

ATOMISTIC BASIS OF FRACTURE IN MATERIALS

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ABSTRACT

The fundamental question in fracture is "How do bonds break?" To answer this question a combination of modeling and experiment is needed. The modeling should be able to suggest the correct energy criterion to describe the geometric change in atomic and molecular positions before and after bond separation. The experimental verification should be robust enough to test quantitatively the tenants of the model. The novel aspect of this research is the application of fractal geometry to explain observed and predicted behavior during fracture. A model based on fractal geometry is suggested as providing the atomic basis of fracture that will fit experimental observations as a result of brittle fracture. The atomic model is based on molecular orbital theory. Molecular dynamics provides the details of the surface created during fracture. It is hypothesized that the fundamental unit of fracture at the atomic scale is a quantity known as a_0 . In turn, a_0 can be related to the fracture energy, γ , and the elastic modulus, E , through a scaling parameter, the fractal dimensional increment, D^* , i.e., $\gamma = \frac{1}{2} a_0 E D^*$. It is suggested that a_0 is a measure of the strain at the crack tip just before fracture and is related to the available free volume for fracture in materials. The characteristic markings of mirror, mist and hackle observed on the fracture surfaces of glasses, ceramics and polymers are related to the fractal dimensional increment: $(Y/Y_j)^{1/2} c/r_j = D^*$, where c is the crack size, r_j , is either the mirror-mist radius ($j = 1$), mist-hackle radius ($j = 2$) or crack branching boundary ($j = 3$), Y and Y_j are constants related to the initial and propagating crack geometry, respectively. The combination of atomistic modeling, experimental measurements and the application of fracture mechanics and fractal geometry leads to a suggested sequence and organization of the brittle fracture process. Brittle fracture, i.e., bond breaking, is a series of bond reconfiguration events at the crack tip dictated by minimum energy configurations. This reconfiguration leads to an increase in free volume all along the crack front. As the crack moves, some of these regions will move either approximately above or below the fracture plane. Nearest neighbor regions of free volume will either add or annihilate. The regions that add, will grow in size. The ones that annihilate each other will return to their approximate original positions. The grown regions will then become nearest neighbors to other regions and the process continues as long as energy is supplied to the system. The addition of regions of free volume will create what is observed on fracture surfaces as mirror, mist and hackle. Macroscopic crack branching is also a fractal process dictated by the energy supplied and the far-field stress. Crack branching patterns are fractal in nature and will provide a description of the size and number of particles created during fracture.

1 INTRODUCTION

The fracture of materials that fail in a brittle manner is a complicated phenomenon that needs the application of several different methodologies in order to better understand the process. Both experimental and analytical approaches are necessary. Within those categories several different techniques need to be applied. Analytically, atomic and molecular models need to be examined. At macroscopic length scales, finite element models and fracture mechanics equations need to be compatible with the atomic and molecular predictions. Modelling has to explain the existence of the fracture surface topography observed, e.g., mirror, mist and hackle in inorganic and organic glasses. Experimentally and analytically, the fracture surfaces needs to be examined at many length scales along with measurements of particle emissions and non-linear crack velocity during propagation. In addition, there are several fundamental questions that need to be answered in order to understand the nature of fracture. How does a bond break? Once a bond breaks, how do the ensembles of bonds, at the tip of a crack, propagate? What are the energetic and geometric steps to fracture? How does energy scale? Is roughness a meaningful parameter for fracture

surfaces? Is there a mathematical formulation which permits insight into the fracture process at all length scales? Although not all of these questions can be answered immediately, insight into some of the answers can be obtained by considering fracture as a fractal process and attempting to compare fractal models at the atomic level with macroscopic experimental measurements. Thus, this paper describes the fractal nature of fracture at the atomic, molecular and macroscopic length scales.

2 ATOMIC MODELLING

The atomic level model for fracture in brittle materials was developed previously using AM1 (Austin Method 1) semi-empirical quantum mechanical molecular orbital theory (West [1]). A set of silica rings were initially optimized to find the ground state geometries and heats of formation. The set of rings included 3-,4-,5- and 6-membered rings in which the silica tetrahedron is the unit member. Each tetrahedron in the ring consisted of two non-bridging oxygens (NBO) terminated with hydrogens forming silanols and two bridging oxygens (BO) connecting neighboring tetrahedra (West [2]). The assumption here is that the atoms along the crack front behave differently than in the bulk because of the free surface and the high energy associated with the crack tip. Thus, there is not as much constraint expected at the crack tip. It was postulated that the atomic and quantum effects at the crack tip control the entire fracture process at the commencement of fracture for homogeneous materials that fail in a brittle manner (West [1]).

