

THE KINETIC NATURE OF THE STRENGTH OF SOLIDS

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Systematic studies of time and temperature dependences of the strength of solids that have been conducted over the last two decades have led to a radical reconsideration of ideas in the physics of failure. It has turned out the materials do not fail by direct mechanical rupture of interatomic bonds, but by separation of atoms owing to thermal fluctuations. That is, mechanical failure of solids is a kinetic phenomenon in which the thermal motion of atoms that gives rise to energy fluctuations plays the decisive role. The experimental bases of the new ideas about failure comprise: first, numerous data from phenomenological studies of endurance (the time until failure) of stressed solids having various structures (metals, polymers, crystals, alloys, etc., amounting to about 100 objects in all), and second, the results of detailed studies of the failure process performed by modern physical methods (infrared spectroscopy, EPR, mass spectrometry, NMR, x-ray diffraction at small and large angles, light scattering, etc.). The latter have been conducted mainly on one of the types of solids: oriented polymers (solids having a "one-dimensional" structure). This has made it possible to trace the development of failure from elementary events of breaking of overstressed interatomic bonds by thermal fluctuations and appearance of nuclei of cracks up to the formation of macro-failure cracks that bring about rupture of the object. The review also discusses briefly developments in the field of the kinetic theory of failure and current problems of further development of kinetic ideas of failure of solids.

INTRODUCTION

AN intensive process of reconsideration and development of the theory of strength of solids is currently going on, in spite of the fact that people have been accustomed to thinking of this field as being practically complete. This process has been caused primarily by a new approach to studying failure of solids: the kinetic approach, in which the thermal motion of atoms and molecules is taken into full account. This article is concerned with presenting and analyzing the experimental data upon which the new kinetic concepts on mechanical failure of solids are based.

Strength characterizes the ability of solid objects to remain intact when acted on by external mechanical loads. For quantitative evaluation of the reaction of solids to mechanical influences, people have introduced the concept of strength as characterizing a certain limiting, critical state of a stressed object, together with the concepts of elastic limit and yield. Initially, study of strength developed within the framework of the mechanics of continuous media. A purely mechanical approach to failure problems persisted even later, when people had begun to consider solids to be structures made of atoms connected by bonding forces. We can distinguish two major junctures in the development

of the physical approach to studying strength and failure of solids.

The first of these involves the creation of the theory of interatomic and intermolecular bonding forces, which made it possible to calculate the strengths of bonds in crystals, glasses, polymers, etc., and to estimate the "theoretical strength" of solids having an ideal structure.^[1-4] Calculation has shown that the theoretical strength is very high, and it exceeds by a factor of hundreds the practical strength of actual solids. This discrepancy has served and is serving as a stimulus to study in the field of strength.

A second step, no less important, in development of physical notions of strength was taken in the fifties, when the kinetic concept of strength was formulated. Here the thermal motion of atoms was cast in the role of one of the fundamental factors directing the failure process. These ideas took into account the fact that the external force does not act on a stationary system of bound atoms, but on a system of particles in vibrational thermal motion, whereby the local stresses on the interatomic bonds vary. The crudest estimate shows that even the average thermal vibrations in a solid produce stresses in the interatomic bonds that are comparable with the rupture strengths of the bonds. However, an especially important role can be played by

inhomogeneity of thermal motion, or energy fluctuations, owing to which individual atoms acquire from time to time a kinetic energy many times greater than the mean.

The aforesaid implies that there is another "extraordinary," mixed way of failure, in addition to the "ordinary," purely mechanical way of breaking interatomic bonds in which the external agent alone pulls the atoms apart when the external force reaches a limiting value equal to the strength of the interatomic bond (the limiting strength was thus derived). Here the atoms become separated at stresses below the strength of the interatomic bonds, and thermal fluctuations complete the rupture of the stressed interatomic bonds. Taking account of the role in failure of thermal motion, and thermal fluctuations is the fundamental content of the new kinetic approach to the problem of strength of solids.

