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SUBCRITICAL CRACK GROWTH OF GLASSY CARBON IN WATER

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The subcritical crack growth characteristics of glassy carbons in water were measured and are correlated with their elastic moduli. It is observed that the susceptibility to fatigue varies inversely with the elastic modulus, which is directly related to the crack growth parameter N. Crack propagation characteristics of glassy carbons are compared with those of silicate glasses and amorphous metals.

1. Introduction

Vitreous or glassy carbon is a disordered, isotropic, non-graphitized carbon that is formed by the pyrolysis of certain organic precursors such as polyfurfuryl alcohol, cellulose or phenolformaldehyde resins [1]. The physical properties of these resulting synthetic carbons are directly related to the specific precursor and the thermal pyrolysis schedule, so that, in general, a wide range of properties are obtainable [2, 3]. Nevertheless, in spite of the many processing variables, this particular form of carbon resembles inorganic silicate glasses in many respects, including low gas permeability, relative chemical inertness, a conchoidal appearance of fracture patterns that exhibit mirrors [4] and a susceptibility to subcritical crack growth [5] which causes fatigue or time-dependent failure as was reported for graphite [6,7]. It is with regard to this latter phenomenon that this study was undertaken. This paper reports the relation of the subcritical crack growth characteristics to the physical properties of glassy carbons. It also compares glassy carbon, silicate glasses and amorphous metals with regard to other fracture characteristics.

2. Materials

The glassy carbons studied in this investigation were commercial products* manufactured according to two different processes (I and II) and pyrolyzed at three different temperatures, 1000, 2000 and 3000°C (labelled 1, 2, or 3). The precursors are not identified. Properties are listed in table 1, where I-2 identifies process I pyrolyzed at 2000°C, etc. Also listed in table 1 is the glassy carbon studied by Nadeau [5] which was pyrolyzed at 1850°C. It probably can be most directly compared with I-2 and II-2. Specimens were received in the form of plates 3–5 mm thick, 25 mm wide and 75 mm in length. All of the specimens were diamond ground, removing equal amounts from each surface and eliminating the compressive surface layers reported by Nadeau [5]. Although it is apparent that the density increases with increasing temperature of pyrolysis, the elastic modulus reaches a maximum value for an intermediate pyrolysis temperature, in the vicinity of 2000°C as was reported previously [2].

X-ray diffraction studies on these six glassy carbons revealed diffuse patterns analogous to those reported by Noda and Inagaki [8] with the exception of I-3. Specimen I-3 had a considerably sharper (002) reflection, indicative of some graphitization during pyrolysis. Its low elastic modulus substantiates this observation.

3. Experimental

3.1. Crack velocity measurements

A graphical description of the fundamental fracture behavior of a brittle material is the ($K_I - V$) diagram, a plot of the opening mode stress intensity factor versus the crack velocity. These diagrams are readily generated via the double-torsion technique (DTT) [9], which has been previously utilized to report similar data on a glassy

Table 1
Properties of the glassy carbons.

Material	Density (g/cm^3)	E(MN/m^2) × 10^{-4}	$-\log A$	N
I-1 (1000°C)	1.47	2.87	795	154
I-2 (2000°C)	1.50	2.91	546	103
I-3 (3000°C)	1.52	1.58	302	57
II-1 (1000°C)	1.45	2.47	370	70
II-2 (2000°C)	1.45	2.67	490	92
II-3 (3000°C)	1.48	2.43	312	59
Nadeau [5]	1.49	3.05	1037	178

* Tokai Electrode Manufacturing Co., Hofu, Japan.

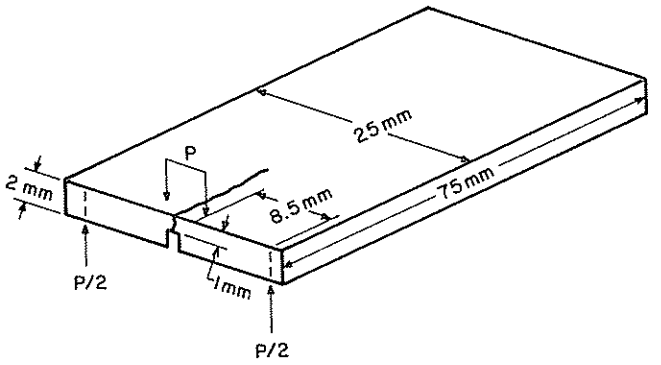

Fig. 1. The double-torsion specimen geometry.

carbon [5] and also on polycrystalline graphites [7]. Fig. 1 illustrates the specimen geometry. Since the environmental factors, temperature and humidity, are well known to affect subcritical crack growth in silicate glasses [10,11], these glassy carbons were all tested submerged in distilled water at 25°C to maintain constancy of those factors.

