

THE NON-THERMAL AND THERMAL PROCESSES OF
FRACTURE AND TIME DEPENDENT STRENGTH OF
BRITTLE SOLIDS

G.M. Bartenev*

ABSTRACT

Non-thermal and thermal (fluctuational) mechanisms of fracture in low-strength brittle solid materials containing sub- and microcracks are discussed. Considered in the non-thermal mechanism of fracture are two types of mechanical losses which are associated with the nature of fracturing, independently of the fact how much the properties of a solid diverge from those of an ideal brittle solid. The non-thermal mechanism of fracture leads to a very poor time dependence of strength regardless of the test temperature.

The fluctuational mechanism leads to the time dependence of strength which is pronounced more markedly, the higher the temperature. Near absolute zero the non-thermal mechanism of fracture is unique.

From the comparison of the two mechanisms it follows that the fluctuational mechanism is responsible for the time dependence of strength experimentally observed in brittle solids. All conclusions are substantiated by numerical calculations mainly as illustrated by a brittle solid polymer.

* Department of Physics of Solids, Lenin State Teachers' Training University, Moscow

Introduction

As far as the mechanism and nature of fracture are concerned, brittle solid materials are represented by all inorganic and some organic glasses at sufficiently low temperatures, may be divided into high-strength and low-strength materials. The main distinction between them lies in the fact that the former are free of sub- and microcracks, while the latter contain submicrocracks. In practice, all engineering brittle materials are low-strength ones. The first physical theory of strength by Griffith as well as many later theories refer to low-strength materials.

Low-strength materials contain microcracks or submicrocracks mainly in surface layers. Therefore, their fracture strength is largely dependent on the size effect and surface-active medium, but practically weakly depends on the chemical composition. A marked scatter of strength value and other characteristics is observed for these materials.

The presence of microcracks in brittle materials gives rise to a mechanism of fracture differing from that for high-strength materials. In glasses containing microcracks the latter commence to grow immediately after application of stresses exceeding the safe stress. Microcracks in brittle solids are characterised by a more or less pronounced distribution in the degree of their danger. Thus, the strength and durability of glasses is determined by a growth of one, more rarely several most dangerous cracks. As a result, low-strength glasses fracture into several macroscopic parts to form mirror and rough zones on fracture surfaces.

High-strength materials were possible to produce only in several cases in laboratory conditions. For instance, the glasses obtained by means of chemical treatment with a fluoric acid [1] practically have no surface microcracks, and their strength amounts to 200-300 kg/mm². Perfect glass fibres [2,3] containing no surface flaws have a strength of 300-350 kg/mm², which is independent of the length and weakly dependent on the diameter of glass fibre; they fracture into a

great number of fragments and even into "dust". As high-strength glasses contain no microcracks, the basic phase of the process of fracture in these glasses is pertinent to the initiation of a great number of microcracks in weak places of the structure by stresses and temperature (the basic factors responsible for fracture). The fracture of high-strength materials comprises two stages: the first is the development of numerous flaws up to the formation of microcracks, and the second is the rapid propagation of microcracks resulting in the final fracture of the specimen into small fragments.

Mechanisms of fracture for low-strength brittle materials are discussed below; accordingly, basic consideration is given to the mechanism of crack propagation in an ideal brittle solid material.

§1. The Molecular Model of a Microcrack and the Mechanism of its Propagation in Brittle Materials

The molecular model of a microcrack (Fig.1) is a development [4,5] of Griffith's and Rehbinder's models of a crack. The breaking of atomic bonds occurs at the boundary between the "bulk" of the material and free surface. Atoms 1-5 are still in the volume of the body, 6-10 and et cetera are already on the free surface; consequently, the act of breaking comes to 5-6. Due to heat agitation and thermal fluctuation, the atoms at the tip of the microcrack get from time to time a certain amount of kinetic energy sufficient to break off or to recombine their bonds, the process of bonds breaking or recombining being accompanied by a loss in the kinetic energy at overcoming potential barriers (Fig.2). Respectively, the kinetic energies of atoms equal to u and u' , are activation energies of processes of bonds breaking and recombination. The difference between potential barriers $u-u'$ is a potential surface energy.