Each of these rings were then strained in 0.01 Å increments to observe their response to the attempt at breaking a bridging Si-O bond. Surprisingly, each of the rings condensed or contracted into the next smaller ring with a single silica tetrahedra being extracted in the direction of the strain (see Figure 1). AM1 UHF PRECISE SADDLE (transition state) calculations on this type of fracture event clearly showed that formation of a pentacoordinate silica as the transition state (Poncelet [3]). The energy barrier to this type of fracture was found to be only +26.1 kcal/mol for the 4-member ring in a vacuum which is approximately one quarter necessary to break a Si-O bond. The 3-member ring has the highest barrier to fracture via ring contraction at + 62.4 kcal/mol and the 5-membered ring has the lowest at + 17.0 kcal/mol. The 6-member ring has an intermediate value of + 40.6 kcal/mol. The effective or average energy barrier to fracture was estimated using the Bell and Dean distribution of ring sizes in amorphous silica (a-silica) (West[1]). Thus, a weighted average barrier could be determined for fracture in vacuum.

Figure 1 shows a schematic of the atomic representation of the change in configuration of a silica ring structure before and after fracture. The initial shape, which represents the structure with strain but before the fracture event, is characterized by “a”, the body diagonal length and “c”, the initial length between two arbitrarily selected reference silicon atoms. After fracture, c deforms to c' so that the strain, ϵ , is $(c' - c) / c$. The ratio of a/ϵ has been identified as a_0 , a structure constant related to the fractal nature of the surface formed (West[1]). The quantity a_0 is most likely a spectral average of all reconfiguration events occurring during fracture. A comparison of the value of a_0 to experimental results will be discussed below.

3 FRACTURE SURFACE ANALYSIS

The observations of the mirror mist and hackle regions on the fracture surface have been known for quite a few decades. As early as 1950, Preston observed that the mirror region contained perturbations from the plane of fracture was not a “smooth” surface (Guilloteau [4]). If we examine the mist and hackle regions of the fracture surface we notice that if we magnify the mist region, it appears similar to the hackle region (Kulawansa [5],Beauchamp [6]). Thus, the process which produces mist evidently is the same as that which produces hackle. This similarity with different magnification is called scale invariance. There have been observations that the “mirror” region, which is apparently smooth, actually contains perturbations from the primary plane of fracture. Examination of the fracture surfaces show that the mist and hackle regions appear self-

similar, i.e., one region appears statistically the same as another region at the same radial distance from the origin. Fractal fracture surfaces are generally self-similar (and in some cases self-affine, Bouchaud [7]), scale invariant, and characterized by their fractal dimension, D . The fractal dimension is a generalization of the Hausdorff dimension, which for surfaces has a value between 2 and 3. The actual value depends on the tortuosity of the surface. Since the decimal portion of the dimension contains all of the surface structural information, we have designated that value as D^* . D is then $2 + D^*$. A value of D^* of 0.06 would be relatively smooth and a fractal dimension of 0.5 would be relatively tortuous.

4. CONTINUUM FRACTURE MECHANICS

Almost all of the mechanically induced cracks can be idealized as a semi-elliptical, sharp crack of depth, a , and half-width, $2b$. The relationship between the stress at fracture, or strength, σ_f , and the fracture toughness, K_{IC} , is:

$$K_{IC} = Y \sigma_f (c^{1/2}) = \sqrt{(2E \gamma_c)} \quad (1)$$

where K_{IC} is the critical stress intensity factor (fracture toughness), Y is a geometric factor which accounts for the shape of the fracture-initiating crack, E is elastic (Young's) modulus for plane stress conditions, and γ_c is the critical fracture energy, i.e., all the energy involved in fracture including the creation of new surface. Y in Eqn.(1) depends on the ratio a/b [$c = (a * b)^{1/2}$]. For surface cracks without local residual stress and those that are small relative to the thickness of the sample, $Y \sim 1.26$.

