLE UHD-A-6A

Treatment	Resonant frequency* (cps)	Dynamic modulus† (10^{10} dyn/cm^2)	Internal friction (10^{-4})
As-machined	13,230	4.197	85
Heated to 562°K	13,241	4.204	56
Stored for 4 months	13,208	4.183	67
Compressed in vise	13,100	4.115	83
Heated to 580°K	13,148	4.145	60
Compressed in vise	13,086	4.106	67
Compressed in vise	12,905	3.993	75
Stored for 2 months	13,137	4.138	57

* ±1 cps.
† The relative values have tolerances of ± 0.001.

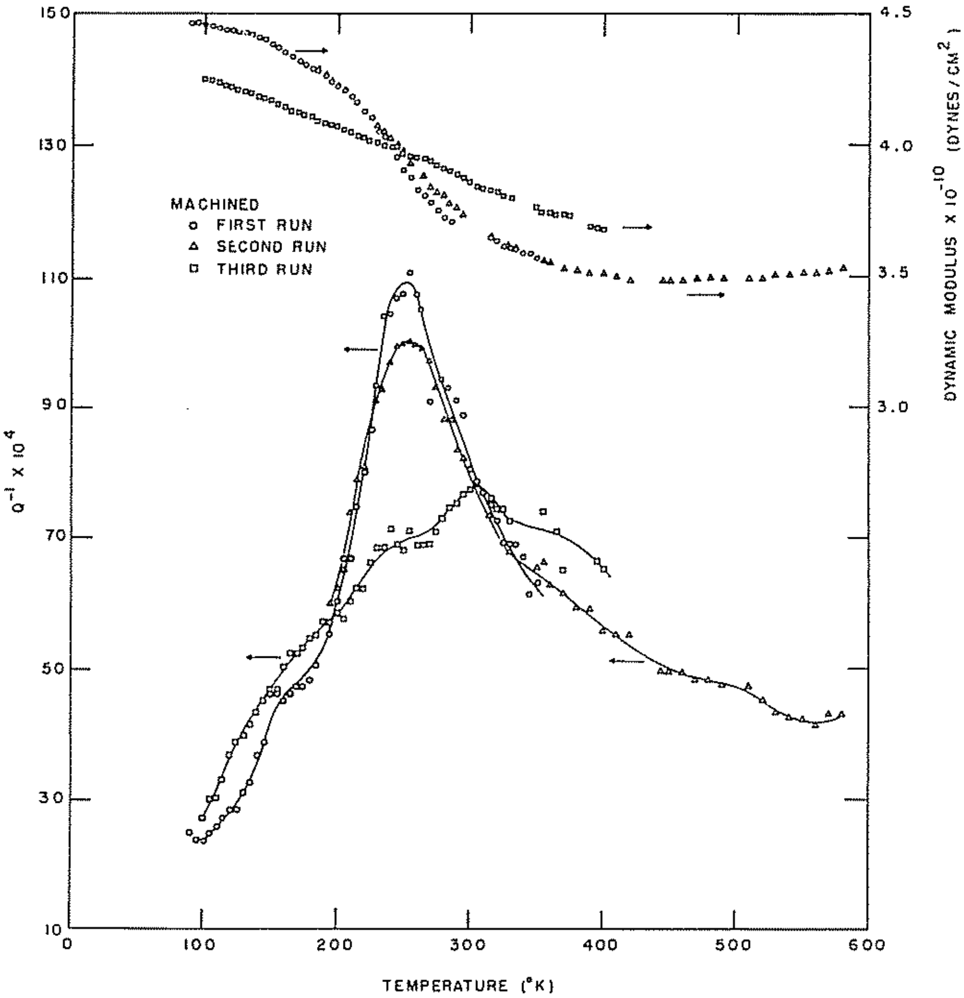

Fig. 5. Internal friction and dynamic elastic modulus of pitch-bonded natural graphite flakes (Sample SP-1V).

still clearly defined. The third run (100–400°K) demonstrated that heating to temperatures above 500°K greatly altered the Q^{-1} peak. When similar samples were annealed at 1800°C, a relatively sharp peak developed much as the sharp peak developed under similar conditions for the 791 grade graphite (Fig. 2).

