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EFFECT OF HEAT TREATMENT TEMPERATURE (HTT) ON DENSITY, WEIGHT
AND VOLUME OF GLASS-LIKE CARBON (GC)*

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Abstract

Room temperature measurements have been made of the density, weight, and linear dimensions of glass-like carbon (GC) that was heat treated in the temperature range of 1000-2700°C for three hours in inert gas atmosphere. The density of GC decreased with increase in heat treatment temperature (HTT), reaching a maximum decrease of 12.4% at 2700°C; and the weight loss increased with increasing temperature to a maximum of about 1.9%. The volume increased and showed a quadratic dependence on the HTT, reaching a maximum value of about 10.2%. Subsequent application of hydrostatic pressures up to 1551 MPa (225,000 psi) produced only a small increase in bulk density. It is concluded that the weight loss is not the major cause of the density decrease, instead the volume expansion of pores is mainly responsible for this behavior.

The weight loss is suggested to be due to the release of the last vestiges of hydrogen and the volume expansion is shown to be due to two

different mechanisms operating in different temperature regimes. A gas pressure mechanism is predominant up to the HTT of 1600°C and at greater HTT thermal stress mechanism predominates. The irreversibility of the dimensional change is proposed to be due to the ratchetlike [1] nature of microstructure that is developed during heating of the GC.

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1. INTRODUCTION

The density of GC decreases when it is heated above its process temperature, the decrease being greater the more the heat treatment temperature exceeds the process temperature [2,3]. Whereas graphite has a density close to 2.25 g/cm^3 , the bulk density of GC previously processed at about 1000°C is close to 1.5 g/cm^3 . The a and c axis lattice parameters of GC are, however, not very different from those of graphite, thus GC must have a large volume of pores. These pores are neither observable by optical, scanning, or transmission electron microscopy, nor by conventional gas absorption methods of characterization [4]. Both N_2 condensation and BET adsorption measurements indicate negligible pore surface area ($< 10 \text{ m}^2/\text{cm}^3$) showing that, in as-received GC, the pores are not interconnected. On the other hand, small-angle x-ray scattering and lattice image studies show that the microstructure has a heterogeneity associated with porosity on the scale of a nanometer [5].

In order to understand the density decrease phenomenon, Fischbach and Rorabaugh [6] examined four different GC materials in the form of 1.35 mm dia rods and 2-3 mm thick plates. They concluded that 80-90% of the density decrease resulted from volume expansion, and the remainder was attributed to weight loss. They suggested that the volume expansion resulted from internal pressure generated by the continued evolution of volatile pyrolysis products and perhaps the release of absorbed material within the closed pore system. Thus, for slow heating rates and/or thin samples there is enough time for the gases to diffuse out as they are generated, so that the increase in internal pressure and the associated volume increase is small. On the other hand, at high heating rates or

with thick samples, pressures large enough to cause large volume increase or fracture would be generated. This analysis is similar to that presented for irreversible expansion observed in heat-treated petroleum coke. In this case, sulfur has been found to be the cause of the irreversible puffing [7-11]. Later, Bragg and Bose [12] obtained similar results and argued that although the gas pressure model for the density decrease in GC can operate, but it may not account for all of the decrease because the pyrolysis is virtually complete at the processing temperature. Similar criticisms for the explanation of the puffing due to sulfur in petroleum coke have also been raised by Collins [7]. It was hypothesized by the authors [12] that the density decrease is due to the volume expansion of pores caused by anisotropic lattice thermal strains. Accordingly, a rough calculation showed that the order of magnitude of the volume change is predicted correctly provided that somehow the expansion is not reversible, thus resulting in the hysteresis effect. This kind of hysteresis in thermal expansion curves has also been observed in polycrystalline noncubic metals [13], ceramics [14], pyrolytic graphite [15], and vitreous carbons [16], and has been explained to arise from internal stresses created due to thermal expansion anisotropy during the thermal cycling of materials.

The objective of this research is to examine the origins of volume expansion and weight loss in heat treated GC. Measurements have been made of the change in density, weight, and volume of heat treated GC. The effect of hydrostatic pressure applied at room temperature on density change in GC has also been determined.