Together with general theoretical considerations, studies on the deformational properties of solids (creep) and relaxation phenomena have also served as bases for molding the ideas of the kinetic conception of failure. Ideas on the determining role of thermal-fluctuation events of atomic and molecular rearrangement in the course of deformation and relaxation processes and on the directionality of these events in the mechanical stress field began to be developed earlier than those concerning failure.^[5-9]

However, the fundamental impetus to development of the kinetic theory of mechanical failure was experimental data on the time- and temperature-dependence of the strength of solids. It was noted relatively long ago that the practical strength of materials ("ultimate strength") is not an invariant quantity, but varies appreciably with the conditions of test. This is indicated by experimental data on dependence of the ultimate strength on the rate of deformation and the temperature in tests in machines that provide a constant rate of deformation,^[10] and also by experiments on creep and endurance (see, e.g., the bibliography in the book^[11]). Time-dependence of the strength under a static load, which has been termed static fatigue of materials, has been observed by many researchers. An effect of the time on strength has been found in silicate glasses,^[12,18] polymers,^[14,15] metals,^[16-18] ionic crystals,^[19-20] etc.

However, no especial attention has been paid previously to all these observations, in spite of their contradiction with the notions of the critical nature of failure. In fact, if rupture sets in only when the stress has reached a limiting value, then it is not clear why the time of testing affects the ultimate strength. The proponents of retaining ideas of the critical nature of rupture in explaining the time-dependence of strength have introduced assumptions of existence of processes that precede or accompany failure. Because of the latter, the strength comes to depend on the time of action of the load. Thus, Orowan^[21] has tried to explain time-dependence of strength by chemical action of the surrounding medium on the material, in particular, for glasses, by formation in the growing cracks of an adsorbed layer that pushes them apart.

Murgatroyd^[22] has advanced the hypothesis of viscoelastic inhomogeneity of solids as a general reason for time-dependence of strength of solids. In a heterogene-

ous system under tension, the stress on the elastic elements increases with time, owing to relaxation of stresses and flow in the viscoelastic micro-regions. The stresses will continue to redistribute until the stress on the elastic elements reaches the ultimate strength of the material, and this will lead to rupture. In essence, this viewpoint ascribes a kinetic nature to a process that accompanies failure, a deformation process, while it denies the kinetic nature of the failure process itself.

However, the cited inner contradictions in the study of strength could also be resolved from the standpoint of treating failure as an independent kinetic process. Systematic studies of the phenomenon of time-dependence of strength have been carried out to determine the validity of these views, mainly in the Laboratory of Physics of Strength of the A. F. Ioffe Physico-Technical Institute of the Academy of Sciences of the USSR. Numerous experiments have shown that the time- and temperature-dependence of strength is not a sporadic phenomenon, but a widespread one that is characteristic of failure of solids that vary in nature and physicochemical properties. This is precisely the experimental result that served as the basis for formulating the kinetic conception of mechanical failure.^[23-30]

In due course, the new views on the nature of failure have aroused a lively discussion. It is not strange that the proponents proved to include the partisans of another kinetic theory, the kinetic theory of deformation. They considered that there is no need to introduce a new kinetic process of failure. The kinetic nature of the deformation process was evident (creep of materials), while the existence of a failure process was not obvious. All of this required setting up special experiments that could prove the reality of the process of gradual failure of solids in order to confirm the truth of the kinetic conception of strength. For this purpose, people have used a series of direct physical methods of study that were unusual in the practice of mechanical testing.

This article reviews the studies concerned with developing the kinetic approach to the problem of failure of solids. Solution of the problem is yet far from completion, and it is as yet too early to speak of a perfected kinetic theory of failure. Many unelucidated and controversial questions still remain. However, the prerequisites have now been amassed for formulating the fundamental assertions of the kinetic theory of failure, and we shall try to reflect this in the article.

The experimental results presented below were obtained by the large collective in the Laboratory of Physics of Strength of the A. F. Ioffe Physico-technical Institute of the Academy of Sciences of the USSR. The initiator and director of these studies is Academician S. N. Zhurkov.

1. ENDURANCE OF SOLIDS UNDER LOAD AND THE FUNDAMENTAL PREMISES OF THE KINETIC CONCEPTION OF STRENGTH

In contrast to the static approach, the kinetic approach treats failure as a real process that develops in time (a process of accumulation of any types whatever of failure). Hence, it is natural to characterize it

either by a certain rate (the rate of accumulation of failures), or by the time in which the process develops to a certain stage and leads to rupture. A characteristic of the strength properties of a material that is very simple and easily determined experimentally, and which simultaneously reflects the kinetic nature of the process is the endurance τ of solid objects under the stress σ , i.e., the time that the specimen exists in the stressed state from the instant of application of the load until rupture. From the standpoint of the kinetic conception of failure, the endurance is a fundamental characteristic of the mechanical strength of a material. We can treat it as a quantity inversely proportional to the mean rate \bar{v} of the failure process. That is, $\tau \sim 1/\bar{v}$.

