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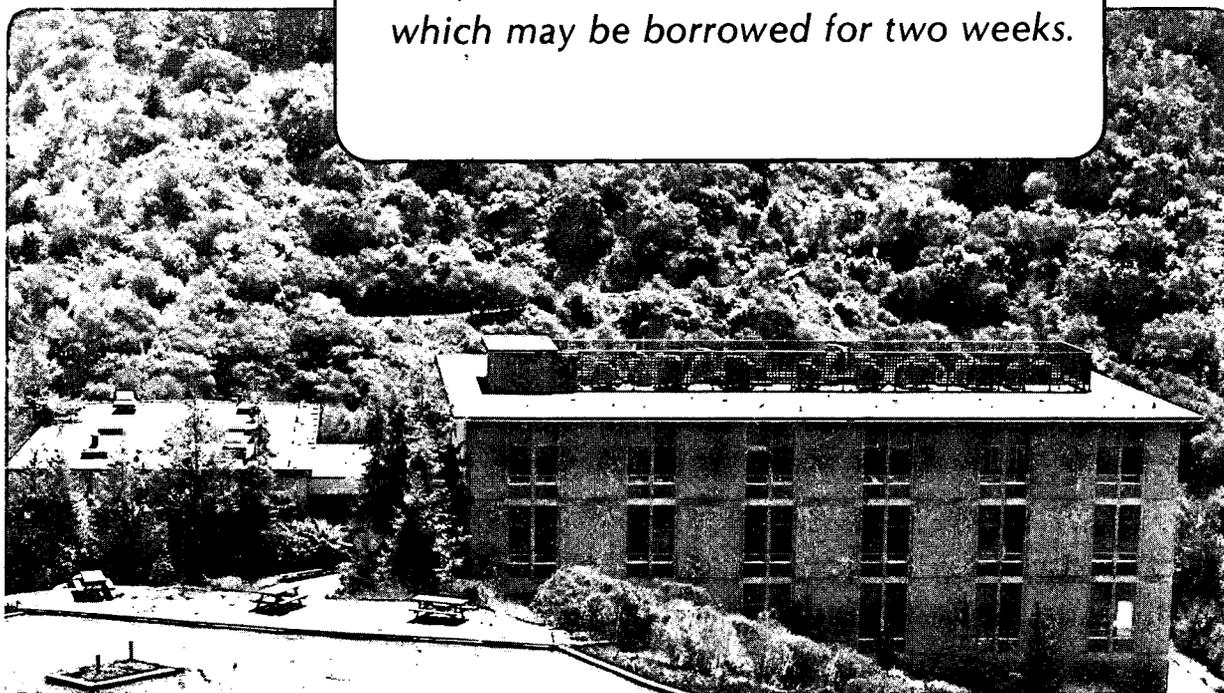
**Nonkinetic Changes in Heat  
Treated Glasslike Carbons:  
Part I — Pore Size and Bulk Dimensions**

J. Lachter, B.N. Mehrotra,  
L.G. Henry, and R.H. Bragg

June 1986

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# NONKINETIC CHANGES IN HEAT TREATED GLASSLIKE CARBONS: PART I - PORE SIZE AND BULK DIMENSIONS\*

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## ABSTRACT

Small angle X-ray scattering measurements have been used to characterize the radius of gyration  $R_g$  of the pores in a glass-like carbon heat-treated between 1000 °C and 2800 °C for periods up to 150 hours. Measurements were also made of the irreversible bulk dimensional changes  $\Delta l$ . In both cases a non-kinetic increase occurs when the heat treatment temperature is increased stepwise to a higher value. The relative changes  $\Delta R_g / R_g$  and  $\Delta l / l$  exhibit a similar three region behavior: an initial increase with the annealing temperature up to 1600 °C, a plateau up to about 2200 °C, and thereafter an increase again. However, the maximum dilatation  $\Delta l / l$  is scarcely 3 percent whereas the increase in  $\Delta R_g / R_g$  is twofold. The first region is attributed to a gas pressure mechanism, and the highest temperature region results from strain relief due to the mismatch of the thermal expansion coefficients in the direction perpendicular and parallel to the layers in graphitic materials. The intermediate region is explained by a combination of both mechanisms.