The potential energy of atoms in the volume, as a function of the distance between atoms, is defined by an interatomic distance x , and that for those present on the

free surface (after the breaking of bonds) by an interatomic distance χ' . When a solid is not stressed, χ_0 is an equilibrium interatomic distance in the volume, and χ'_0 in the surface layer. Consequently, the left-hand minimum (Fig.2) corresponds to an equilibrium state of atoms in the volume being far from the microcrack, while the righthand minimum to an equilibrium state of atoms on the microcrack surfaces.

The maximum on the potential curve is due to the fact that the nearest neighbouring atoms present in adjacent atomic layers affect the process of bonds breaking. Their interaction with the atoms emerging to the microcrack surface after the breaking of bonds, is defined by the interatomic distance χ' , which has a maximum at the tip of the microcrack (Fig.1).

For a stress-free material the probability of finding atoms in the lefthand minimum on the potential energy curve is greater than in the righthand one. If corrosion processes, surface-active media and internal stresses, i.e. factors which are not discussed in this paper, are absent, the crack, after removal of stresses, closes up to a flaw on which it has grown.

For a stressed material the tensile stress facilitates the breaking of bonds and prevents their recombination, consequently the kinetic energy necessary for the breaking of bonds is lower than that for their recombination, under stress-free conditions. At low stresses, the assymetry of the potential curve is slightly reduced, but at high stresses the sign of assymetry changes to the opposite one. For this reason the breaking of bonds becomes more propable, and the crack continues to grow. The stress σ_0 at which the potential curve becomes symmetrical and probabilities of bonds breaking and recombination are the same, is called a safe stress.

§2. The Non-Thermal Mechanism of Fracture and Time Dependence of Strength

At very low temperatures near absolute zero heat agitation is practically absent. Therefore the kinetic energy necessary for the transfer of one minimum of the potential

energy to another to occur, is also absent (Fig.2). Under these conditions microcracks do not grow at any stresses below the critical stress σ_K to which the critical overstress σ_K^* at the microcrack tip corresponds.

Above the critical stress the microcracks grow and the solid fractures. If, following Griffith, the mechanical losses discussed in our other paper prepared for this Conference, can be neglected, the starting velocity of microcrack growth, when the stress passes through the level σ_K , immediately becomes critical, and equal in the order of magnitude to the velocity of transverse elastic waves propagating through a solid body. But if one takes into account the dissipation of the elastic energy depending on the velocity of crack propagation, the ultimate velocity will be reached not at σ_K , but at higher stresses.

Further consideration is given to ideal brittle solid materials in which two basic types of mechanical losses are observed in the process of fracture: 1) partial dissipation of the elastic energy by the breakdown of bonds at the crack tip; 2) transformation of a part of elastic energy into the kinetic energy from moving the walls of the crack apart, which then dissipates. The deformation losses which are relatively small for brittle solid materials, will be neglected for simplification of the problem.

The first type of mechanical losses does not depend on whether the microcrack starts to grow slowly or rapidly. These losses are dependent on the number of bonds being broken per unit area of the cross-section.

Mechanical losses from moving the walls of the crack apart, according to Mott [6] and Bateson [7] depend on the velocity of the crack growth. At $\sigma = \sigma_K$, the starting velocity of the microcracks and the 2nd type losses are equal to zero; at $\sigma > \sigma_K$, the starting velocity increases rapidly according to Bateson's equation:

$$v = \frac{V}{\sqrt{2(1-\mu)}} \left[1 - \left(\frac{\sigma_K}{\sigma} \right)^2 \right]^{1/2} \quad (1)$$

where V is the velocity of transverse elastic waves in a solid; μ is Poisson's ratio. As is seen, at $\sigma > \sigma_k$ the velocity of crack growth increases, reaching, at $\sigma \rightarrow \infty$ an ultimate value $U_\infty = V/\sqrt{2(1-\mu)^{1/2}}$. The numerical calculations will give the value of U_∞ rather close to those observed experimentally. Thus, for quartz glasses $V = 3510$ m/sec, $\mu = 0.17$; consequently, $U_\infty = 2290$ m/sec, whereas from the measurements by H.Schardin the ultimate velocity is 2155 m/sec.

