

RELATIONSHIP BETWEEN PREFERRED ORIENTATION, THERMAL EXPANSION,
AND MOLDING PRESSURE OF SOME EXPERIMENTAL GRAPHITES*

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Introduction

Efforts to improve the overall thermal stress resistance of specialty graphites have centered upon increasing the isotropy of the graphite structure. In order to effectively determine the effect of these various methods of isotropy improvements, objective quantitative methods of anisotropy measurements are necessary and are the secondary topic of both this and the succeeding paper.

It should be understood that graphite has both a crystallographic and a defect anisotropy which affect physical properties. These are generally inter-related and are strongly influenced by the fabrication procedure. While the effects of crystallographic anisotropy are reasonably understood^(1,2,3), the effects of defect anisotropy on the physical properties are vague. These defects will strongly affect both the thermal expansion as well as the mechanical properties, thus having a strong effect on the overall thermal resistance.

In the present study, CTE's of a series of graphites were found to vary regularly with molding pressure. These graphites have been examined to determine whether the CTE differences were due to orientation or structural differences resulting from the modifications in the fabrication procedures.

Orientation effects were determined by use of an X-ray diffraction technique conceived by Jetter and Borie⁽⁴⁾ and applied to graphite by Cavin⁽⁵⁾. This technique directly yields the crystallite orientation processing variables. Values of the preferred orientation parameter R were also calculated from both CTE and electrical resistivity data. Thus, direct comparisons were made between the actual crystallographic preferred orientation, the CTE anisotropy with a c -axis accommodation type of defect structure and the resistivity anisotropy with a defect structure that hinders conductivity in the a -axis.

Experimental

A. Sample Preparation

The H2 graphites were fabricated from high quality acicular green coke supplied by Great Lakes Carbon Corporation. After addition of 20. pph of 30-m pitch obtained from Allied Chemical Corporation, the mixture was slurried in benzene, stirred until dry and then mikropulverized. After firing for 1 hour at 325-350 C, the modified coke was again mikropulverized. Appropriate quantities of A-240 binder pitch (obtained from Ashland Oil Company) were dry mixed with the modified filler and subsequently slurry blended using benzene until reasonably dry. After grinding to -120 mesh, the mix was warm molded at approximately 95 C and at pressures of 1000, 1500, 2000, and 3000 psi. The 1.6-in.-diameter blocks were placed into restraining holders. After carbonization to 1000 C on a controlled 3-day cycle, the carbonized blocks were removed from the restraining

holders and heated to 2800 C on a 1-day cycle. The graphitized bodies were then machined to obtain samples for the physical and orientation property measurements.

B. Property Measurements

The CTE's (room temperature to 1000 C) were calculated using data obtained from a TemPres TD-710 dilatometer.

X-ray diffraction data, obtained from spherical samples machined on one end of a cylindrical stem, were determined by use of a North American Phillips X-ray diffraction unit. Readings of intensity of the diffracted beam at various orientations of the anisotropic sphere and of the background radiation were made by the ORTEC Model 432A Digital Rate Meter and recorded on teletype tape.

Orientation parameters were subsequently calculated from (1) X-ray diffraction data⁽⁵⁾, (2) from CTE measurements⁽⁴⁾ using

$$\frac{1}{R_{\parallel}} = 0.5 \frac{CTE_{\parallel}}{CTE_{\perp}} + 1.0$$

and (3) from electrical resistivity (ρ) values⁽⁴⁾ using

$$\frac{1}{R_{\parallel}} = \frac{\rho_{\parallel}}{\rho_{\perp}} + 0.5$$

Accommodation factors were calculated using⁽²⁾

$$\sigma_{oz} = R_{oz} \sigma_{oz} + (1 - R_{oz}) \gamma_{oz} \sigma_c$$

Results and Discussion

Properties of the experimental graphites are listed in Table 1.

As indicated in the Table and in Figure 1, the binder content did not noticeably affect the CTE measurements of the graphites. However, the within-grain CTE shows a constant value with increasing mold pressure while the across-grain CTE increases with molding pressure. Thus, the degree of CTE anisotropy is directly proportional to mold pressure. The direct dependence of anisotropy on molding pressure was a reflection of a corresponding increase in the degree of preferred orientation with mold pressure. This would indicate a decrease in the orientation parameter R measured in the direction of molding. However, when the samples were analyzed by X-ray diffraction, no change in R in either direction was observed to occur with varying molding pressure (Figure 2). A change in CTE with no change in crystallite orientation must be attributed to a change in the degree of accommodation. Thus, as shown in Figure 3, γ_{\parallel} increases and the degree of formation of microcracks which accommodate thermal expansion in the parallel direction decreases with increasing molding pressure.