## I - INTRODUCTION

Investigations of the kinetics of the structural changes in glass-like carbon (GC) materials have usually not taken account of non-kinetic factors [1]. BOSE and BRAGG studied the kinetics of changes in surface area of a GC material [2] and were the first to point out that the data must be corrected for these non-kinetic changes prior to any kinetic analysis. For example, they found that the specific surface area of as-received GC previously processed at 1000 °C decreased instantaneously from  $1150\text{m}^2/\text{cm}^3$  to about  $500\text{m}^2/\text{cm}^3$  when the sample temperature was increased stepwise from room temperature to 2700 °C. However, their study of the surface area kinetics was performed for heat treatment temperatures above 2000 °C and the authors did not analyze the data in terms of the radius of gyration  $R_g$ . LACHTER et al [3] showed that the pores in a GC material similar to that used by the previous authors can

be approximated by ellipsoids of revolution, and HENRY et al [4] monitored both the size and the shape of the pores as they are affected by heat treatment time (HTt) and temperature (HTT). The purpose of the present paper is to investigate the low temperature region (HTT < 2000 °C) not previously studied and to analyze the non-kinetic structural changes as they are related to the radius of gyration and bulk dimensions for HTT's in the range 1000 °C-2800 °C.

## 2 - RESULTS

Experimental details related to the preparation, heat treatment and characterization of the samples used in the present investigations can be found elsewhere [4,5]. The isothermal variations of the radius of gyration  $R_g$  as a function of HTt are plotted on Figure 1. LACHTER et al [6,7] showed that the pore growth kinetics in GC materials can be described in terms of a coarsening theory

where the cube of  $R_g$  is proportional to the heat treatment time HTt. The  $t^{1/3}$  law is evident in Figure 2 where it should be emphasized that the extrapolated values at zero time  $R_{g_0}$  do not coincide for different HTT's but range between 9Å at 1000°C and 24Å at 2800°C. This figure also shows that below  $\text{HTT} = 2200^\circ\text{C}$ , there are no time dependent changes up to about  $\text{HTt} = 100$  hours (150 hours for  $\text{HTT} = 1000^\circ\text{C}$ ), but  $R_g$  increases with both HTt and HTT above  $\text{HTT} = 2200^\circ\text{C}$ . The effect of HTt on the average linear bulk dimensions of the samples is shown on Figure 3 for different HTT's. Since it was found that the average changes in linear dimensions were isotropic, the sample volume  $V$  to the  $1/3$  power was used as a measure of the bulk linear dimensions. The relative variations of  $R_g$  are illustrated on Figure 4 where  $\frac{\Delta R_{g_0}}{R_{g_0}(1000)}$  expressed in percent is plotted versus HTT, curve (a). Here,  $\Delta R_{g_0}$  represents the difference  $R_{g_0}(\text{HTT}) - R_{g_0}(1000)$ , where  $R_{g_0}(\text{HTT})$  is the extrapolated value at zero time at a given HTT and  $R_{g_0}(1000)$  is the extrapolated value at zero time for the processing temperature, i.e., 1000°C. Curve (b) in Figure 4 shows the relative variations of the corresponding macroscopic dimensional changes  $\Delta l/l$  of the samples. It should be noted that  $R_g$  increased nearly twofold whilst the bulk dimensions only increased by about 3 percent. Figure 5 shows data reported by MEHROTRA et al [8]. These in-situ results indicate that when GC is heated at a steady rate it undergoes a reversible expansion up to its process temperature, about 1000°C. In the range  $1000^\circ\text{C} < \text{HTT} < 1600^\circ\text{C}$  the thermal expansion is more rapid, and above 2200°C it is roughly parabolic with HTT. Upon cooling the material contracts along a different path and sustains an irreversible volume expansion. Also the material retraces the cooling curve when re-heated.

### 3 - DISCUSSION

The non-kinetic changes in the pore size as represented by the radius of gyration  $R_g$  have not been reported prior to the present work. As shown in Figure 3, these relative non-kinetic changes exhibit the same