When calculating σ_k , it is necessary to take into account the first type of losses, because the 2nd type of losses at $\sigma = \sigma_k$ is equal to zero.

Henceforth, comparison of various mechanisms of fracture will be made numerically on the basis of some typical data. For an unoriented brittle solid polymer in the form of a strip specimen of the width $L = 10$ mm containing an edge transverse microcrack of a small length, data [8] are given below, which are in agreement with the polymer structure and some experimental determinations: the safe stress $\sigma_0 = 1$ kg/mm²; the critical stress $\sigma_k = 12$ kg/mm²; Young's modulus $E = 600$ kg/mm²; Poisson's ratio $\mu = 0.3$ (Shear modulus $G = 230$ kg/mm²); the density $\rho = 1.2$ g/cm³; the frequency of thermal vibrations $\nu_0 = 10^{12}$ sec⁻¹; the distance between polymer chains is 4 Å, and the coefficient of stress concentration at the microcrack tip $\beta = 10$.

An essential simplification is that it was assumed for the model of the microcrack under examination that the coefficient of stress concentration β does not depend on either the stress σ or the microcrack length l . The only justification still now is the good agreement between theory and experiment.

The velocity of transverse elastic waves $V = (G/\rho)^{1/2} = 1400$ m/sec; consequently, the ultimate value of U at $\sigma \rightarrow \infty$ will be $U_\infty = 900$ m/sec, which is in agreement with the experimental data on the maximum velocity of fracture in glass-like polymers.

A curve showing the dependence of the starting velocity of crack growth on the different value of tensile

strength $\sigma = \text{const}$ according to equation (1) is given in Fig.3. The curve is almost of the same form at 0°K and 300°K, as the constants in equation (1) are weakly dependent on temperature.

As the edge microcrack penetrates to the inside of the specimen, the stress σ' in the still unfractured cross-section rises from σ to ∞ , because the tensile stress σ is assumed to be constant during the test. At the same time the velocity of the crack growth increases from the starting to the ultimate according to equation (1), in which σ must be substituted for σ' . The relationship between these stresses for the strip is given by an equation:

$$\sigma' = \sigma / (1 - \frac{l}{L}) \quad (2)$$

where l is the length of the microcrack.

The time dependence of strength in the case of a non-thermal mechanism of fracture may be found from equation (1) in which σ is replaced for σ' . The durability τ at a given tensile stress σ is equal to

$$\tau = \int_0^L \frac{dl}{U} = \tau_\infty \frac{\sigma}{\sigma_k} \text{ArcSin} \frac{\sigma_k}{\sigma} \quad (3)$$

where $\tau_\infty = L/U_\infty$. The initial length of the microcrack being neglected, the lower limit of integration is therefore at zero.

In semi-logarithmic coordinates (Fig.4) the durability equation (3) is represented by Curve 1. As is seen, the non-thermal time dependence of strength is expressed weakly. At $\sigma < \sigma_k$ the durability is equal to infiniteness, while at $\sigma = \sigma_k$ it is equal to $\frac{\pi}{2} \tau_\infty$, and at $\sigma \rightarrow \infty$ it tends to approach the value τ_∞ .

Thus, the non-thermal process of fracture actually does not lead to the time dependence of strength. The process of non-thermal fracture itself is almost of critical nature: below σ_k there is no fracture, but slightly above the fracture is rapid. Therefore the observed time dependence of strength cannot be explained by the non-thermal mechanism of fracture.

§3. The Thermal (Fluctuational) Mechanism of Fracture and Time Dependence of Strength

Near absolute zero thermal fluctuation is infinitesimal, therefore the non-thermal mechanism of fracture is realised in its pure form. With increasing the temperature heat agitation and the fluctuational mechanism of fracture have still greater effect on the process of fracture, the higher the temperature.

The general idea of the fluctuational mechanism of fracture in solids was repeatedly stated long ago (A.Smecal and others). Later, in connection with these or other specific ideas of the fluctuational mechanism of fracture various authors proposed different theories of the time dependence of strength. Critical discussion of these theories is outside the scope of this paper. The principal theses of theory proposed by the author [9] on the basis of the molecular model of a microcrack (Fig.1 and Fig.2) will be considered and developed below.