For double-torsion testing, the aforementioned plates were side grooved 1 mm deep with a diamond saw and notched 1 cm at the end to be loaded. The specimen was loaded on a commercial testing machine at constant crosshead speed until the specimen "precracked" itself from the sawed notch. The initial crack propagation was easily detected from the deviation of the load-time trace from linearity. Once the load reached a constant value, the cross-head was arrested and the crack extension monitored through the load relaxation. Stress intensity factors were calculated from [9]

$$K_I = PW_m \left[3(1+\nu)/Wt^3 t_g\right]^{1/2}, \quad (1)$$

where P is the load, W_m the moment arm, W the specimen width, t the sample thickness, t_g the sample thickness at the groove and ν Poisson's ratio. Crack velocities were calculated from:

$$V = (P_o\dot{y}/P_oB)(\dot{P}_i/P_i^2), \quad (2)$$

where V is the crack velocity and the subscripts o and i refer to the original and subsequent conditions respectively for the load $\dot{P}$, and the relaxation rate P. The crosshead speed prior to relaxation is $\dot{y}$, which was 0.005 in/min, and B is related to the specimen compliance. Note that the application of this technique to the determination of $(K_I - V)$ diagrams does not require knowledge of the crack length.

3.2. Fracture measurements

Fracture toughnesses, K_{Ic}'s, were determined from double torsion specimens by rapidly loading precracked specimens in an inert environment. Specimens were pre-

cracked in ambient air, then enclosed in a dry argon environment and rapidly loaded, 0.1 in/min, to failure. The fracture toughness was calculated by eq. (1). These fracture toughnesses are referred to as K_{Ic} (DTT) in later discussions.

Two other fracture tests were performed by three-point bend tests over a $\frac{1}{2}$ in. span at a crosshead speed of 0.01 in/min. These were on $\frac{1}{8}$ in. square bars that were diamond sawed and diamond ground. Fracture strengths were calculated from the standard mechanics formula

$$\sigma_f = 3PL/2bh^2 , \tag{3}$$

where σ_f is the fracture strength, P the fracture load, L the test span, b the specimen width and h the specimen height. Notched beam fracture toughnesses were also measured on similar bars that were diamond sawed halfway through with a 0.010 in. lapidary diamond blade [12, 13]. These fracture toughnesses, referred to as K_{Ic}(NBT), were calculated from

$$K_{Ic} = (3PLC^{1/2}/2bh^2)(T) , \tag{4}$$

where C is the length of the precrack and T is a geometrical constant equal to about 2.3 for these specimens. Elastic moduli were measured by resonance techniques as discussed by Spinner and Teft [14].

4. Results and discussion

4.1. Subcritical crack growth

Subcritical crack growth data on $(K_I - V)$ diagrams can frequently be described by the relationship [15]

$$V = AK^N \quad \text{or} \quad \log V = \log A + N \log K . \tag{5}$$

Fig. 2 indicates the valid application of this relation to these glassy carbons in water. Nadeau [5] similarly observed satisfactory straight-line agreement with the log-log relationship in ambient air. Regression analyses of the data from fig. 2 yields N and $\log A$ values for these glassy carbons. These values are listed in table 1 along with the densities and elastic moduli. It is apparent that the two glassy carbons pyrolyzed at 2000°C, namely I-2 and II-2, occupy the positions furthest to the right on the $(K_I - V)$ diagram. This indicates that compared to the others, these two require higher values of K_I to produce a given crack velocity V. This is consistent with the general observation that some mechanical properties of glassy carbons are maximized by a pyrolysis near 2000°C [16]. Clearly, for a given K_I, the 2000°C pyrolysis appears to yield the slower crack velocities for a given processing.