qualitative behavior as the macroscopic relative dimensional length changes  $\Delta l/l$ : an initial increase for  $\text{HTT} < 1600^\circ\text{C}$ , a plateau-like region for  $1600^\circ\text{C} < \text{HTT} < 2200^\circ\text{C}$ , and a roughly parabolic high temperature region for  $\text{HTT} > 2200^\circ\text{C}$ . The GC used in the present work contained about 0.3 weight percent hydrogen as the only significant impurity and this was reduced to 0.01 weight percent at  $\text{HTT} = 2500^\circ\text{C}$ . It is to be noted that HENRY et al [4] showed in their study of the characterization of the pore shape and size in the same GC samples used in the present investigation that the pore size increased as the specific surface area decreased with HTT throughout the heat treatment temperature range, 1000°C-2800°C and the total pore volume is found to depend only on HTT and not on HTt. MEHROTRA et al [8] and MEHROTRA [9] also showed that the density decreases continuously from about  $1.5 \text{ gr/cm}^3$  at  $\text{HTT} = 1000^\circ\text{C}$  to  $1.3 \text{ gr/cm}^3$  at  $\text{HTT} = 2600^\circ\text{C}$ . Since the dimensional changes are isotropic on a macroscopic scale on the one hand, and since most of the residual hydrogen is released at low temperatures ( $\text{HTT} < 1600^\circ\text{C}$ ) on the other hand, the gas pressure mechanism suggested by FISCHBACH and RORABAUGH [10] is the most likely explanation for the volume expansion in this low temperature region. Indeed, increasing temperature causes a volume expansion due to the pressure generated inside the pores from the continuous release of volatile pyrolysis products, hydrogen or hydrocarbons, and perhaps the exolution of adsorbed gases within the closed pore system. BOSE and BRAGG [11] however argued that even though the gas pressure model for density decrease may operate in GC, it cannot fully account for all the density decrease because the pyrolysis of the initial precursor is virtually complete at the processing temperature. Thus, there must be another source of volume expansion and the mechanism was identified as anisotropy in the thermal expansion coefficients in the laths of GC. The thermal expansion coefficient of glass-like carbon materials perpendicular to the layer planes is about  $28 \times 10^{-6}/^\circ\text{C}$  whereas the coefficient parallel to the layer planes is only about  $1 \times 10^{-6}/^\circ\text{C}$ . It is suggested that the gas pressure mechanism operates only up to about  $\text{HTT} = 1600^\circ\text{C}$ ,

the temperature where there is an onset of a plateau in Figure 4 for both  $\Delta R_g/R_g$  and  $\Delta l/l$ . This plateau-like region ( $1600^\circ\text{C} < \text{HTT} < 2200^\circ\text{C}$ ) corresponds to the irreversible changes observed in many studies of volume expansion in carbons and graphite [12-16] and must represent a combination of the end of the gas pressure mechanism and the beginning of the anisotropic thermal expansion contribution. This anisotropy has been shown to be responsible for causing internal stresses during cool-down from a higher temperature, and consequently permanent thermal expansion in many polycrystalline non-cubic materials [17], ceramics [18], pyrolytic [19] and vitreous carbons [20,21]. The effect of the HTT behavior of the thermal stress, small below about  $1600^\circ\text{C}$  and increasing almost parabolically up to the highest HTT, would be expected if the thermal expansion coefficient  $\bar{\alpha}$  is a statistical average  $\bar{\alpha} = \frac{1}{3}\alpha_c + \frac{2}{3}\alpha_a$ , where  $\alpha_c$  and  $\alpha_a$  are the thermal expansion coefficients in the  $c$  and  $a$  directions respectively. Using values from KELLY and TAYLOR [22], one calculates  $\bar{\alpha}T = 9.82 \times 10^{-6}T + 0.50 \times 10^{-9}T^2$ , where  $T$  is the annealing temperature. Thus, since the pressure increases as  $T$  and the thermal stress increases as  $T^2$  for large values of  $T$ , the thermal stress mechanism must dominate at high HTT's. Assuming that all the weight loss is solely due to hydrogen, the pressure  $P_g$  generated inside the pores can be calculated on the basis of the perfect gas law. The internal stress  $\sigma$  can be estimated according to  $\sigma = E \bar{\alpha} T$ , where  $E$  is the Young modulus. The results are plotted on Figure 6 along with the ultimate tensile stress  $UTS$  whose values are taken from the literature [23]. It is seen that below  $\text{HTT} = 1600^\circ\text{C}$ , the pore pressure mechanism is predominant. For  $1600^\circ\text{C} < \text{HTT} < 2200^\circ\text{C}$ , there is a combination of both the pore pressure and the thermal stress which takes over above  $\text{HTT} = 2200^\circ\text{C}$ .

The magnitude of  $\Delta R_g/R_g$  is remarkable in that modest bulk strains are accompanied by changes in mean pore dimensions nearly two orders of magnitude larger. An explanation must be sought in the unique microstructure of GC. It has been described in terms of interwound laths of 5-10 graphitic

layers 30-50Å wide [24]. However, the model of OBERLIN [25] is probably more nearly correct, i.e., the pores in GC are regions enclosed by wrinkled and folded sheets of materials. The relaxation of the thermal stresses has been shown to occur either through microfracture [26], reversible phase transformation [27] or a plastic deformation if the material is fine grained [28]. Since no reversible phase transformation or microfracture are detectable in GC materials whose pore structure is fine, it seems that the kinetic component of the plastic deformation must be due to the relaxation of internal stresses in the lattice through plastic deformation which is accommodated to some extent in the pores.