4. DISCUSSION

4.1 *The α peak*

A study of the Q^{-1} data for the various commercial graphites and pitch-bonded natural crystals revealed that a reasonably consistent pattern was obtained for all polycrystalline graphites studied. A broad internal friction peak (which will be referred to as the α peak) was present near *RT* in machined samples of the as-received material. The α peak, with an associated hump on its low-temperature side, was invariably accompanied by a relaxation in the dynamic modulus. In contrast, the Q^{-1} data for as-deposited pyrolytic carbon and vitreous carbon are an order of magnitude less ($< 10^{-3}$) and contain no large peaks. Since the crystal struc-

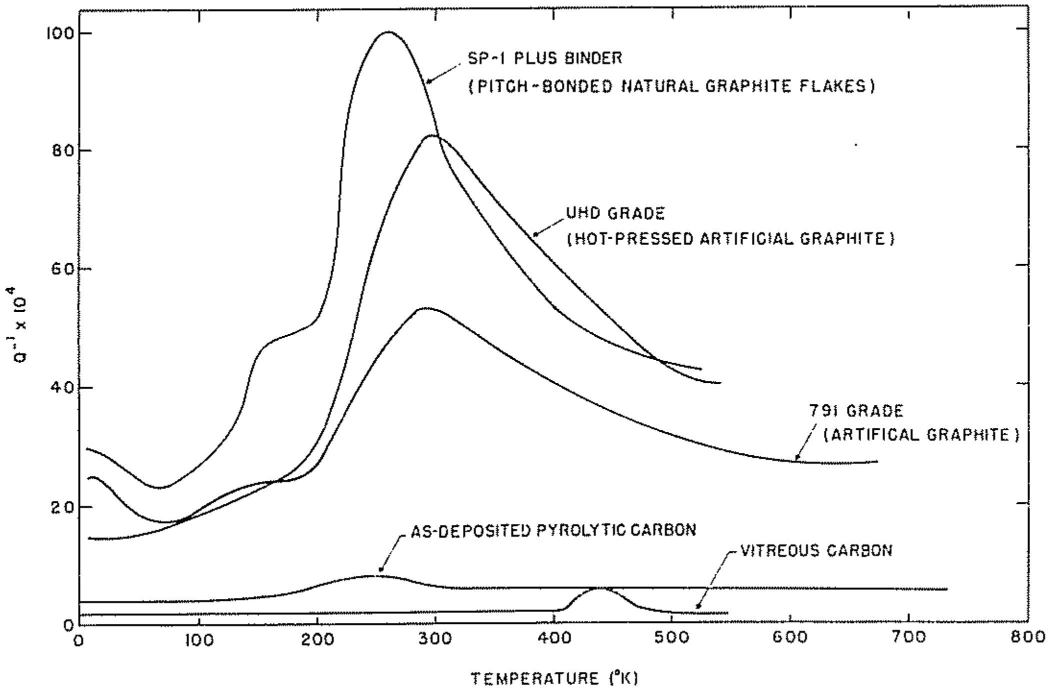

Fig. 6. Typical internal friction results for various types of graphites and carbons.

ture is almost non-existent in vitreous carbon and very poor in as-deposited pyrolytic carbon, this strongly suggests that the α peak is associated with a process which occurs in the crystallites and for it to occur these crystallites must have a significant amount of three-dimensional order. Typical summary data for various graphites and carbons(10, 11) are shown in Fig. 6.

The height of the α peak was apparently related to crystallite size and quality. Its maximum was about 50×10^{-4} for samples of the commercial graphites, about 90×10^{-4} for samples of UHD and about 100×10^{-4} for pitch-bonded natural crystals. From the relationship between average crystallite diameter (L_a) as obtained from the interlayer spacing(18) (given in Table 1), it is seen that the average crystallite diameter for the UHD and SP-1 material is appreciably greater than that for the 791, 787S, MI and reactor grades.