It is also evident from the data in table 1 that some form of relationship exists between the N's, that is the slopes of the $(K_I - V)$ curves, and the E's, the elastic moduli of the glassy carbons. With the exception of I-3, those materials with higher

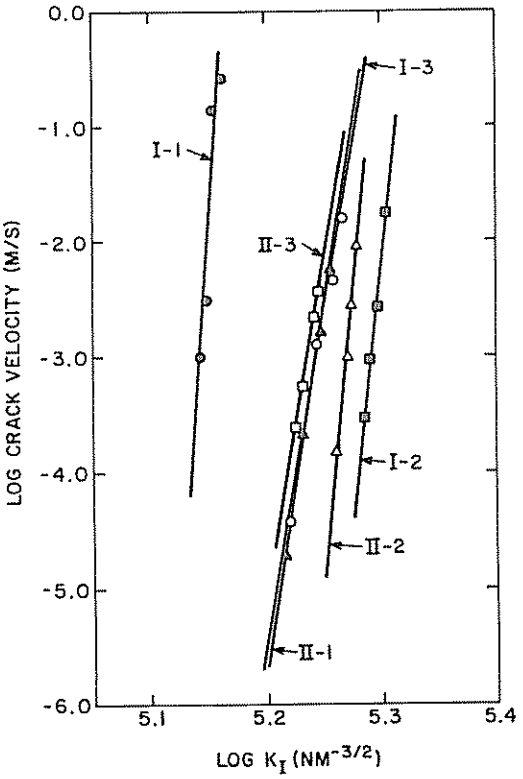

Fig. 2. The (K_I–V) curves of the glassy carbons.

E's have higher N's, and this includes the material measured by Nadeau [5] in air. Fig. 3 illustrates this relationship and also the clear separation of the partially graphitic, I-3 material from the glassy carbons. It is obvious that the (K_I–V) behavior of graphite [7] is different than that of glassy carbon.

This relationship between N and E for glassy carbon can be tentatively explained in terms of the usual interpretation of subcritical crack growth phenomena in silicate glasses. It is generally accepted that the mechanism of slow crack growth in silicate glass is one of a chemical reaction of moisture in the environment with the highly stressed crack surface or flaw tip [10]. Details of the reactions are not specified, but they are all usually written to involve some form of autocatalytic effect. In any event, the relationship between N and the susceptibility to fatigue is an inverse one: that is, silicate glasses with large N's are less susceptible to the fatigue reactions. In an analogous fashion, glassy carbons with larger N's also have larger E's. The higher the elastic modulus of glassy carbon, the less its reactivity or susceptibility to subcritical crack growth. The higher modulus glassy carbons are more resistant to the subcritical crack extension reactions, presumably because the carbon atoms are more strongly

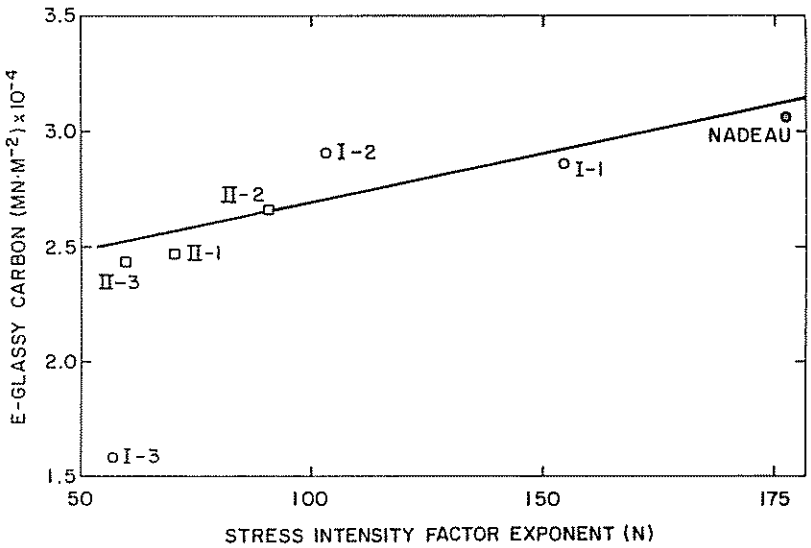

Fig. 3. Correlation of N and E for glassy carbons.

bonded to each other. It would be of interest to attempt a similar correlation of silicate glasses, unfortunately the limited range of available N and E values for silicate glasses does not readily lend itself to such an analysis.

There is also a correlation of the crack growth parameters $\log A$ and N, as evidenced in table 1 and illustrated in fig. 4. The relationship is a linear one, where the slope has units of stress intensity and the intercept those of velocity. Their values are 1.26×10^5 $Nm^{-3/2}$ and 1×10^{-14} m/s respectively. In terms of the fundamental parameters of $(K_I - V)$ diagrams, these strongly resemble values of K_0 and V_0, the fatigue limit, as has been reported to exist for soda–lime–silicate glasses [12]. This information, coupled with the large displacement of the curves from K_{Ic}, strongly suggests that region I subcritical crack growth is being observed for these glassy carbons in water.