#### 4 - CONCLUSION

The evolution of the pores ( $\Delta R_g/R_g$ ) and the bulk dimensions ( $\Delta l/l$ ) in glass-like carbon materials heat treated between  $1000^\circ\text{C}$  and  $2700^\circ\text{C}$  for periods up to 150 hours has been shown to depend on both heat treatment time and temperature. Below  $1600^\circ\text{C}$ , the changes are non-kinetic and the gas pressure mechanism operates causing the small changes in pore size and bulk dimensions. The abrupt increases seen above  $\text{HTT} = 2200^\circ\text{C}$  for both  $\Delta R_g/R_g$  and  $\Delta l/l$  are associated with thermal stress and strain relief.

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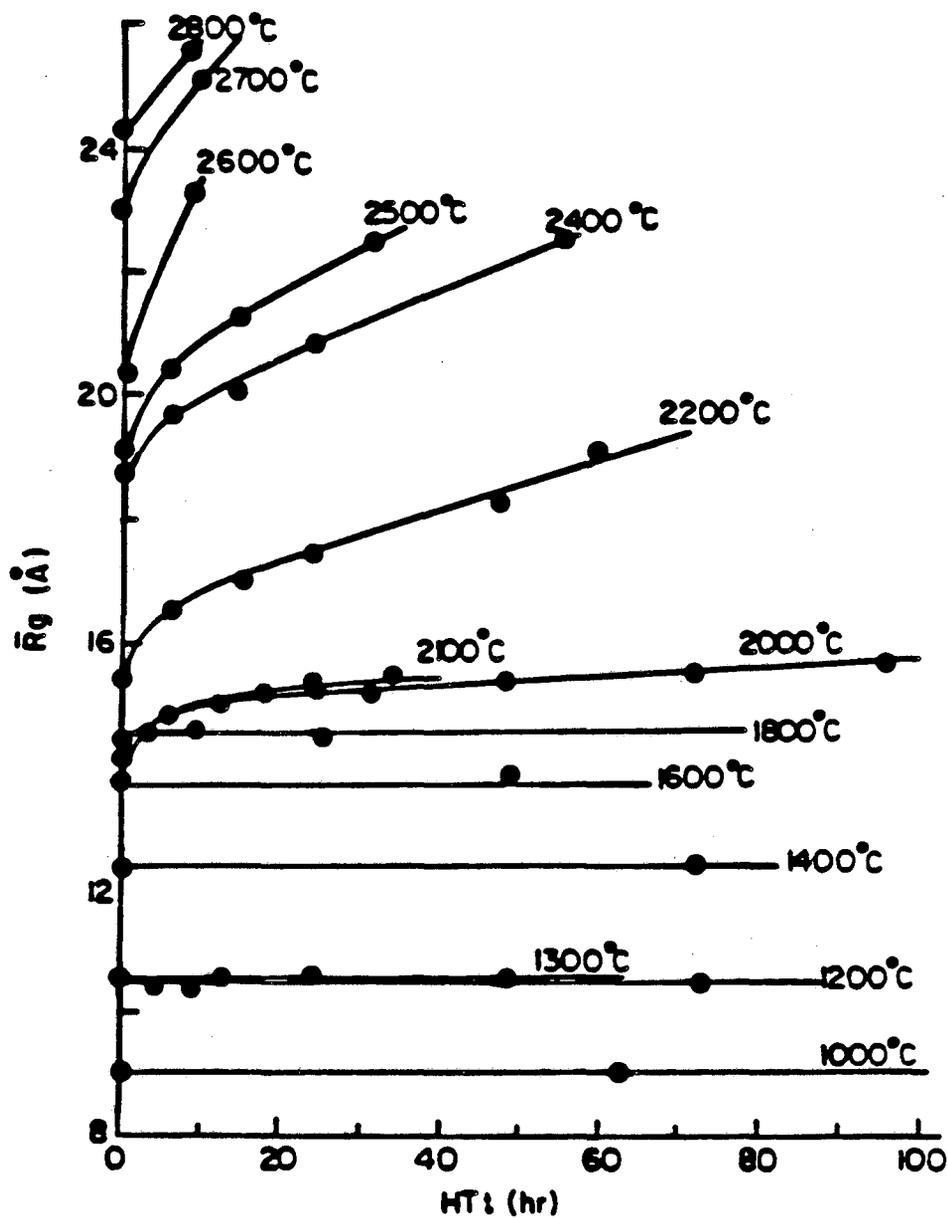
*Part of the work presented in this paper is contained in the Ph.D dissertation of B. N. Mehrotra, University of California, 1986.*