At a safe stress σ_0 probabilities of bonds breaking and recombination are identical. Therefore, at stresses $\sigma \leq \sigma_0$ the growth of microcracks will not occur at any temperature. At stresses $\sigma > \sigma_0$ the probability of bonds breaking will be greater, the higher the stress and temperature.

Based on the fluctuational mechanism of fracture the starting velocity of the microcrack is $v = v_1 - v_2$ where v_1 and v_2 are fluctuational velocities of the growth and collapse of the microcrack, depending on the probabilities of the process of bonds breaking and recombination at a given stress σ and temperature T . According to our calculations [8,9]:

$$v = v_k \left\{ e^{-\frac{u - \omega \beta \sigma}{kT}} - e^{-\frac{u' + \omega \beta \sigma}{kT}} \right\} \quad (4)$$

Here, $v_k = \lambda v_0$ is the critical velocity of the microcrack growth, k is Boltzmann constant, ω the fluctuational microvolume equal to $\lambda \lambda' \lambda_m$, where λ is the path element corresponding roughly to the interatomic or intermolecular distance to which moves a section of the microcrack front enveloped by fluctuation; λ' is the section element of the microcrack perimeter; λ_m is the distance between the maximum and the minimum on the potential energy curve (Fig.2). The distance λ_m is a magnitude slightly greater than the shift of atoms at the moment of bonds breaking to which corresponds the maximum of the quasielastic force acting between atoms.

The activation energy of the process of fracture is dependent on absolute temperature

$$u = u_0 - aT \quad (5)$$

where, for polymers, $a = 30$ cal/mole.grad [8]. As u_0 is determined experimentally [10], u is readily calculated at a given temperature.

The activation energy of bonds recombination may be defined if the safe stress σ_0 is known. At $\sigma = \sigma_0$, $v = 0$ and from (4) it follows that

$$u - u' = 2\omega \beta \sigma_0 \quad (6)$$

In the work [10] it is shown that the "zero" activation energy u_0 almost practically coincides with that of the thermal destruction of polymers in vacuum. This means that during the process of fracture of the polymer only one chain (or bond) is broken at each fluctuation. Consequently, the fluctuational microvolume ω is related to a single broken chain, and therefore $\lambda = \lambda'$.

For an unoriented solid polymer it can be assumed approximately that every third polymer chain is broken on the way of the growing crack, because one of three chains, on the average, is oriented in the direction of stretching of the strip specimen. As the distance between chains is 4 Å, we find that $\lambda = 12$ Å. The stretching of a C-C bond in the poly-

mer chain at the moment of bonds breaking is approximately equal to the distance between carbon atoms in the polymer chain [11], which is 1.54 Å. Therefore, $\omega = 2.22 \cdot 10^{-19}$ mm. This value is in good agreement with an experimental value [8].

The dependence of the starting velocity of the microcrack in the polymer on stress is shown in Fig.3. The calculated from equation (4) at 300°K and the following values of constants: $\lambda = 12$ Å, $v_0 = 10^{12}$ sec⁻¹, $u = 37$ kcal/mole, $u' = 31$ kcal/mole, $\omega\beta = 2.22 \cdot 10^{-18}$ mm³. At absolute zero $v = 0$ at every $\sigma < \sigma_k$, and differing from zero at $\sigma = \sigma_k$, when $u - \omega\beta\sigma_k = 0$. Hence, the critical stress calculated from equation

$$\sigma_k = \frac{u}{\omega\beta} = \frac{u_0 - \alpha T}{\omega\beta} \quad (7)$$

appears to be dependent on temperature: at 300°K it is equal to 12 kg/mm², at 0°K - to 14.6 kg/mm². These values correspond to the critical overstresses at microcrack tips in an unoriented solid polymer, which is equal to 120 and 146 kg/mm². Thus, these values are approximately equal to the theoretical strength of an unoriented amorphous polymer at 300°K and at absolute zero.

