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The fracture energy of brittle crystals

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Abstract An expression is derived for the fracture energy, γ, in brittle crystals, namely, $\gamma = kd_0E$, d_0 being the lattice spacing, E Young's modulus perpendicular to the fracture plane, and k is a constant. The value of γ obtained through this expression is compared to experimental data for cubic crystals. Despite the fit, we conclude that because the fracture energy is dominated by the elastic constant, comparisons between a computed γ and experimental data cannot be used to distinguish between bonding functions.

Introduction

The resistance to fracture of a brittle material, i.e., its fracture energy, γ, is governed by the energy needed to form the two fracture surfaces. If the fracture process involves no other energy-absorbing mechanisms, i.e., plastic deformation, heat, surface bond reconstruction, etc., the energy required to form these surfaces is that required to separate two atomic planes. Under these conditions, if the stress–strain expression, i.e., bonding function governing the behavior of the material is known, one should be able to calculate the fracture energy through the integration of the function as the planes are separated.

A number of stress–strain functions have been suggested to apply to inorganic crystals, including the sine function used by Gilman [1], a Morse type function used by Tromans and Meech [2] to model the fracture toughness of ionically bonded minerals, a Born model used by these same authors to calculate the fracture energy of covalent materials [3], and the Universal Binding-Energy Relation [4, 5]. Based on dimensional considerations, the form of the final expression for fracture energy is expected to be similar for all such functions.

In this article, we will demonstrate that while there is good correspondence between models and experimental data on cubic systems, this agreement alone cannot be used to verify the accuracy of such models.

Modeling fracture

Fracture can be modeled as two planes being separated by a tensile stress applied perpendicular to them. If this process is carried out reversibly such that no energy is lost to other processes, e.g., dislocation generation, heat loss, etc., the energy needed for plane separation is the fracture energy. Note that the presence of a crack serves to concentrate stress on the bonds at a crack tip, but is not a fundamental requirement of the model.

The separation, δ, of two planes of atoms from their equilibrium value, d_0, is given by

$$2\gamma = U(\infty) - U(d_0) = \int_{d_0}^{\infty} \sigma(R)\mathrm{d}R \qquad (1)$$

$U(d_0)$ is the equilibrium energy of the crystal, and $U(\infty)$ is the energy at complete separation. $R \equiv d_0 + \delta$, and $\sigma(R)$ is the particular restoring stress governing separation of the planes.

We define $\varepsilon \equiv \delta/d_0$. Then, under plane strain conditions,

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$$\left.\frac{d\sigma}{d\varepsilon}\right|_{\varepsilon=0} = E \tag{2}$$

where E is Young's modulus, whose value is calculated perpendicular to the plane of fracture. For any $\sigma(R)$ we might choose, there exists a strain ε_m for which the restoring stress $\sigma_m = \sigma(\varepsilon_m)$ is a maximum.

As an example, we examine the sine function, which is the simplest, and therefore a popular choice, for a bonding expression. It has a well-defined integration limit, the point of failure. The sine law can be expressed as

$$\sigma(\varepsilon) = \sigma_m \sin\left(\frac{\pi\varepsilon}{2\varepsilon_m}\right) \quad \text{for } 0 \le \varepsilon \le 2\varepsilon_m \tag{3}$$

$$\sigma(\varepsilon) = 0 \quad \text{for } 2\varepsilon_m \le \varepsilon \tag{4}$$

Equation 2 gives

$$E = \frac{\pi\sigma_m}{2\varepsilon_m} \tag{5}$$

Equation 1 then gives

$$2\gamma = \sigma_m d_0 \int_0^{2\varepsilon_m} \sin\left(\frac{\pi\varepsilon'}{2\varepsilon_m}\right) d\varepsilon' = \frac{4\varepsilon_m\sigma_m d_0}{\pi} \tag{6}$$

Combining Eqs. 5 and 6 gives

$$\gamma = \frac{4}{\pi^2}\varepsilon_m^2 d_0 E \tag{7}$$

or

$$\gamma = k d_0 E \tag{8}$$

k is a numerical constant, whose value depends on the particular stress–strain function. We make the point that integrating other expressions, e.g., the Born function, will lead to an equation of the same form.