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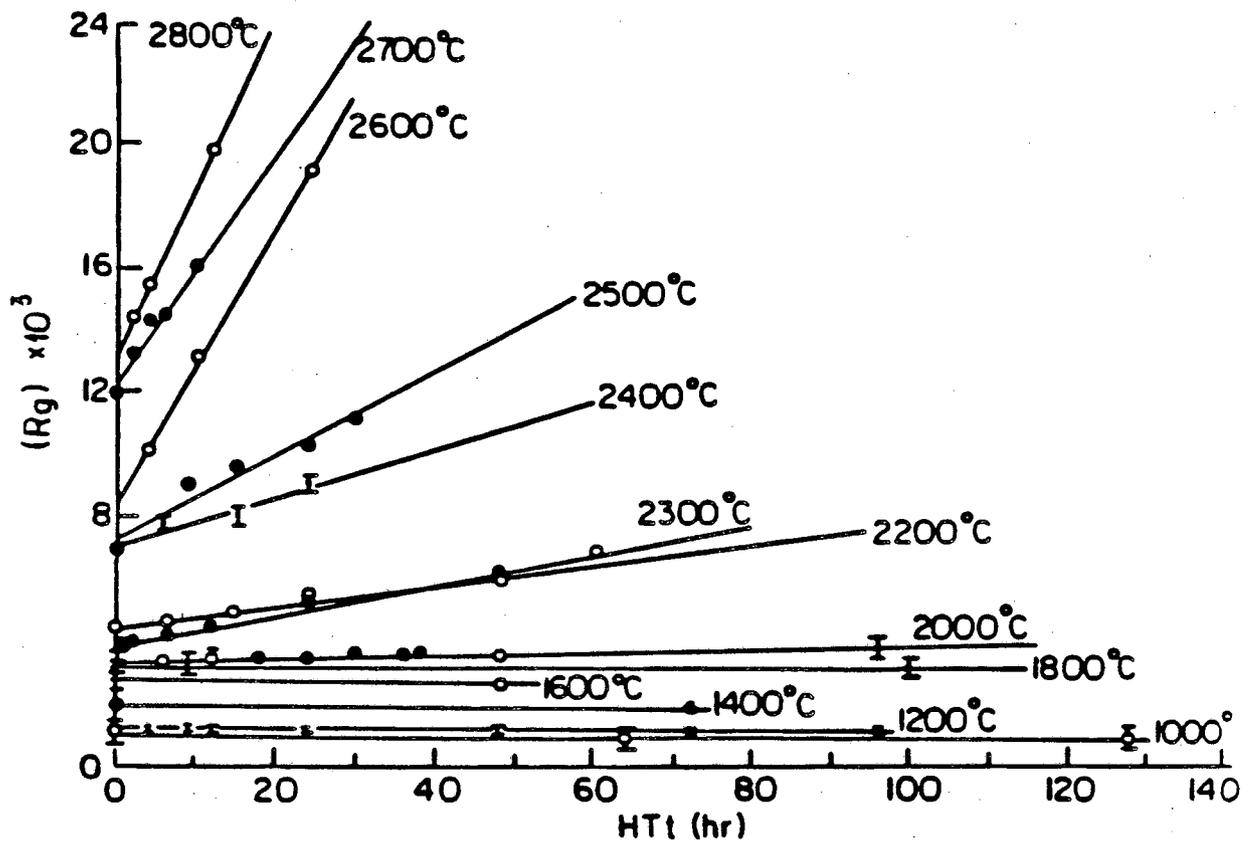
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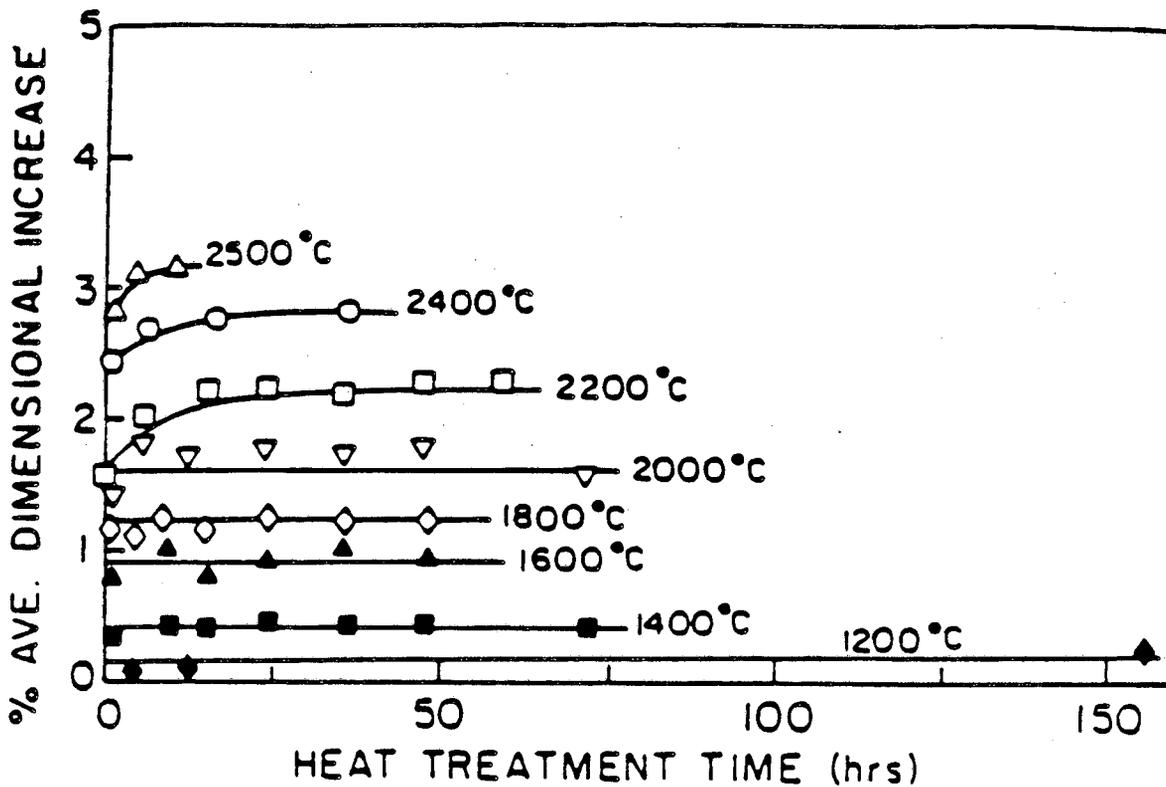
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Fig. 1: Isothermal variations of the radius of gyration  $R_g$  as a function of heat treatment time.