Now, if we replace σ for σ' in equation (4), then an equation can be obtained describing the rise in the velocity of the crack deepening into the material at the given stress $\sigma = \text{const}$. If from the very beginning $\sigma' < \sigma_k$, the fracture of the specimen is going through two stages. At the first stage the initial microcrack grows at the velocity increasing from the starting to that close to the critical velocity (a smooth zone is formed on fractured surface). At the second stage, the initial crack grows at a velocity which is determined by the non-thermal mechanism of fracture. As at the second stage the stress in the remained cross-section of the specimen, excluding the microcrack, becomes greater than the critical σ_k , secondary cracks start growing simultaneously, producing at their meeting cleavages, blisters and other defects on the surface (rough zone).

As it follows from equation (4), at $\sigma = \sigma_k$ the critical velocity is calculated from the expression $v_k = \lambda v_0$. Considering that $\lambda = 12$ Å and $v_0 = 10^{12}$ sec⁻¹, obtain $v_k = 1200$ m/sec for solid polymers. This value is bigger than the ultimate velocity $v_\infty = 900$ m/sec predicted by the non-thermal mechanism of fracture, and therefore cannot be realised. Equation (4) becomes inexact at stresses σ or σ' close to the critical σ_k .

The time dependence of strength due to the fluctuational mechanism of fracture, for a statically stressed strip specimen (at various $\sigma = \text{const}$) with a negligibly small-length microcrack, is calculated from equation (4) in which σ is substituted for σ' . The durability of the specimen acted upon by the given stress $\sigma = \text{const}$ in the range of stresses σ_0, σ_k consists of the times of fracture at Stages 1 and 2:

$$\tau = \int_0^{l_k} \frac{dl}{v} + \int_{l_k}^L \frac{dl}{v_k} = \quad (8)$$

$$= \frac{1}{v_k} \int_0^{l_k} \left\{ \exp\left(-\frac{u - \omega\beta\sigma(1-l/L)}{kT}\right) - \exp\left(-\frac{u' + \omega\beta\sigma(1-l/L)}{kT}\right) \right\}^{-1} dl + \frac{L - l_k}{v_k}$$

where:

$$l_k = L \left(1 - \frac{\sigma}{\sigma_k}\right)$$

The substitution for the above values in equation (8) leads to the time dependence of strength for the polymer at 300°K, which is shown in Fig.4 (Curve 2). The practically straight-lined shape of the durability curve with a slope tangent being $-\omega\beta/2.3kT$ is practically observed on the curve AB. The approximate durability equation conforming to the curve AB is as follows (taking into account equation (5) and $n = \lambda^{-1}$ being equal to the number of bonds broken per unit length of the microcrack path)

$$\lg \tau = \lg \tau_0 + \frac{1}{2.3kT} (U_0 - \omega \beta \sigma) \quad (9)$$

$$\tau_0 = \frac{nLkT e^{-a/k}}{v_0 \omega \beta \sigma} \cong 10^{-12} \text{ sec} \quad (10)$$

The simple equation (9) is well substantiated by numerous investigations of the time dependence of strength [8].

As it follows from equations (8) and (9) the slope of the curve AB becomes steeper with decreasing the temperature. At absolute zero the durability curve transforms into a vertical line $\bar{\sigma} = \bar{\sigma}_K$, and the time dependence of strength disappears.

Strictly speaking, the curve AB is not linear, as at $\bar{\sigma}$ in the range of 2 to 9 kg/mm² $\lg \tau_0$ changes very slightly with changing the stress. From the above given comparison of the two mechanisms of fracture it follows that the thermal (fluctuational) mechanism of fracture is responsible for the time dependence of strength in brittle solids.

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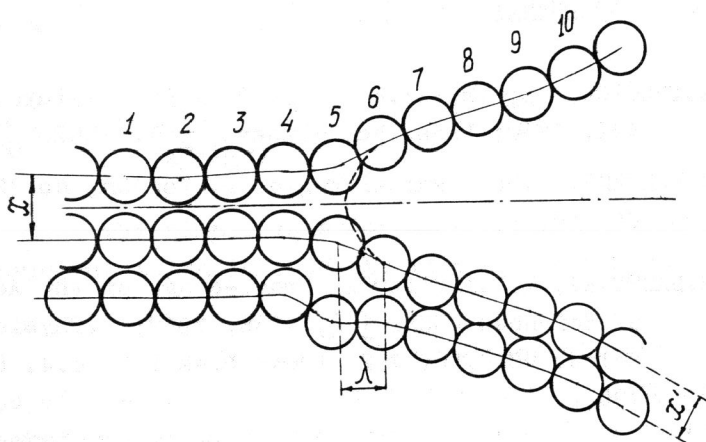


Figure 1. Molecular model of a microcrack in a brittle solid.