Any stress–strain function must have the same basic features:

- An initial slope defined as Young's modulus, E
- A maximum stress, σ_m, at some strain, ε_m
- A parameter that defines the range over which the function operates
- An area under the stress–strain curve $\sim 2\gamma/d_0$

Each function contains an unknown numerical parameter, either ε_m or a failure criterion. Without detailed atomistic calculations it is not possible to assign values to these parameters. While Gilman [1] attempted to rectify this situation by assigning a value to the failure criterion, i.e., the period of the sine function, as being one-half of the radiuses of the atoms in the fracture plane, we can find no physical basis for this choice. Despite our lack of knowledge regarding the value of k, we can use Eq. 8 to compare models with experimental data.

Comparison between prediction and experiment

To compare Eq. 8 with fracture experiments, we chose a set of materials having a common (cubic) crystal structure for which experimental fracture energy data were available. No attempt was made to differentiate between good and poor cleavages, or to discriminate between selections based on the perceived quality of the test procedure or the experimental data. Values of the elastic constant pertinent to the particular fracture system for each material were calculated by rotating the $E = 1/S_{11}$ values reported in the literature [6] to the direction perpendicular to the fracture planes (Table 1). The equilibrium plane spacing, d_0, was calculated from the reported lattice parameter and the crystal structure for the relevant set of fracture planes (Table 1). When data were taken from the literature, reported values of fracture toughness (as opposed to fracture energy) were converted to γ through suitable expressions [7].

Our approach was to make no attempt to assign a value to the numerical constant k, but instead to assume that the plane separation process was independent of any other material properties or structure. We first compare the predictions of the model to the experimental data in Fig. 1, by plotting measured values of γ versus $E \cdot d_0$, as suggested by Eq. 8.[1] Notice that this approach is reasonable based on a dimensional analysis. The challenge is to state what the distance, d_0, is relative to the structure.

The line in Fig. 1 is a best linear fit to the data, yielding a value of $k = 0.04$. Because, in the ultra-low elastic constant regime, it was assumed that other types of bonding would apply, we did not force the fitted lines through the origin. Note that the differences in atomic bonding in the materials ranging from completely ionic (e.g., KCl, CaF_2) to completely covalent (e.g., Si, Ge, diamond) [20] do not affect the fit of the data.

There seems to be a single k common to the entire range of cubic materials. However, because k contains an unknown parameter (either the failure criterion or the point of maximum stress), this alone cannot be used to identify the particular stress–strain function that best applies. We also recognize that there are limitations to this analysis because of the lack of experimental data for cubic materials in the intermediate range of 4–10 J/m^2.

The observation from Table 1 that the range of plane spacing's (d_0) for this group of materials is quite small compared to the range in elastic properties suggested that we examine a graph of γ versus the elastic constant (Fig. 2).

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[1] We recognize that experimental values of γ were not obtained reversibly as defined in Eq. 1, so should lead to greater than predicted values of fracture energy.

Table 1 Data used in comparison of measured and calculated values of fracture energy

Material	Plane	d_0 (nm)	E (GPa) rotated	Gamma (J/sq m)	References
KCl	100	0.31	22.90	0.25	[10]
KCl	100	0.31	22.90	0.11	[11]
BaF	111	0.27	66.20	0.35	[8]
ZnSe	110	0.25	78.60	0.6	[12]
CaF	111	0.24	88.40	0.51	[8]
ZnTe	110	0.3	63.90	0.56	[9]
GaAs	110	0.24	121.50	0.87	[9]
GaP	110	0.27	144.60	0.94	[9]
Ge	111	0.25	137.70	1.1	[13]
Si	111	0.24	174.80	1.2	[14]
MgO	100	0.21	335.90	2.4	[15]
MgO	100	0.21	335.90	1.2	[16]
MgO	100	0.21	335.90	1.2	[17]
MgAl203	100	0.19	363.80	3.3	[18]
Diamond	111	0.2	1207.0	10	[19]