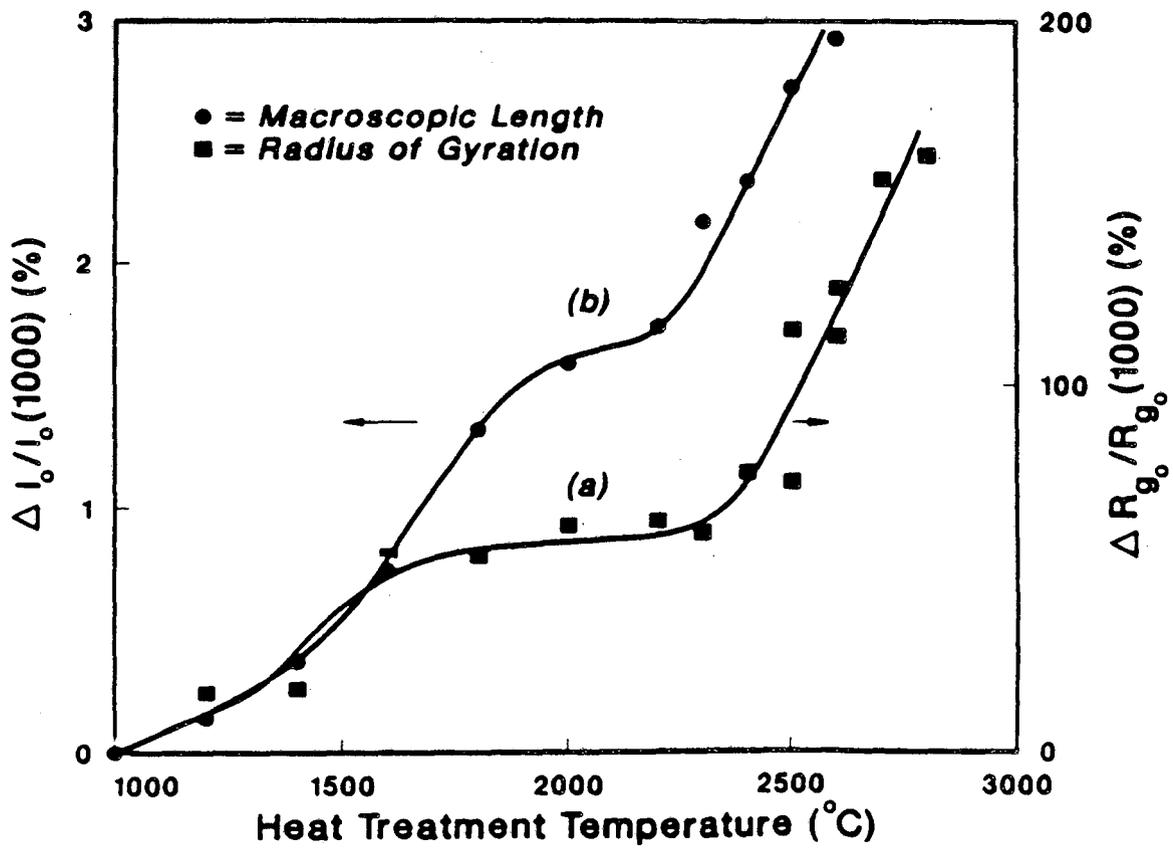
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Fig. 2: Variations of the cube of  $R_{g_0}$  as a function of Heat treatment time,  $R_{g_0}$  being the extrapolated value of  $R_g$  at zero time.