2. EXPERIMENTAL PROCEDURE

As-received plates of GC (Polycarbon, Inc., North Hollywood CA, Process temperature said to be 1000°C) were cut into specimens of 5 cm x 2.5 cm x 0.25 cm, and heat treated in an Astro furnace for three hours at various temperatures in the range of 1000-2700°C. The samples were heated either by initially positioning them inside the hot zone (15°C/min heating rate) or pushing a specially constructed carousel samples holder containing a workload of about 10 samples into the hot zone quickly (heating rate > 80°C/min). After the heat treatment, the samples were dropped individually from the hot zone by rotating the sample holder over a bottom hearth assembly into a lower chamber attached to the bottom of the furnace. The temperature was measured with a disappearing filament optical pyrometer calibrated for temperatures up to 2800°C, and was controlled to $\pm 20^\circ\text{C}$ at the highest temperature (2800°C). The atmosphere inside the furnace during low-temperature (< 2000°C) heat treatments was pure argon, and for higher temperature it was extra-pure helium. The density was measured by weighing the sample in water and air to an accuracy of $\pm 0.0001 \text{ g/cm}^3$. Weight loss was measured to an accuracy of 0.0001 g using a single pan analytical balance. A traveling microscope was used to measure dimensional changes to an accuracy of $\pm 0.0004 \text{ cm}$ in the samples where the sample shape remained unaffected after the heat treatment. The foregoing measurements were made at room temperature. A few dilatometric measurements have also been made (at Thermophysical Division, Southern Research Institute, Birmingham Alabama; J.R. Koenig, Head) wherein the lengths were measured in-situ during a full heating/cooling cycle (RT $\rightarrow$ 2700°C).

The samples heated at higher heating rates ($> 80^{\circ}\text{C}/\text{min}$) often fractured into small pieces or fragments of material chipped off from their surfaces. The density of the fragments varied appreciably and was always lower than those of materials that survived. Some of these samples were placed in a plastic bag and compressed in an isostatic compaction unit using 20 wt turbine oil as the working fluid. Pressures up to 1550 MPa (225,000 psi) were applied for a period of between 5-60 min. On the other hand, the samples heated at lower rates ($15^{\circ}\text{C}/\text{min}$) and heat treated for three hours at HTT, were used for density weight loss and dimensional change studies.

3. RESULTS

The density measurements obtained from several experiments in the present work are shown in Fig. 1. The two sets of experimental data in this figure were obtained from different batches prepared by the same vendor and agree fairly closely but differ from those reported by Fischbach and Rorabaugh [6], the latter displaying a more rapid decrease as the temperature is increased. It should also be noted that different heating rates ranging from $15^{\circ}\text{C}/\text{min}$ to $75^{\circ}\text{C}/\text{min}$ had little effect on the resulting densities for present data. Figure 2 displays the effect of isochronal heat treatments on weight loss and length increase, where the values for 1000°C have been taken as reference values. These data show that no appreciable weight change occurs for $\text{HTT} > 2000^{\circ}\text{C}$, but the volume (length x width x thickness) continues to increase up to the highest HTT. This figure also shows that the dimensional change can be taken as isotropic on a macroscopic basis. The data obtained from in-situ measurements are plotted in Fig. 3. It is noted from this

figure that the as-received sample followed one curve during heating up to the process temperature (ca. 1000°C), thereafter expanding much more sharply up to 2700°C. Upon cooling, the sample contracts less sharply and follows a curve roughly parallel to that found during the initial low-temperature heating, resulting in a permanent expansion of 3%. Similarly, the dimensional changes at other temperatures can be calculated by assuming that upon cooling from a given temperature (heating rate is the same in all cases), the sample contracts along the curve parallel to the upper curve of Fig. 3. The values thus obtained are plotted in Fig. 4 along with the average linear expansion values calculated from Fig. 2. The value of permanent set at 1000°C is taken as zero, as has been observed experimentally [16] for GC. This can be explained on the basis of stress relief phenomena, as discussed in detail later.

If the density decreases are attributed to the volume expansion and weight loss, then one can also calculate the average dimensional change from density decrease by correcting it for weight loss at each HTT. This is obtained from

$$\Delta\rho/\rho - \Delta w/w = -\Delta V/V = -3 \Delta\ell/\ell_0 \quad (1)$$

Figure 5 shows such a comparison of the average dilation obtained in this way from experimental data of Fig. 1 (density) and Fig. 2 (weight), and measured data of Fig. 4. The close correlation indicates that the pycnometric measurements are not affected by the ingestion of fluid, and the observed weight and volume changes account for density changes.

The results of the isostatic compression measurements are shown in Fig. 6. The density of the as-received material was unaffected by pressures up to 1550 MPa (225,000 psi) as was the case for materials heated at 1000°C. At intermediate temperatures up to 2700°C, a small density increase was observed. The density increases were in fact only slightly dependent upon applied pressure and prior heat treatment.