A decrease in the height of the α peak and in the magnitude of the dynamic modulus relaxation resulted from heating in the 550 to 700°K range. Subsequent heating of selected samples to 1800°C changed this weakened and broadened peak to a relatively sharp peak centered near 260°K (Fig. 2). This peak was similar to the α peak since it also had an auxiliary hump associated with its low-temperature side. However, the peak formed during the 1800°C anneal was not destroyed by subsequent heating to 500°K.

Although data were not obtained as a function of temperature, the results given in Table 2 for a sample of UHD graphite indicated that the α peak can be at least partially restored, following a low-temperature anneal, by an appropriate cold working process.

The height of the α peak and the magnitude of its associated modulus relaxation were greatly reduced by relatively low-dose neutron irradiation (threshold near 10^{15} nvt for the SP-1 material). This effect will be discussed in detail in a subsequent paper.(19)

The foregoing characteristics of the α peak strongly suggest that it is similar in almost every respect to the peak first discovered by BORDONI(21) in copper. These internal friction peaks have been subsequently observed(20) to occur in some cold-worked metals at a temperature near one-third of the Debye temperature. Experimental observations(20) of the Bordoni peaks in metals show that:

1. They are relatively broad. (However, it seems likely that this broadness in a given case should be judged relative to the temperature in °K at which the peak occurs.)
2. A smaller subsidiary peak or hump is generally observed on the low-temperature side of the main peak.
3. They have an associated modulus relaxation, and the relative magnitude of the relaxation increases with increasing peak height.
4. The peak height is reduced by annealing.
5. Irradiation reduces the peak height.
6. The height of the peak increases with increasing cold work (for deformations up to two per cent).
7. The height of the peak and the temperature at which it occurs are approximately strain–amplitude independent.
8. They exist in both single crystal and polycrystalline specimens.
9. They occur at about one-third the Debye temperature.
10. The temperature at which the maximum occurs is lower if the friction is measured at lower frequencies.
11. Impurities reduce the peak height.
12. The peak has been observed in fcc metals (and possibly hcp) but thus far not in bcc metals.

A comparison of the characteristics of the α peak in graphite to the above known observations concerning the Bordoni peak will be presented. The experimental results obtained on the α peak during the present work have already been demonstrated to be in accord with the first five of the listed observations concerning the Bordoni peak, i.e. that the peak is relatively broad, that it tends to have a hump on the low-temperature side, that it has an associated modulus relaxation which depends on the peak height, and that the peak height is reduced by either low-temperature annealing or by relatively low-dose irradiation. Although Q^{-1} data for a cold-worked sample of grade UHD were obtained only at room temperature, the results presented in Table 2 imply agreement with the sixth observation, i.e. cold working tends to increase the peak height. (Samples of other grades of graphite were too fragile to withstand the amount of cold working required to significantly alter their DMP.)

The height of the α peak and the temperature at which the maximum occurs were investigated at several strain amplitudes using the longitudinal apparatus. Although increasing the strain amplitude increased the overall level of the Q^{-1} values at all the temperatures investigated, the peak height obtained by subtracting the background from this level was found to be nearly strain–amplitude independent. No shift in the temperature at which the maximum occurred could be detected when the strain amplitude was increased. Excellent agreement in the Q^{-1} peak heights observed for the same graphite sample with both the longitudinal and transverse apparatus also implies the lack of an appreciable strain–amplitude dependency for the α peak, because the strain levels and strain distribution are different in the two pieces of apparatus. Thus, the behavior of the α peak agrees with the seventh observation concerning Bordoni peaks.

The low Q^{-1} values obtained on vitreous carbon compared to peak values obtained on commercial graphites probably indicate that the large α peak observed in the pitch-bonded natural graphite crystals is associated with the crystals and not with the binder. While the natural crystals are not single crystals, selected area electron diffraction studies usually produce single crystal patterns.(14) These observations are compatible with the eighth observation concerning Bordoni peaks in metals, i.e. they exist in relatively well-ordered regions in both single crystal and polycrystalline specimens provided that the crystals exceed a minimum size and quality.