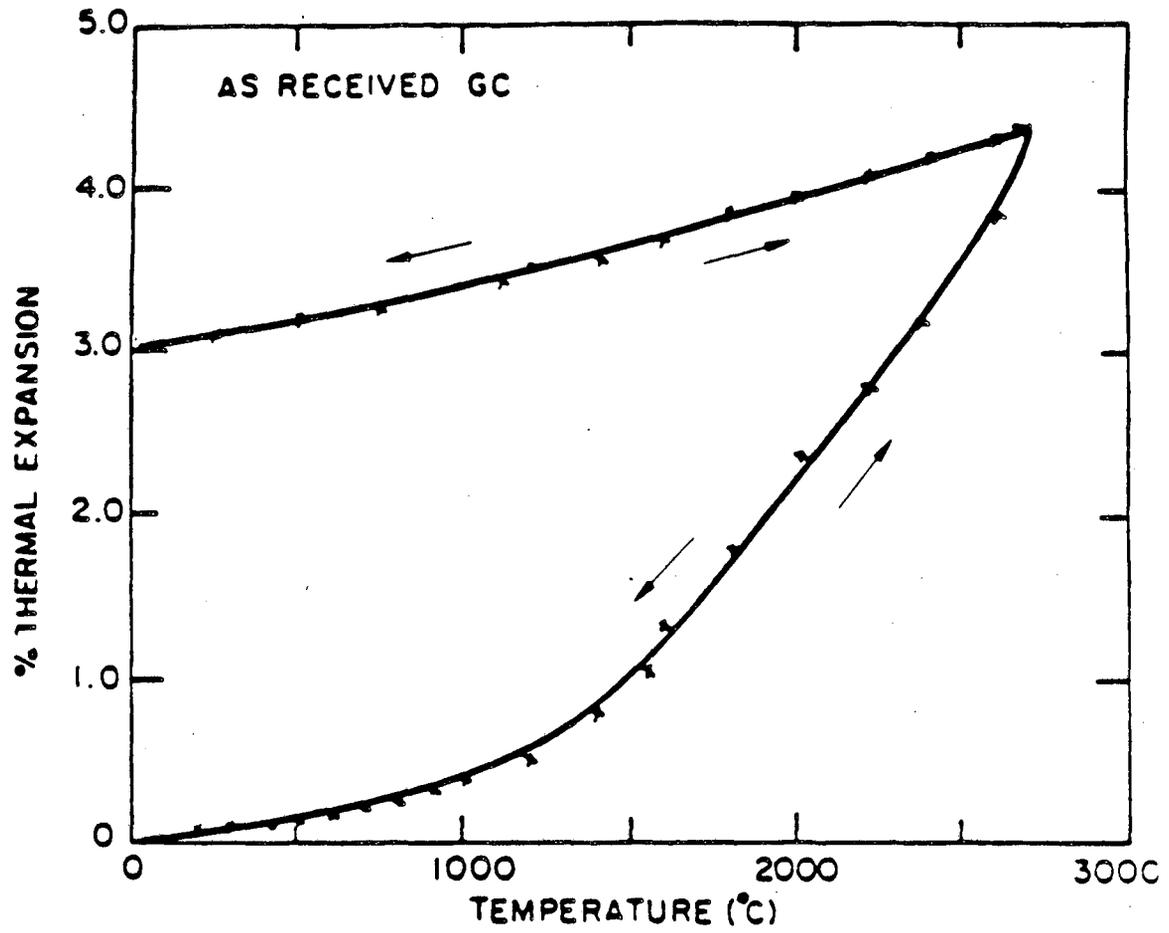
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Fig. 3: Variations of the bulk linear dimensions  $l_0$  as a function of heat treatment time for different annealing temperatures.