In order to characterize the strength properties of some particular material from the standpoint of the kinetic approach, we must have information on the relation of the endurance of specimens of this material to the applied stress σ and the temperature T of the test. This same information also permits one to draw conclusions on the nature of the strength.

The cited ideas have led to the conclusion that one must design systematic studies of the relation to the applied stress and temperature of the endurance of solids that are most varied in structure and physical properties. This complex of studies has been conducted, mainly in uniaxial tension on specimens cut out of thin films or foils, or taken in the form of a bundle of fibers.

As a rule, the tests were performed at some chosen temperature T under the condition that the applied stress σ was held constant throughout the experiment. The endurance τ was measured under these conditions. A large series of experiments (tens or hundreds of experiments) was set up to find the relation of τ to σ and T , and different values of σ and T (but constant for a given experiment) were established for each of the specimens. The experiments were conducted over a broad range of temperatures and stresses in an endurance range of up to ten orders of magnitude (from thousandths of a second to many months).

The studies were performed on many substances of various structures and types of bonding forces. They studied polycrystalline metals, [29,31-43] single crystals, [44-47] non-metallic compounds, [25-48] polymers, [29,32,23,49-56] alloys, [33,38-40,57] and complex, composite materials. [58,59,25] About a hundred different materials were studied in all. These experiments led to establishment of laws that are general for solids relating the endurance τ to the acting stress σ and the temperature T (see below).

For example, Fig. 1 gives the experimental data on the relation of τ to σ for tests of different materials at constant temperature. We see that materials that are most varied in structure and properties obey the following endurance-stress relation: the endurance declines with increasing stress (polycrystalline metals and alloys in Figs. 1a and b, single crystals of metals and alkali halides in Fig. 1c, polymers in Fig. 1d, and composite materials in Fig. 1e). In order to determine whether the time-dependence of the strength involves action of the surrounding medium, studies were performed in a high vacuum. Figure 1f shows the results.

