RELATIONSHIP BETWEEN PREFERRED ORIENTATION, THERMAL EXPANSION, AND COKE PREPARATION TEMPERATURE 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 improvement, 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 coke preparation temperature. 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 H1 graphites were fabricated from experimental green cokes prepared from A-240 petroleum pitch obtained from Ashland Oil Company. The green cokes were prepared by fusing approximately 1800 g of A-240 pitch in carbon boats for 1 hour at 575, 600, 650, or 675 C under an inert atmosphere. After firing, the cokes were ground and dry-mixed with appropriate amounts of A-240 pitch binder and subsequently slurry-blended with benzene until reasonably dry. After grinding to -120 mesh, the mix was warm molded at approximately 95 C at a pressure of 2000 psi. The 1.6-inch-diameter blocks were cooled under pressure and placed in restraining holders. After heat treatment 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 for physical and orientation property measurement specimens.

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 Figure 1, the binder content did not noticeably affect the CTE measurements. But a significant decrease in the CTE parallel with the molding direction, accompanied by an equivalent change in the perpendicular direction, occurred with increasing heat treatment temperature. As shown in Figure 2, no change in crystallite orientation was revealed by X-ray analysis. As illustrated in Figure 3, the accommodation factor showed a significant decrease with increasing heat-treatment temperature.

Thus, the CTE differences were due to structural differences resulting from the heat-treatment temperature variation in that the development of an internal microcrack defect structure increased with increasing coking temperature.

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* This work was funded by the U.S. Naval Surface Weapons Laboratory under the REVMAT Program.

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Operated for the Energy Research and Development Administration by Union Carbide Corporation.

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TABLE 1. EFFECT OF HEAT TREATMENT TEMPERATURE ON PHYSICAL PROPERTIES OF GRAPHITE

Sample Number	A-240 Binder Content (pph)	Molding Pressure (psi)	Heat Treatment Temperature[a] (C)	Orientation Parameter $R_{\parallel}$[a] (from X-ray Measurements)	Measured CTE (C^{-1}, x 10^6) $\parallel$	Measured CTE (C^{-1}, x 10^6) $\perp$	$R_{\parallel}$ (from CTE Values)	Accommodation Factor $\gamma_{\parallel}$	Measured Electrical Resistivity (ρ $\mu\Omega$-cm)		$R_{\parallel}$ Calculated (from Electrical Resistivity)
H1-78B	10	2000	575	0.5717	7.0	5.1	0.5930	0.53	1730	1110	0.4858
H1-78C	12	2000	575	0.5645	8.2	5.0	0.5495	0.62	1690	920	0.4279
H1-78D	14	2000	575	0.5980	7.4	4.8	0.5647	0.60	1550	830	0.4224
H1-80A	12	2000	600	0.5735	6.9	4.0	0.5369	0.53	2000	1240	0.4733
H1-80B	14	2000	600	0.5650	6.6	4.2	0.5600	0.49	1620	1080	0.5000
H1-80C	16	2000	600	0.5903	6.8	4.2	0.5526	0.54	1750	1030	0.4547
H1-82A	12	2000	650	0.5597	5.8	3.7	0.5606	0.43	2920	1370	0.3800
H1-82B	14	2000	650	0.5894	5.8	3.7	0.5606	0.46	2650	1550	0.4526
H1-82C	16	2000	650	0.5790	5.8	3.7	0.5606	0.45	2080	1290	0.4734
H1-84C	12	2000	675	0.5755	5.2	3.2	0.5517	0.39	3110	--	--
H1-84D	14	2000	675	0.5851	5.2	3.2	0.5517	0.40	2620	1560	0.4588

[a]From x-ray diffraction data.

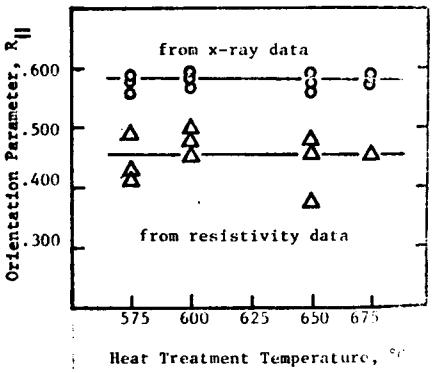

Fig. 2. Orientation Parameter as a Function of Heat-Treatment Temperature.

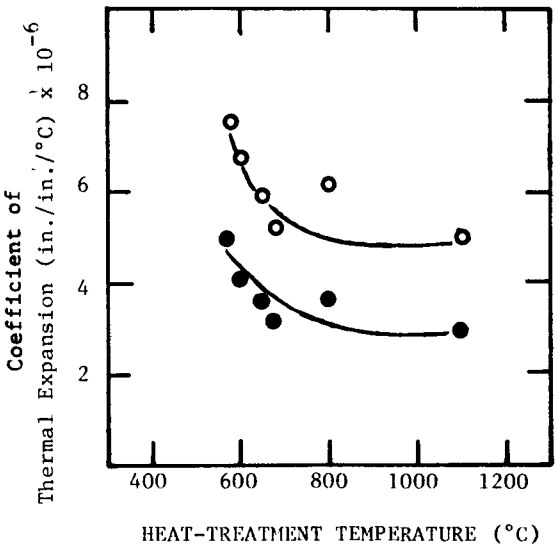

Fig. 1. The Effect of A-240 Pitch Heat-Treatment Temperature on the Coefficient of Thermal Expansion of Graphites Fabricated from A-240-Derived Cokes.

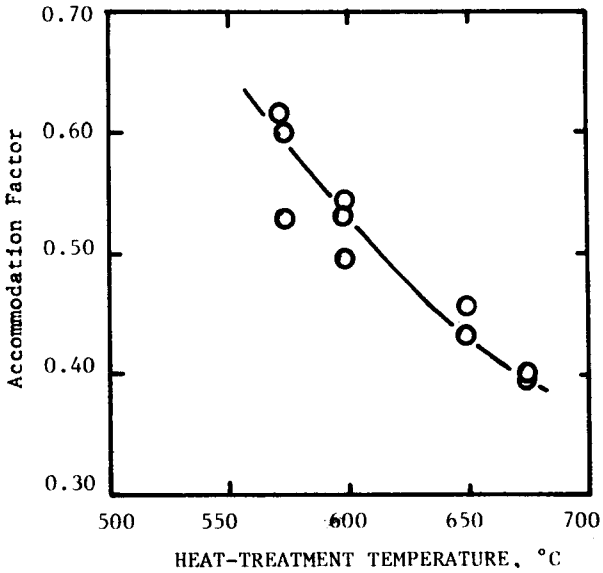

Fig. 3. Accommodation as a Function of Heat-Treatment Temperature.