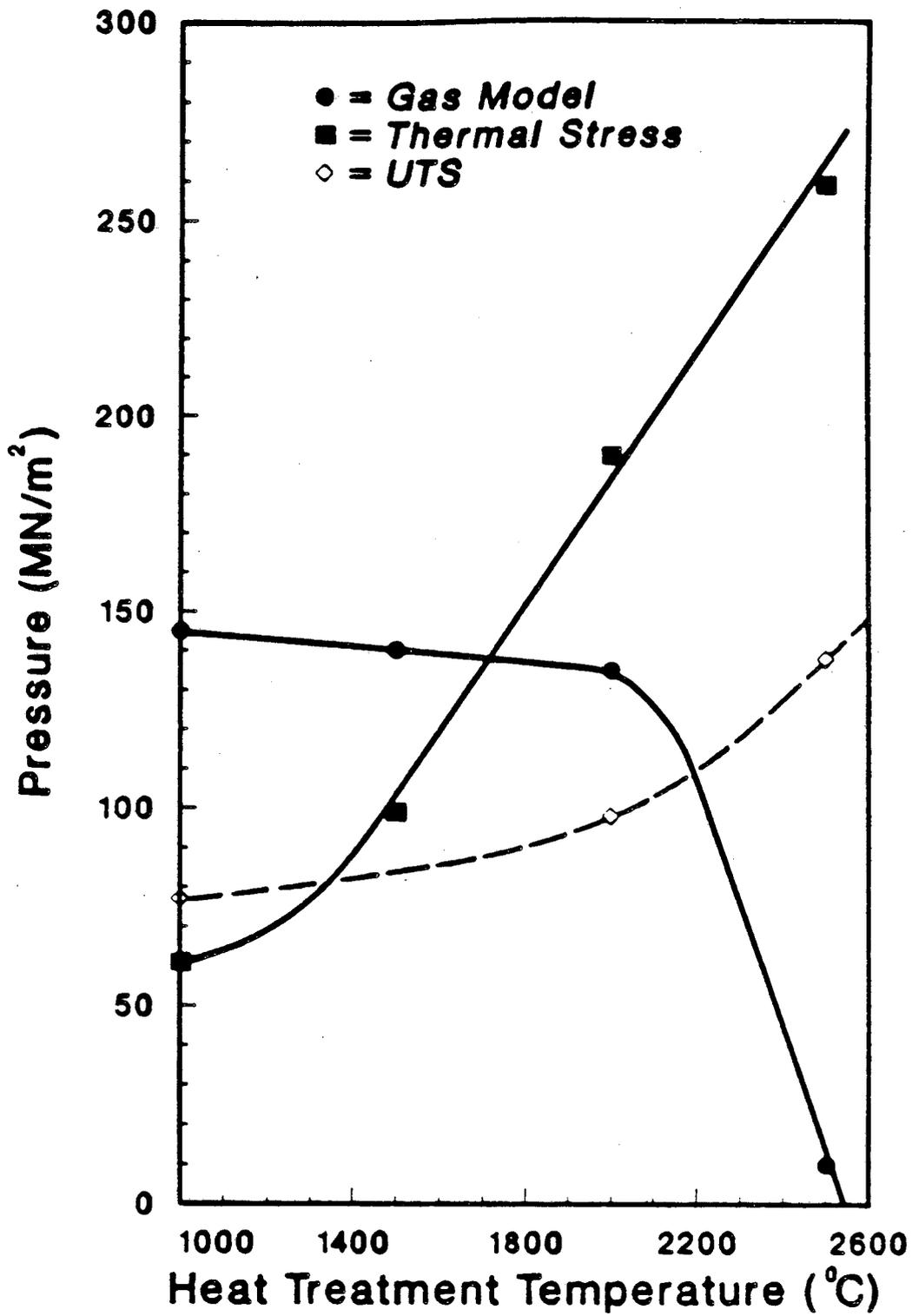
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Fig. 4: Relative variations of  $R_{g_0}$  (a) and  $l_0$  (b) as a function of heat treatment temperature.



XBL 8710-4460

Fig. 5: In situ dimensional changes as a function of heat treatment time for an as-received glass-like carbon sample annealed at 1000°C.



XBL 8710-4461

Fig. 6: Pressure generated inside the pores, pressure due to thermal stress and ultimate tensile strength plotted as a function of the heat treatment temperature.

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