We observe that from the fracture origin, the crack propagates in a relatively smooth plane (the mirror region) to the boundary, r_1 , and progressively gets rougher by deviating slightly out of plane in a region that resembles mist (the mist region), between r_1 and r_2 . Finally, the crack deviates locally from the main plane of fracture (the hackle region), between r_2 and r_3 , getting very rough and finally branching into two or more cracks at r_3 . Beyond macroscopic crack branching, the process can repeat itself on each branch of the propagating crack. These regions are all related to the applied (far field) stress at fracture, σ_f :

$$\sigma_f r_j^{1/2} = \text{constant} = K_{Bj} / Y'(\Theta) = \sqrt{(2E\gamma_{Bj})} / Y'(\Theta), \quad (2)$$

where $r_j = r_1, r_2$ or r_3 corresponding to the different regions in an analogous equation to Eqn. (1). K_{Bj} is the crack branching stress intensity and $Y'(\Theta)$ is a crack border correction factor where Θ is the angle from the surface to the interior, i.e. $\Theta = 0$ to 90° . Note that K_{Bj} is proportional to K_{IC} , i.e. $K_{Bj} = \lambda K_{IC}$ where λ is 3-5 (for $j=1$) for most ceramic materials. γ_{Bj} is the branching energy associated with the different regions, respectively, and E is the same as above.

Fundamental relationships can be derived between the fractal dimensional increment, D^* , and the fracture toughness of a material in the form of the critical stress intensity factor, K_{IC} :

$$K_{IC} = E a_0^{1/2} D^{*1/2} = Y(\theta) \sigma_f c^{1/2}, \quad (3)$$

where E is the Young's modulus and a_0 is a parameter having the units of length. The discussion of the meaning of a_0 is a key element of this paper and will be discussed in detail later. The relationship between K_{IC} and D^* is based on experimental observations and the relationship between K_{IC} and c is based on fracture mechanics and experimental confirmation. The measurement of D^* is an average property of the entire fracture surface and a measure of its tortuosity. The flaw size is a linear measure of the critical flaw area locally around the fracture origin.

It can be shown that (Mecholsky [8]):

$$(Y / Y_j)^{1/2} c / r_j = D^*. \quad (4)$$

where Y_j is a geometric constant for the propagating crack corresponding to the three boundaries.

Fractal dimensions for fracture surfaces of glasses, ceramics, glass-ceramics, single crystals, intermetallics and polymers have been measured. Atomic force microscopy studies have shown that the fracture surface is not smooth at the atomic level for many materials (Guilloteau [4]) and has the same tortuosity at the atomic level as at the macroscopic level. Thus, the crack front is neither smooth nor continuous. A fundamental relationship between basic materials constants, fractal geometry, and fracture parameters has been shown to exist for brittle materials:

$$\gamma_c = \gamma_s + \gamma_t + \gamma_i = \gamma_o + \frac{a_0 D^* E}{2} \quad (5)$$

where γ_c = critical fracture energy (toughness), γ_s = surface energy created during fracture, γ_t = thermal energy during fracture, γ_i = summation of all other energy contributions during fracture, γ_o = fracture energy for a flat surface ($\gamma_o \sim 0$), D^* = fractal dimensional increment of the fracture surface, E = Young's modulus and a_0 = a material structure constant.

The variables D^* , E , and γ_c are independently measurable; a_0 can be calculated from these three variables without introducing any adjustable parameters. Eqn. (5) can be considered representative of the toughness-tortuosity relation for glass, Ocala chert, intermetallics, ceramics and glass ceramics, i.e., the toughness increases as the tortuosity (Mecholsky [8]). Note that a crack propagating through a perfectly homogeneous material with thermal vibrations will not result in a smooth surface. Thus, we should not expect any fracture surface that involves fracture of primary bonds to be smooth if the fracture occurs above absolute zero! Thus, the value of γ_c in Eqn. (5) can be thought of as the fracture toughness, inclusive of all contributing terms

The quantity a_0 is a representation of a length on the scale of the structure of the material. It is most likely the expected average, $\langle a_0 \rangle$, of all of the configurations of bonds at fracture related to a linear unit, similar to the crack "size" represented as a length. The fracture energy and the elastic modulus can be measured using standard techniques on macroscopic structures. Several techniques have been suggested (Meisel[9], Russ[10], Mandelbrot[11]) for the measurement of D^* . The author prefers the slit island analysis because it offers the most reliable values, if sufficient care is taken to protect the surface during contour polishing and the sections are taken approximately perpendicular to the original fracture surface (Hill [12]). The value of a_0 , at this time, cannot be measured. The value is calculated from independently measured values of γ , E and D^* (e.g., West [1]). This calculation is based on relatively macroscopic measurements, i.e., length scales on the order of microns. The estimation of the magnitude of a_0 can also be made from Molecular Orbital (MO) calculations. A comparison of a_0 values calculated using macroscopic, experimentally measured values of E , γ_c and D^* (Eqn. 5) are compared to MO calculations in Table 1.