4. DISCUSSION

4.1 Density Loss. As noted from Fig. 1, the initial density of the GC used in this study was higher than that studied by Bose and Bragg [12], but both materials experienced about the same density change for a given HTT. In the absence of weight-loss data and volume expansion in the former case, it is suspected that the material used by Bose and Bragg had undergone a slightly longer heat treatment at 1000°C than that of the present work. On the other hand, the difference between the density change behavior of essentially Lockheed GC-1000 and the Sigri GC could be attributed to the difference in precursor material and processing parameters. This density decrease is best understood in terms of the weight loss and volume expansion, as discussed in the following subsections.

4.2. Weight Loss. The weight loss in heat-treated carbon materials at $\text{HTT} > 1000^\circ\text{C}$ has mainly been attributed to the loss of hydrogen [17-19]. It has also been proposed that expulsion of the last vestiges of hydrogen is probably responsible for the beginning of graphitization in turbostratic carbons [19] as indicated by sudden drop in d_{002} at $\approx 2200^\circ\text{C}$. The indirect effect of a sudden decrease in d_{002} would

possibly be a drastic increase in dimension and thus a decrease in density. The rate of increase of weight loss however is far lower than that of density decrease, and also the weight loss ceases for $HTT \geq 2000^\circ C$ (Fig. 2). This argument thus leads to the conclusion reached by Fischbach and Rorabaugh [6] that the weight loss cannot fully account for the density decrease in GC and the volume expansion must be responsible for most of the observed decrease in density.

4.3. Volume Expansion. Heat treatment of GC samples causes an increase in volume that shows a quadratic temperature dependence (Fig. 2). The dimensional change calculated from this curve is comparable to that obtained by dilatometry (Fig. 4), except that the values determined by the present authors are a bit higher. This difference is attributed to the longer period of annealing employed (3 h vs 0 h) in the present case before cooling down the samples. The origin of this dimensional change can be explained by examining the gas pressure [6] or lattice thermal expansion [12] mechanisms as following.

According to the gas pressure model, the volume expansion is caused by the stress generated in the pores due to pressure of evolving gases. The maximum stress thus created can be calculated following Lieberman [20], and is given as

$$\sigma_{\max} = 7.82 \left(\frac{mT}{M} \right) \frac{MN}{m^2} \quad (2)$$

where m = the mass of expelled gas, M = molecular weight of gas, and T = temperature ($^\circ K$).

The values thus calculated at different temperatures are presented in Table I, along with the tensile strength values obtained from literature [21]. The corresponding elongation for fracture are values given in column 6 and are compared with the observed strain values given in column 5. In the last column, the strain generated due to anisotropy in thermal expansion are presented that have been calculated following Kelly and Taylor [22] from Eq. (3).

$$\epsilon_T = 9.82 \times 10^{-6} T + 0.50 \times 10^{-9} T^2 \quad (3)$$

The main features of Table I are

(i) The irreversible strain observed at 1000°C is negligible in comparison to the calculated value of 1.03% (lattice expansion). This observation can be explained by the gas pressure model because the fracture strength is larger than that of the stress generated in the pores, so that no strain is generated. One more possible explanation for this behavior is that at this temperature there is no relaxation of internal (thermal) stresses because the sample has originally been processed at 1000°C so that there should be no significant strain. These thermal stresses are generated due to anisotropy of lattice thermal expansion, and so the mechanism [12] is also defined as a thermal stress mechanism.

(ii) The strain observed at 1500°C is better explained by gas pressure mechanism than by thermal stress mechanism. These conclusions are similar to that reached by Collins [7] for irreversible expansion in petroleum coke.

(iii) The strain observed at 2000°C and above is better explained by a thermal stress mechanism. This is in accordance with the

observation that there is very little extra weight loss after 2000°C heat treatment, and therefore the strain should have little contribution from gas pressure.

It is inferred from the above analysis that both mechanisms can explain the observed permanent set, but in different temperature regimes.

During further examination of these mechanisms, it is noted that the gas pressure mechanism can explain the fracture of thick GC samples at high heating rates, but it cannot explain the buckling of thin samples (<0.5 mm) observed by the present authors at the heating rates ($>15^{\circ}\text{C}/\text{min}$). The later behavior can however be easily understood on the basis of the thermal stress mechanism. The stresses on the sample surface are in compressive mode and are in tensile mode in the center during heating. These modes get reversed during cooling and thus would cause buckling of thin samples and fracture of thick samples [23]. The fracture at high heating rates on the other hand could also be possibly due to poor thermal shock fracture resistance (R). According to Gangler [24], the parameter (R) of the material increases as $k\sigma/\alpha E$ increases, where k is thermal conductivity, σ is tensile strength, α is thermal expansion coefficient, and E is Young's modulus. This parameter has been modified to $\sigma/\alpha E(R')$ by Kingery [23] for high heating rates. Table II shows the calculation of these parameters, where the standard values are taken from Jenkins and Kawamura [25]. It is noted that for low heating rates, R increases with increase in temperature, as has been observed experimentally. At high heating rates, however, R is maximum for 1000°C and less

for higher temperatures, suggesting that the chances of thermal shock fracture at high heating rates are greater. These suggestions are similar to the conclusions reached by Sato et al. in their thermal shock fracture studies of soft carbon materials [26].

