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by

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EFFECT OF HEAT TREATMENT TEMPERATURE ON BINDER THERMAL CONDUCTIVITIES

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ABSTRACT

The effect of heat treatment on the thermal conductivities of a pitch and a polyfurfuryl alcohol binder residue has been investigated. Graphites specially prepared with these two binders were used for the experiments. Measured thermal conductivities were treated in terms of a two-component system, and the binder thermal conductivities were calculated. Both binder residues showed increased thermal conductivity with increased heat treatment temperature.

INTRODUCTION

Analysis of heat transfer in the high-temperature gas cooled reactor (HTGR) fuel rods has indicated that increased thermal conductivity (λ) in the fuel rods would improve the thermal performance of the reactor core significantly.¹ Although it has long been recognized that λ in artificial graphite can be affected by thermal treatment, quantitative information about the effect of heat treatment temperature on λ of graphites of interest was not to be found in the literature. In particular, because HTGR fuel rods are made using pitch or a similar binder, it is the thermal conductivity of the binder residue that is of primary interest. Experiments performed to determine the binder λ as a function of heat treatment temperature are described in this report.

EXPERIMENTAL

As is so often the case with graphites, it is difficult to establish a single-valued cause-and-effect experiment. This work was no exception. Direct λ measurement in a specimen made using pitch or thermosetting resin binder (the two candidates of interest) is an awkward task because pyrolysis and subsequent graphitization with increasing heat

treatment tend to degrade the structural integrity of the sample. We decided to use compacts made from a well-graphitized graphite filler and a binder of interest. We reasoned that because the filler had been graphitized at higher temperatures than those to be used in the λ experiments, any increases in λ would be due to changes in the λ of the binder component only.

We used two molded graphites, S-7 and S-8. Although both were made of the same filler flour, S-7 contained 35 parts per hundred (pph) of pitch and S-8 contained 28 pph of partially polymerized polyfurfuryl alcohol (PFA),² catalyzed with 4% maleic anhydride. The specimens were hot-molded at 13.8 MPa (2000 psi) to 1173 K in graphite dies, then baked to 1773 K in helium. Some properties of these graphites are as follows.

	S-7	S-8
Bulk density (g/cm ³)	1.86	1.83
Binder residue		
Per cent of original binder	52.3	35.3
Per cent of baked specimen	15.5	9.0
Preferred orientation		
Bacon anisotropy factor	1.188	1.147-1.151
Electrical resistivity ($\mu\text{ohm-cm}$)		
WG ^a	1762	1298
AG	2207	1713
Thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)		
WG	59	70

^aWG = with grain, AG = across grain.

Four specimens were used for the study, one oriented with and one across the grain of each graphite. These specimens were heat-treated together; the treatment consisted of 3.6-ks (1-h) exposures in vacuum at 2046, 2270, 2491, 2674, and 2869 K.

The heater assembly geometry is such that the temperature uniformity within the samples and from sample to sample should be approximately 0.5 K.³ The temperature accuracies are probably within ± 5 K at the lowest temperatures and ± 15 K at the highest.

After each heat treatment, the samples were removed from the furnace and their thermal diffusivities were measured at room temperature.⁴ The thermal diffusivity (α) was obtained using a thermal transient method, and it is related to the specimen dimensions by

$$\alpha = \text{constant} \times \text{thickness}^2 \times (\text{characteristic time})^{-1}.$$

The thermal conductivity is obtained from α by using

$$\lambda = \alpha \rho C_p.$$

where ρ = density and C_p = specific heat. During the course of the heat treatments, the densities and thicknesses changed; so did the specific heat, although the amount of change is difficult to assess. Therefore, we used a constant value, $0.721 \text{ J g}^{-1} \text{ K}^{-1}$, for C_p . Linear interpolation based on initial and final measurements was used to determine ρ and thickness after each heat treatment.

RESULTS

The thermal conductivities obtained are plotted against heat-treatment temperature in Fig. 1. As expected, λ increases monotonically with heat-treatment temperature. The rate of increase of λ with heat-treatment temperature is faster in the pitch-bonded graphite than in that made with PFA. This is more significant than the fact that the λ of the pitch-bonded material is lower, initially, than that of the PFA graphite. This lower initial value results from use of nonoptimized binder-flour ratios for the experimental graphites. The reasons for the scatter in the λ data (i.e., a curve connecting the points would look "wavy") are not clear; possibly it results from the various simplifying approximations used in calculating λ .

Fig. 1.
Effect of heat treatment temperature on the thermal conductivity (300 K) of two graphites.

To determine the thermal conductivity change in the binder alone, we first corrected the measured λ s for porosity⁵ by using

$$\lambda (\text{for } 100\% \text{ density}) = \lambda (\text{measured}) \frac{2 + P}{2(1 - P)},$$

where $P = 1 - \rho/\rho_0$ = fractional porosity, ρ = density of the artifact, and ρ_0 = theoretical density. The calculated λ s were then used to obtain the binder thermal conductivities by assuming that the graphites were two-phase systems in which the graphite particles were the dispersed "phase" and the binder was the continuous matrix. The thermal conductivity of the system is related to those of the components by⁶

$$\lambda = \lambda_b \left[\frac{1 - 2V_g(\lambda_b - \lambda_g)/(2\lambda_b + \lambda_g)}{1 + V_g(\lambda_b - \lambda_g)/(2\lambda_b + \lambda_g)} \right],$$

where λ_b = thermal conductivity of the binder (the continuous phase), λ_g = thermal conductivity of the graphite (the dispersed phase), and V_g = the volume fraction of the graphite. Because the graphite flour had been fully graphitized, λ_g was assumed to be 150 W/mK. The binder mass fractions after pyrolysis were 0.155 in the pitch- and 0.09 in the PFA-bonded graphite samples, respectively. Assuming that these values also represented the volume fractions, V_g was 0.845 in the pitch-bonded graphite and 0.91 in that made with PFA. Using these values, we solved the above equation for λ_b .

The thermal conductivities of the two binders are shown as functions of heat treatment temperature in Fig. 2. Published data on pitch residues¹ show λ at 300 K to be about 10 W m⁻¹ K⁻¹ in materials heat treated at 2073 K. This is the nominal value used for λ in the HTGR fuel rods after 2073 K thermal treat-

ment. Our values for pitch residue heated to 2073 K are 11 and 13 W m⁻¹ K⁻¹. On the average, λ values for the PFA binder residue are lower than comparable values for the pitch binder. This is to be expected because the natural product (pitch) tends to graphitize more readily than the synthetic polymer at these temperatures. As Fig. 2 shows, heat treatment affects the thermal conductivities of the binders very markedly. Both binders are affected about equally (λ increases of 7-10 X) by the thermal treatment.

SUMMARY

Assertions that increasing graphite binder processing temperatures improves their thermal conductivity have been verified. Within the limits imposed by our experimental and calculational approach, changes in λ (measured at 300 K) due to changes in heat treatment temperature have been quantified.

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Fig. 2.

Effect of heat treatment temperature on the thermal conductivity (300 K) of two binders.

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