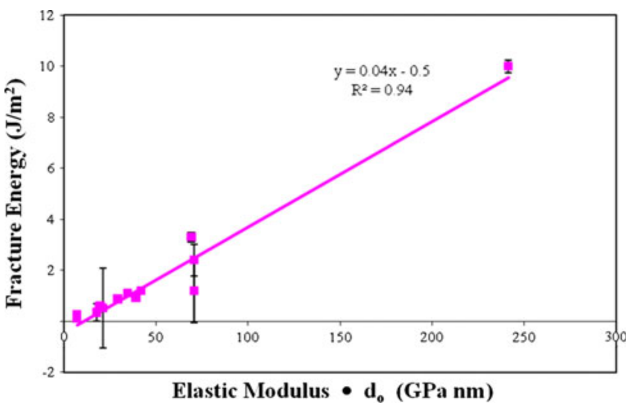

Fig. 1 Measured fracture energies plotted versus $E{\cdot}d_0$ as suggested by Eq. 8

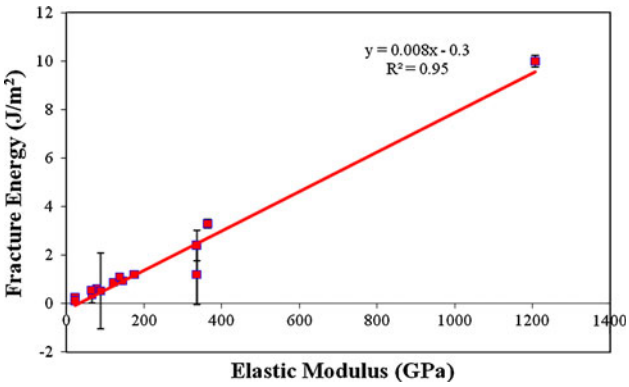

Fig. 2 Measured fracture energies graphed versus Young's modulus, E

Again the fit of the data between measured fracture energy and E is quite good, indicating that the equilibrium interplanar spacing in the crystal plays only a minor role in determining resistance to fracture. The relationship between γ and E emphasizes the fact that this approach as described in Eq. 8 provides no insight into the reason for the relationship. E is equilibrium bond energy per unit volume, whereas γ is the non-equilibrium fracture energy per unit area. Although dimensionally one needs the d_0 value for "correctness," the fact that E can be used alone emphasizes the point that the equilibrium values are almost the same for many single crystal structures and that the elastic modulus is the important parameter in bonding. However, the main point of Figs. 1 and 2 is that graphing the variables in this manner provides no insight into reasons for the relationships. One would need quantum level calculations to understand fracture at the atomic level, as well as the corresponding experimental measurements.

Based on the above graphs, we can conclude that if the elastic properties and the fracture planes in a cubic material are known, a reasonable estimate of its resistance to fracture can be obtained. Indeed, the insertion of any stress–separation function into Eq. 1 will prove to be equally effective in predicting fracture energy. The functional form of the relationship between γ and E dictates that any equation selected cannot be used to distinguish between various models of potential energy. Note that there is nothing in the model that allows one to predict the effect of direction within a set of fracture planes, even though experimental data indicate that fracture energies are different depending on the propagation direction of a crack on a given plane [21]. Thus, the potential energy approach used by many investigators which shows correlations between γ and E or $E{\cdot}d_0$ does not demonstrate any understanding of the process of bond rupture nor does it provide insight into fracture behavior. The main point of the article is that either approach, i.e., one based on "theory" or one based on experimental observation, provides little insight into the fracture behavior of single crystal materials. One needs to use quantum level calculations along with atomic level measurements in order to gain insight into fracture behavior at the atomic level.

Summary

A general expression relating the fracture energy of a brittle material to its elastic properties and crystal structure was formulated based on integration of the stress–separation relation between the fracture planes. A number of possibly applicable stress–strain functions reduce to the expression

$\gamma = kd_0E$

Unlike previous studies which assigned a value to the separation distance at which failure occurred, no quantitative value of a failure criterion was assigned. Instead, it was assumed that k is invariant over the range of cubic materials whose fracture energies range from 0.25 to 10 J/m^2. A good correlation was obtained between the calculated values of fracture energy and those obtained from experiment. It is also shown that there is a correlation between fracture energy and elastic constants *ignoring any contribution from* d_0.

The primary conclusion we draw from this study is that the selection of any stress–separation function, whether simple or sophisticated, will not provide insight into the behavior of materials. Because of the dominance of the elastic modulus in the function, a fit to experimental data, no matter how good, will not be helpful in making the choice of functions. Any models used to predict failure mechanisms must account for specific deformations at the atomic scale, and the models must be verified experimentally using measurements at atomic length scales.

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