It can be concluded from the above analysis that the observed irreversible thermal expansion at $HTT > 1600^{\circ}C$ is mainly due to thermal stresses present in the material, similar to observations of other anisotropic materials [13,14,15,16]. These thermal stresses have been found to increase with the increase in cooling rate for the same grain size material and with increase in grain size for the same cooling rate in alumina [27]. Relaxation of internal stresses could occur either through microfracture [28] or reversible phase transformation [29], depending upon the grain size and/or cooling rate.

Recently, yet another method of stress relaxation has been proposed by Holcombe [1] for fine grain ($< 20 \mu m$) tantalum tungstates. He argued that these thermal stresses would cause plastic deformation in the material if reversible phase transformation or microfracture are absent in the material. These arguments, strengthen the proposal that the presence of fine pores ($< 10 \text{ nm}$) and internal stresses [30] in GC is responsible for the dimensional change observed at room temperature after cooling from a designated HTT. This is based on the observation that there is no detectable reversible phase transformation in GC and heat treatment does not cause any opening of pores [31]. The heating of GC would cause the relaxation of internal stresses through plastic deformation that is accommodated in the pores [32] and in the new microstructure, developed at higher HTT. This microstructure has a ratchetlike [1] nature and so the strain is irreversible.

Finally, if the permanent expansion (set) is ascribed to internal (thermal) stresses, then it is easier to understand that the permanent set is reduced after subsequent thermal cyclings, as has been reported by Koenig [16] for GC. This is because possibly during thermal cycling some annealing of internal stress can occur that would reduce the plastic strain in subsequent heat treatments.

5. CONCLUSIONS

1. The density and weight of GC decrease with increase in heat treatment temperature (HTT), while the volume increases.

2. The weight loss reaches a plateau at $\approx 2000^{\circ}\text{C}$, while the density decrease and volume increase show quadratic temperature dependence.

3. The typical values of density decrease, weight loss, and volume expansion at 2700°C are 12.4%, 1.9%, and 10.2%, respectively.

4. It is shown that the weight loss is not the major cause of density decrease. This loss is suggested to be due to the release of residual hydrogen.

5. The density decrease is shown to be mainly due to volume expansion that can be attributed to gas pressure for HTT up to 1600°C and to thermal stress for $\text{HTT} > 1600^{\circ}\text{C}$.

6. The mechanism responsible for the permanent dimensional change is suggested to be ratchetlike, wherein the new microstructure developed during heating is not rearranged during cooling.

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Table I. Experimental and Theoretical Strain Values in Heat Treated GC.

Table II. Thermal Shock Fracture in Heat Treated GC.

Table I. Experimental and Theoretical Strain Values in Heat Treated GC.

HTT	% Wt loss (hydrogen)	$\sigma_{\max}$ (MN/m ²) (Eq. 2)	UTS (MN/m ²) [21]	% Irreversible Strain		
				Observed	Fracture	Lattice (Eq. 3)
1000	0.85	42.	77	0.10	Not available	1.03
1500	1.45	100.	51	0.80	0.35	1.585
2000	1.95	173.	98	1.75	1.90	2.16
2500	1.80	195	138	2.85	10.50	2.77
2700	1.90	220	122	3.25	27.00	3.02

Table II. Thermal Shock Fracture in Heat Treated GC.

temperature (°C)	k cal/cm/sec/°K	σ MN/m ²	α' /°K	E (GN/m ²)	(R') $\sigma / \alpha' E$ 10 ³	(R) $\sigma k / \alpha' E$
1000	0.01	77	1.6×10^{-6}	30	1.60	12.80
2000	0.02	98	3.0×10^{-6}	28	1.16	23.20
2700	0.03	122	3.6×10^{-6}	26	1.30	39.00

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XBL 827-6010

Fig. 1

XB L 828-6423

Fig. 2

XBL 827-6011

Fig. 3

XBL827-6012

Fig. 4

XBL 812-5145

Fig. 5

XBL8012-13463

Fig. 6

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