The Bordoni peak in metals has commonly been centered at about one-third of the Debye temperature (ninth observation). No theoretical explanation for this behavior has been advanced beyond the remark of Bordoni(21) that a statistical treatment suggests that changes in sliding time become large when $T = \theta_D/3$. Krumhansl and Brooks(22) showed that the Debye temperature (θ_D) associated with atomic vibrations normal to the layer planes in graphite is about 900°K, while the Debye temperature associated with atomic vibrations in the plane is about 2500°K. Thus, the α peak occurs at about one-third the out-of-plane Debye temperature.

The temperature of the maximum of the α peak was about the same whether the samples were measured with the longitudinal apparatus (9000 to 13,000 cps) or the transverse apparatus (500 to 1000 cps). This frequency difference may not have been sufficient to discern a possible shift in temperature position if the average activation energy is not small. However, measurements by another investigator,* using a torsional apparatus at about 3 cps on a sample of our reactor grade graphite, indicated that the maximum of his α peak occurred at a somewhat lower temperature than we observed. This result(23) is in agreement with the tenth observation concerning the Bordoni peak.

The effect of impurities on the height of the α peak was not systematically investigated. In observations of the Bordoni peaks in metals, the impurity effect on the Q^{-1} behavior is qualitatively similar to the irradiation effect. However, in the absence of a systematic study, the effect of impurities on the height of the α peak must be considered as unknown.

In order to relate the twelfth observation concerning general characteristics of Bordoni peaks to the characteristics of the α peak in graphite, the proposed mechanism which gives rise to the Bordoni peak must first be considered. According to Seeger's mechanism,(24) the Bordoni peak in metals is due to a relaxation process involving dislocations which run parallel to one of the close-packed directions in the crystal. Seeger(24) derived the following expression for the maximum values of the internal friction associated with this relaxation process:

$$Q^{-1}_{(\max)} = \frac{P}{2\,(1+P)^{1/2}} \tag{1}$$

where:

$$P = \frac{2N_0\, a\underline{b}^2\, sG}{kT} \left[\frac{\pi a E_0}{2\underline{b}\tau_p}\right]^{\frac{1}{2}} \left(\frac{1}{3\pi}\; l_n\, \frac{16\tau_p}{\pi\tau} + 0.3\right) \tag{2}$$

N_0 is the number of dislocation loops per unit volume contributing to the process, s is the mean area swept out by one dislocation look, $\underline{b}$ is the Burgers vector, a is the lattice spacing, E_0 is the dislocation line tension, τ_p is the Peierls stress, and τ is the applied stress. A lower limit for the Bordoni peak is obtained by substituting $s = L \cdot a$ where L is the average length of the dislocation loop. It has been shown that Seeger's theory as outlined by the above relationships has given a good account of the Bordoni peak in metals.(20)

In the case of reactor grade graphite, N_0 can be roughly estimated to be 5×10^{15} cm^{-3} and L is estimated to be 10^{-6} cm.(25) By using these values and setting $E_0 = 1/2\ G\underline{b}^2$, $a = \underline{b}$, $\tau_p = 4 \times 10^{-4} G$,(4) and $\tau = 0.01\ \tau_p$,(25) a value of $Q^{-1}{}_{(\max)}$ of 300×10^{-4} is obtained, compared to the observed value of 50×10^{-4}. Considering the available estimates of the parameters involved and the limitations on the approximations required, Seeger's theory concerning the Bordoni peak accounts for the magnitude of the α peak reasonably well. Since the peak center position is near 300°K, rather than at lower temperatures as in many metals, this may suggest that basal plane dislocations in graphite are relatively less mobile.

It is also of interest to examine the shape of the α peak. Zener(26) has shown that for a single relaxation process:

$$Q^{-1} = \frac{\Delta E'}{E'}\,\frac{\omega\,\xi}{1 + (\omega\xi)^2}, \tag{3}$$

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* Courtesy of Dr. S. Turley, Dow Chemical Company, Midland, Michigan.

where ξ is the relaxation time, ω is the circular frequency and $\Delta E'$ is the change in Young's modulus due to the relaxation process. Q^{-1} becomes a maximum at $\omega\xi = 1$, so that:

$$Q^{-1}_{(max)} = \frac{1}{2}\frac{\Delta E'}{E'}. \tag{4}$$

The values of $Q^{-1}_{(max)}$ for polycrystalline graphite calculated from equation 4 are about an order of magnitude larger than the observed values.