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TABLE 1. EFFECT OF MOLD PRESSURE ON PHYSICAL PROPERTIES OF GRAPHITE

Sample Number	A-240 Binder Content (pph)	Molding Pressure (psi)	Heat Treatment Temperature (°C)	Orientation Parameter R_{\parallel} ^b (from X-ray Measurements)	Measured CTE ($^{\circ}\text{C}^{-1} \times 10^6$)		R_{\parallel} (from CTE Values)	Accommodation Factor γ_{\parallel}	Measured Electrical Resistivity (ρ $\mu\Omega\text{-cm}$)		R_{\parallel} Calculated (from Electrical Resistivity)
					\parallel	\perp					
H2-BE2	9	1000	-	0.5764	7.30	5.13	0.5843	0.563	1320	800	0.4651
H2-10A2	10.5	1000	-	0.5819	7.30	5.13	0.5843	0.570	1240	800	0.4878
H2-12A2	12	1000	-	0.5876	6.88	4.97	0.5910	0.543	1180	770	0.4920
H2-8F1	9	1500	-	0.5869	7.04	5.13	0.5931	0.556	1230	740	0.4625
H2-10B1	10.5	1500	-	0.5824	7.04	5.13	0.5931	0.550	1170	780	0.5000
H2-12B2	12	1500	-	0.5974	6.92	5.26	0.6032	0.560	1160	760	0.4935
H2-8C1	9	2000	-	0.5637	7.30	4.93	0.5766	0.567	1260	730	0.4492
H2-10C1	10.5	2000	-	0.5783	7.53	5.01	0.5709	0.584	1190	710	0.4595
H2-12C2	12	2000	-	0.5219	7.45	5.00	0.5731	0.511	1170	680	0.4503
H2-8D4	9	3000	-	0.5777	7.67	5.04	0.5679	0.594	1310	770	0.4543
H2-10D4	10.5	3000	-	0.5941	7.54	4.92	0.5910	0.607	1180	770	0.4920
H2-12D2	12	3000	-	0.5656	8.06	5.17	0.5620	0.609	1380	830	0.4624

^aAs-received coke was fired at 500°C for 1 hr (H2 series).

^bFrom x-ray diffraction data.

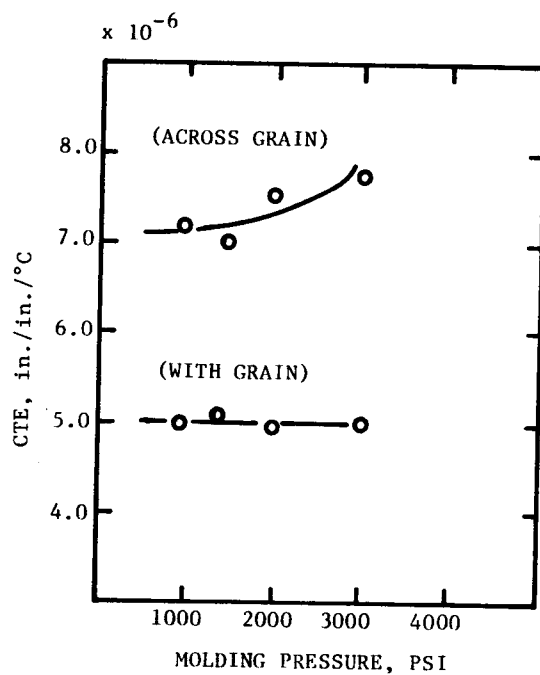


Fig. 1. The Effect of Mold Pressure on the CTE of Experimental Graphites.

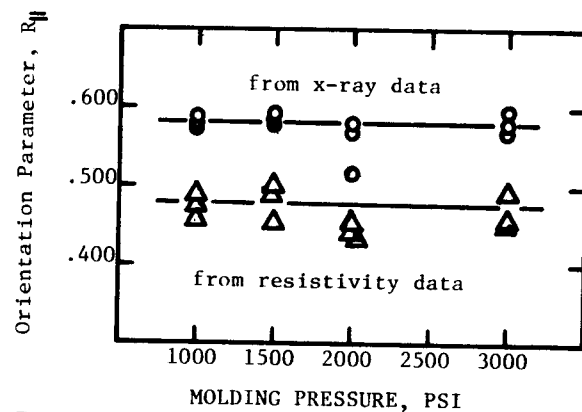


Fig. 2. Effect of Molding Pressure on the Orientation Parameter R_{\parallel}

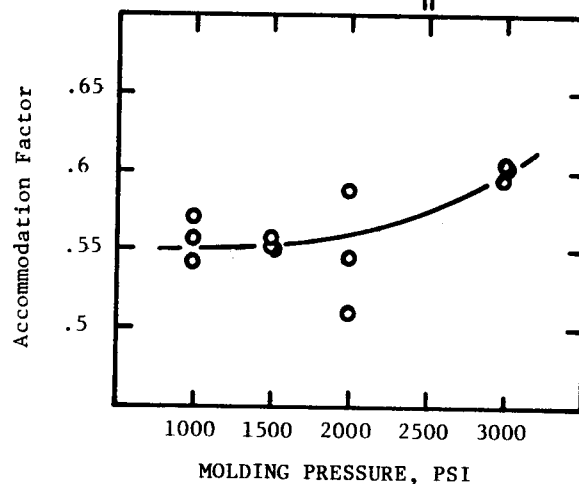


Fig. 3. The Effect of Mold Pressure upon the Accommodation Factor.