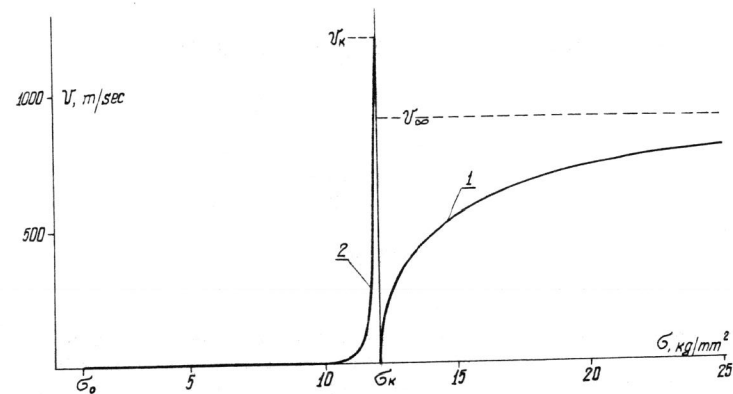
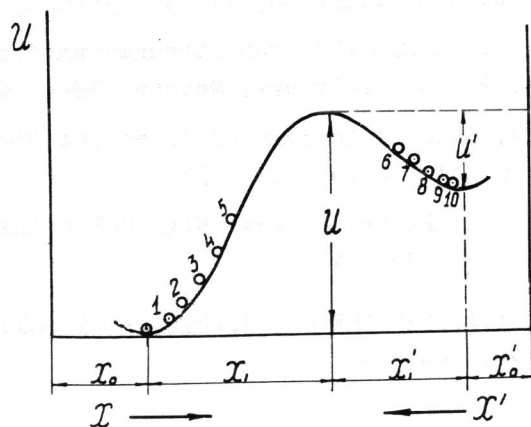


Figure 3. Dependence of the starting velocity of the microcrack on the value of tensile stress for a strip specimen made of unoriented brittle polymer: 1 - a curve corresponding to the non-thermal mechanism of fracture, according to equation (1); 2 - a curve corresponding to the fluctuational mechanism of fracture, according to equation (4) at 300°K.

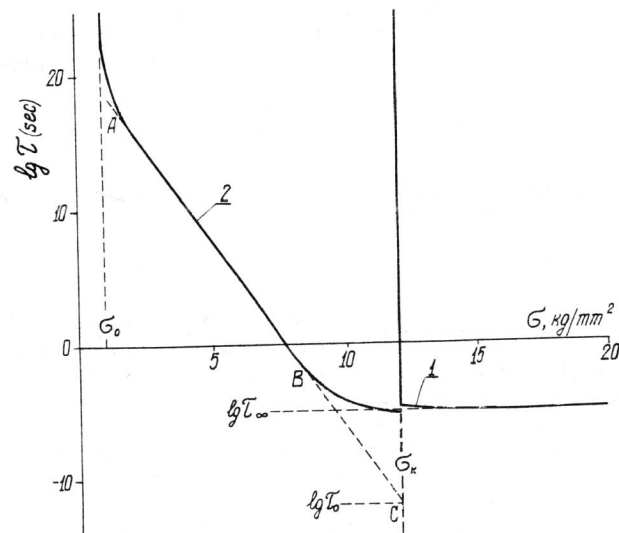


Figure 4. Theoretical durability curves for a strip specimen made of unoriented brittle polymer: 1 - a curve according to equation (3); 2 - a curve according to equation (8) at 300°K ($\tau_{\infty} = 1.1 \cdot 10^{-5}$ sec; $\tau_0 = 10^{-12}$ sec.).