The fact that the Q^{-1} peak height calculated from the modulus relaxation is significantly greater than the observed peak height and the fact that the α peak is relatively broad both suggest that more than one relaxation time is involved.(20) It may be possible to decompose the observed peak into a number of constituent peaks, each associated with a particular relaxation time and a given activation energy, by assigning a part of the modulus relaxation to each process. In a similar case for a copper single crystal, THOMPSON and HOLMES(27) were able to obtain a reasonable fit to their experimental data for the Bordoni peak in copper by adding together seven separate contributions.

The relation of the α peak to the twelfth observation concerning Bordoni peaks, i.e. that they have only been observed in fcc metals, will now be examined. First, it should be noted that there appears to be nothing in SEEGER's theory which tends to limit Bordoni peaks to the fcc lattice. In fact, BRUNER(29) has criticised SEEGER's(28) theory on the grounds that it should be equally applicable to bcc metals whereas his measurements suggest that no Bordoni peak occurs in iron. However, the dislocation behavior for bcc crystals is known to differ from that observed in fcc crystals.(30) In bcc metals, slip has been observed in the (110), (112) and (123) planes.(30) Of these, the (110) plane is most nearly closest-packed, and there is some evidence that the slip usually attributed to the (112) and (123) planes is actually the resultant of slip on several different (110) type planes.(30) A perfect dislocation on a (110) bcc plane can be split into three partial dislocations in a manner which is analogous to the creation of two partial dislocations from a perfect dislocation on the (111) planes in fcc crystals.(30) Actual observations by electron microscopy of split dislocations in bcc crystals are a great rarity.(30)

The situation for graphite is analogous to that for fcc crystals since slip in graphite occurs on the layered planes and the dislocations also occur as partials separated by relatively wide faulted regions.(31) Thus, it is conceivable that the same mechanism that gives rise to Bordoni peaks in fcc crystals could be operative in graphite. If we assume that the α peak is a Bordoni peak, it would appear that the requirements for such a peak include a reasonable dislocation density, an easy glide plane and a small stacking fault energy (i.e. partial dislocations separated by a relatively wide faulted region).

Alternate possible explanations for the α peak should be considered. These possibilities include the thermoelastic effect, grain boundary viscosity and stress-induced ordering of impurities. The theory for the thermoelastic internal friction(26) indicates that the thermoelastic damping is usually small for bars vibrating longitudinally, but that it may become appreciable for flexural vibrations unless care is taken in selecting specimen size. Calculations using the sample geometries, thermal diffusivities, specific heats and frequencies encountered in the present work indicated that the thermoelastic damping should not make a significant contribution in polycrystalline graphite. The close agreement between the results obtained with the longitudinal and transverse apparatus and the lack of dependence of Q^{-1} on sample geometry also appear to rule out a significant thermoelastic contribution.

A low-temperature (550°K) anneal would probably have little effect on grain boundary regions, and low-dose (3×10^{15} nvt) irradiation is not expected to produce an appreciable effect in the grain structure of polycrystalline graphite because of the low density of defects produced. Consequently, grain boundary viscosity is not a likely mechanism to explain the decrease in

α peak height by annealing or by neutron irradiation. The increase in α peak height with cold working of sample UHD-A-6A (Table 2) also supports the conclusion that the α peak is associated with dislocations rather than grain boundaries.

Internal friction peaks (Snoek peaks) due to interstitial atoms are often observed in bcc crystals, and the mechanism involved has been rather well explained.(20) In an unstressed crystal, the interstitial atoms are randomly distributed; but, upon applying a tensile stress, the energy of an interstitial atom becomes less in certain sites because of the distortion produced by the applied stress. Hence, the stress produces a preferential redistribution of the interstitial atoms. When an alternating stress is applied this gives rise to an internal friction peak.(20) The height of the Snoek peak depends upon the impurity level at certain locations in the structure.(32) However, the peak heights were about the same for samples of grades 791 and 787S as compared to the reactor grade sample although the impurity levels were believed to be significantly different. It is therefore suggested that the α peak is not a Snoek peak. This is further supported by the observations that the Snoek peaks are relatively sharp and tend to have a single relaxation time compared to the broadness of the α peak, that they should not be markedly affected by low-dose irradiation, and that they should not tend to increase with cold working as observed herein.