5 SUMMARY

Brittle fracture is a series of quantized, bond reconfiguration events related to the production of free volume at the crack tip. A series of these reconfigurations along the crack front, due to thermal vibrations and lowest energy configurations, develop into a mirror-mist-hackle pattern. The pattern that develops is started at the atomic scale with the quantized ring contractions based on minimum energy. These ring contractions occur in discrete steps all along the discontinuous crack front. In some locations the contractions stabilize and in other locations two or more rings supplement each other and become larger in a fractal manner. The value of a_0 represents an indirect measure of the size of the initial crack advance. These enlarged groups, in turn, annihilate and supplement other similar groups either to subside or to percolate into large structures, respectively. D^* is a scaling factor for both the fracture energy and the geometry of the fracture surface created. Such structures are suggested to percolate in a self-similar (or self-affine) manner and produce the structure we observe as the fracture surface. At some point, dictated by the type

and strength of bonding, more energy is available than necessary for propagation. At this point, the crack branches macroscopically. The angle and nature of the macroscopic branching depends on energy levels, geometric atomic structure, far field stress, and lowest energy pathways.

On the macroscopic scale, continuum (fracture) mechanics is used. The crack size-to-mirror size ratio is a constant equal to the fractal dimensional increment, D^* . The c/r_1 ratio relates the initiation of crack propagation with the resulting fractographic features quantified by Eqn. (2). On the molecular scale, MD modeling describes the creation of the fracture surface (Swiler [13]) and has been shown to compare well with the experimental observations by using the AFM (Kulawansa [5]) and by a comparison of the fractal dimensions. At the atomic level we can use quantum mechanics to describe fracture as a series of quantized ring contractions dictated by minimum energy and creation of free volume. The geometry of the structure formed is the basis for the structure of the ensuing crack propagation. Many of the calculated critical parameters such as D^* and a_0 derived from the models can be verified experimentally.

6 CONCLUSION

The fracture process for materials that fail in a brittle manner begins with the separation of primary bonds at the atomic level. The bonds separate and can be described as a quantized ring contraction dictated by minimum energy and creation of free volume. At the start of the fracture process along the crack front, the individual bonds either act in concert and increase in amplitude, or subside, depending on chaotic probability. The collective bonds grow in amplitude in a fractal manner to form the features well-documented on brittle fracture surfaces: mirror, mist, hackle and macroscopic crack branching. Fractal geometry can be used to link the atomic bond breaking process to the creation of mirror, mist, hackle and macroscopic crack branching.

7. References

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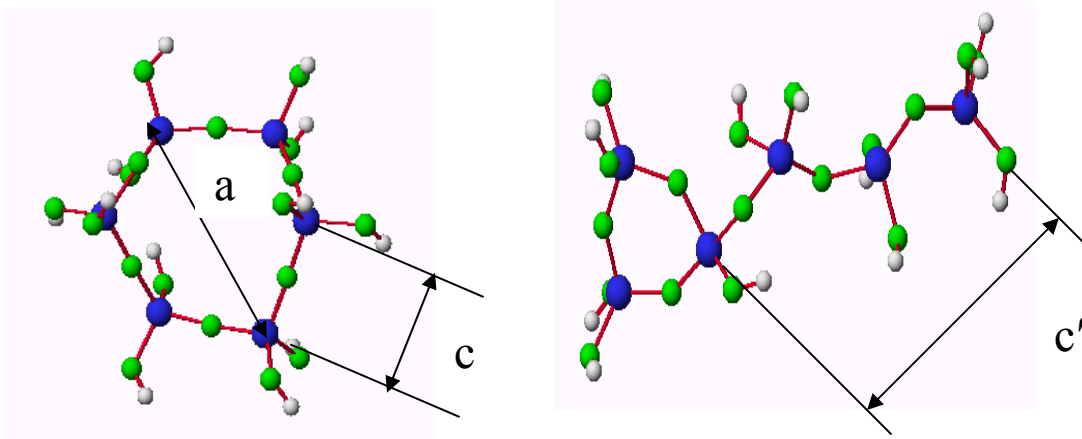


Figure 1 – Schematic of Atomic Reconfiguration Obtained From Molecular Orbital Calculations. (A.) a is the “ring” diameter, c is the distance between two atoms before extension due to stress and (B.) c' is the distance after extension.

Table 1. Comparison of Experimental and Theoretical Values of a_0

Material	γ_c (J/m^2)	E (GPa)	D^*	(exp) a_0 (Å)	(MO) a_0 (Å)
SiO2 glass	4	70.0	0.11	10	11.4
Si (110){100}	4	130.0	0.10	6	7.2
Si (100){110}	6	169.0	0.16	4	7.2
Si (111){110}	3	169.0	0.06	6	7.2
Al2O3	19	406.0	0.31	3	2.8