4.2. Strength and fracture toughness

Strength and fracture toughness data are summarized in table 2. Several points of interest are evident. For both processes I and II, the strength maximum occurs at, or near, a pyrolysis temperature of 2000°C, similar to the elastic modulus trend and the shifting of the $(K_I - V)$ curves. Clearly, there is some form of mechanical property maximization for a pyrolysis in the vicinity of 2000°C. The calculated flaw sizes are interesting; however they reveal little or nothing about the glassy carbon itself, for their magnitude clearly suggests that they are the result of machining damage.

The fracture toughness data agrees in magnitude with that reported by Nadeau

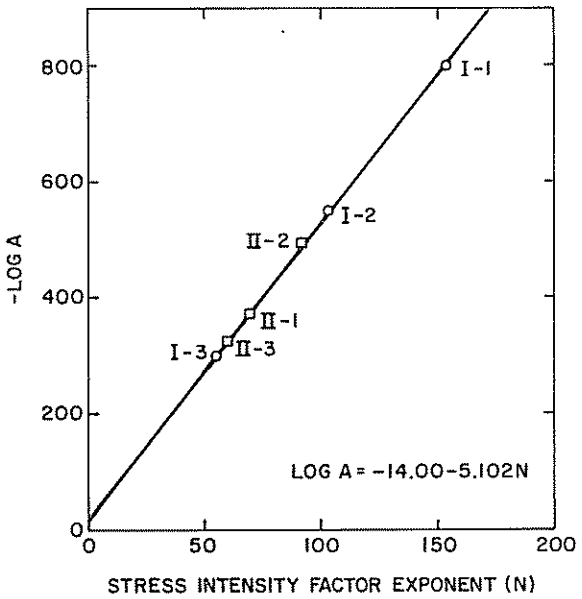

Fig. 4. Correlation of crack growth parameters log A and N for glassy carbons.

[5]; however, his technique differences are not apparent in these results. From these results, the fracture toughness does not appear to possess a maximum at the 2000°C pyrolysis.

4.3. Comparison with other glasses

It is interesting to compare the fracture characteristics of glassy carbon with other glassy or amorphous materials. Ready comparisons can be made from the

Table 2
Strengths and fracture toughnesses.

Material	K_{Ic} (DTT) [a]	K_{Ic} (NBT) [a]	σ_f [b]	Flaw size (μm)
I-2	10.6	10.9	9.4 ± 0.8	43
I-2	10.2	9.1	11.9 ± 2.5	19
I-3	10.5	13.3	11.2 ± 1.2	45
II-1	–	8.1	11.8 ± 0.9	15
II-2	–	9.9	14.5 ± 0.3	15
II-3	–	12.8	11.7 ± 1.3	38
Nadeau [4]	7.6	10.8	11.7 ± 1.4	27

a) $\times 10^{-5}$ $Nm^{-3/2}$.
b) $\times 10^{-7}$ N/m^2.

($K_I - V$) diagrams of glassy carbon and silicate glasses [17]. The overall stress intensities and crack velocities fall in the same general regions for both materials; however, the crack growth kinetics differ substantially. These differences are clearly evident through the descriptive crack growth parameters, most readily N, but $\log A$, too, if desired. The N's are generally much smaller for silicate glasses, lying between approximately 10 and 35, while those of glassy carbons vary from about 50 to 200. Clearly, the range and magnitude of the N's are considerably smaller for silicate glasses than for glassy carbons. On the basis of the magnitudes of N values, glassy carbons have a greater resitance to fatigue than silicate glasses, particularly in water or a moist environment. The ranges of N's possible for these two types of glasses further indicate that glassy carbon can be prepared with a wider range of subcritical crack growth characteristics.

No ($K_I - V$) data is currently available for amorphous metals; however, since there is published fracture toughness data [18] in the form of K_{IIIc} values, it is possible to compare that fracture characteristic with K_{Ic} values for glassy carbons and silicate glasses. It becomes immediately obvious that amorphous metals are essentially ductile compared to glassy carbon and silicate glasses. On that basis amorphous metals are nearly 10^2 times tougher than either glassy carbons or silicate glasses. Both glassy carbon and silicate glasses have comparable fracture toughnesses, about 1 $MN/m^{-3/2}$. However, the elastic modulus of most silicate glasses is about two to three times that of glassy carbon [19], so that the fracture surface energy of glassy carbon must be correspondingly larger than silicate glasses. It might be surmised that the reason for this higher fracture surface energy for glassy carbon is the interaction of the propagating crack with the fine pore structure [20]. By comparison, this very fine pore structure has no comparable structural analog in silicate glasses.

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