TSUZUKU postulated(2, 3) that the peak which he had observed around 50°K in a sample of reactor grade graphite (Fig. 3) was a Bordoni peak, but he later(5) decided that it was not. In their review article TSUZUKU and SAITO(5) stated that no evidence for a Bordoni type relaxation had yet been found. However, in view of the marked similarity between the behavior of the α peak observed in the present graphite studies and the Bordoni peak as reported in the literature,(20) and the lack of a suitable alternate explanation, it is believed that the α peak should be considered to be a Bordoni peak.

4.2. *Low temperature peak*

An internal friction peak (or at least a change in level) as well as a definite modulus relaxation was observed at low (<60°K) temperatures in the 791 (Fig. 1) and 787S grades and in the pitch-bonded natural graphite material. In the pyrolytic carbon (Fig. 6), the reactor grade (Fig. 3) and the UHD material (Fig. 4), this Q^{-1} peak and the modulus relaxation were either much less in magnitude or were not detected. There appeared to be no simple correlation between the low-temperature behavior and the height of the α peak. For example, a definite relaxation was noted for SP-1C and a much smaller relaxation was observed for UHD-A-6 although these samples had relatively high α peaks. Also, a marked relaxation was observed for sample 791-G-3, while a relatively small relaxation occurred in the reactor graphite sample, although the α peaks for both materials had approximately the same height.

It appears possible that the low-temperature behavior may be related to impurities. The relatively low impurity content of the reactor grade material compared to that of grades 791 and 787S would then be consistent with the smaller relaxation for the reactor grade material (as observed). Presumably the UHD material was somewhat purified during the high temperature densification process, and this again is in accord with the relatively small relaxation observed at low temperature. Pyrolytic carbon, which is also relatively pure, exhibits no detectable relaxation in tests thus far conducted.(19) Although the SP-1 crystals were relatively pure, the impurity content of the formed body was undoubtedly increased due to the pitch binder. Therefore, if impurities were responsible, the pitch-bonded material could have had a moderate relaxation below 60°K (as observed).

The data from all materials tested may also suggest that the low-temperature DMP behavior is associated with the relatively disordered regions. For instance, it is observed in vitreous carbon. If this is true, it would explain the lack of correlation between the low-temperature behavior and the height of the α peak, and would also explain the presence of a relaxation in the pitch-bonded natural graphites. Since no definitive study of the low-temperature (<80°K) DMP behavior was made during the course of the present work, it should be emphasised that the foregoing association of the low-temperature DMP behavior with impurities and/or disordered regions is merely an hypothesis, and that other mechanisms may be responsible for the observed behavior.

4.3 *Sharp internal friction peaks near 340°K*

An extremely sharp Q^{-1} peak of substantial height was observed for UHD graphite during the initial run above 295°K for one sample. Subsequent heating or machining destroyed this peak. A similar sharp peak at 340°K has recently been observed by another investigator with one sample of our reactor grade material.(33) Using an aluminum sample, BIRNBAUM and LEVY(34) have previously observed a series of very sharp peaks superimposed on a monotonically increasing background. However, upon repeating the measurement, only the smooth background was observed. Thus, the heat treatment during the first series of measurements was apparently sufficient to anneal out the structure responsible for the peaks. Similar behavior has also been reported in aluminum by FILMER *et al.* (35) and in copper by several workers.(20) The fact that these sharp peaks are often removed by annealing suggests that they may be due to an unstable dislocation configuration.(20)

Although only the sharp peak at 340°K was observed in the present work, the fact that several sharp peaks have been observed with aluminum and copper also suggests the possibility that the sharp peak at 50°K observed by TSUZUKU(2, 3) with a sample of reactor grade graphite may have been related to a similar process.

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