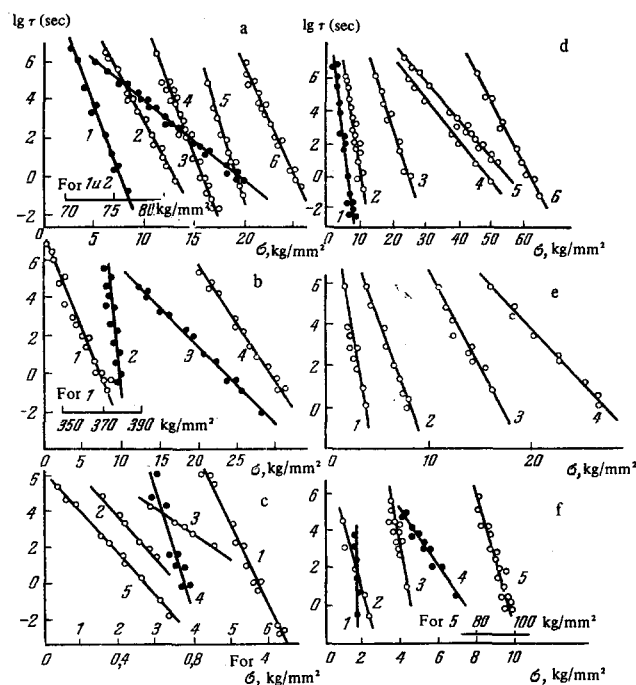


FIG. 1. The endurance τ of different solids under the load σ . [25] a) Polycrystalline metals: 1—niobium, 2—vanadium, 3—aluminum, 4—zinc, 6—silver (1—4 and 6, room temperature); 5—platinum (300°C). b) Alloys: 1—molybdenum-rhenium (18°C); 2—aluminum with 0.75% copper (70°C); 3—silver with 2.5% aluminum (300°C); 4—aluminum with 4% copper (100°C). c) Single crystals: 1—aluminum (18°C); 2 and 3—zinc with varying orientations of the stress with respect to the basal plane (2—35°C; 3—20°C); 4—rock salt (18°C); 5—aluminum (300°C). d) Polymers (room temperature): 1—plexiglas (polymethylmethacrylate); 2—polystyrene; 3—polyvinylchloride (fiber); 4—viscose (fiber); 5—capron (polycapromamide, fiber); 6—polypropylene (fiber). 3) Heterogeneous (composite) materials (room temperature): 1—paper; 2—composite (stressed along the fiber axis); 3—cement, 4—fiberglass. f) Endurance in vacuo (10^{-7} Torr): 1—silver chloride (18°C); 2—aluminum (300°C); 3—aluminum (18°C); 4—polymethylmethacrylate (18°C); 5—oriented capron (18°C).

We see that time-dependence of the strength persists also in a vacuum.

As Fig. 1 implies, the relation of the endurance to the stress is uniform in nature: $\log \tau$ depends linearly on σ . However, the linearity of the $\log \tau - \sigma$ relation breaks down as $\sigma \rightarrow 0$ (see the upper part of the curve in Fig. 2). This is natural, since otherwise the object would have a finite lifetime in the absence of a load. However, if we are not dealing with the region of small stresses,* the $\log \tau - \sigma$ relation remains linear over a rather broad range of stresses, and this fact is used in the following analysis.

The prevalence of the relation of τ to σ for all solids shows that fracture requires a time during which certain processes occur in an object under a tensile load that cause it to fall apart.

The fact that processes of gradual accumulation of failure actually occur with time in a stressed object has been demonstrated by experiments involving interrupted loading. The specimen proved to weaken after being under load for a certain time: its subsequent

*The $\log \tau - \sigma$ relation approaches infinity as $\sigma \rightarrow 0$, owing to recombination processes [25] and other factors. [208-216]

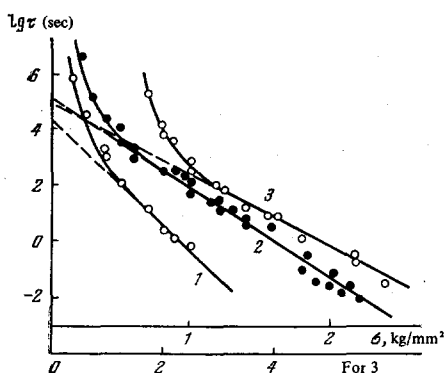


FIG. 2. Endurance-stress relation in the small-stress region. [25] 1—silver chloride (200°C); 2—aluminum (400°C); 3—polymethylmethacrylate (70°C).

endurance (as measured from the instant of reapplication of the same load) is reduced. [15,29]

The effect of temperature on endurance under load has been studied in order to elucidate the nature of the processes that lead the object to failure. It turned out that if one performs the measurements at a series of temperatures, then the $\log \tau(\sigma)$ relation remains linear for each of them, but the slopes of these lines vary regularly (Fig. 3). The slopes of the $\log \tau - \sigma$ lines decrease with increasing temperature, and increase and approach the vertical with decreasing temperature.

It is a highly essential fact that the family of linear $\log \tau - \sigma$ relations at different temperatures is a pencil of straight lines that intersect at a single point, or pole (see Fig. 3). In this regard, this pole was shown to occur at practically the same endurance value, $\sim 10^{-13}$ sec, for all types of solids. This constancy is satisfied with logarithmic accuracy ($\log \tau_0 \approx 13 \pm 1$, where τ_0 is the endurance at the pole), since the pole is found by a rather long extrapolation (see Fig. 3).

The relations obtained experimentally between the endurance τ , the stress σ , and the temperature T have made it possible to establish analytical relationships between these quantities.

The endurance of solids proves to obey the expression [23,26]

$$\tau = \tau_0 \exp(U(\sigma)/kT), \quad (1)$$

where

$$U(\sigma) = U_0 - \gamma\sigma, \quad (2)$$

k is the Boltzmann constant, and T is the absolute temperature.

Some evidence of the applicability of Eqs. (1) and (2) to describe the experimental endurance data is given by a test based on the fact that Eqs. (1) and (2) can be rewritten in the form

$$U(\sigma) = U_0 - \gamma\sigma = kT \ln(\tau/\tau_0). \quad (3)$$

Then the "fanlike" families of lines like those shown in Fig. 3 should collect into single lines when plotted in the coordinates $kT \log(\tau/\tau_0)$ and σ .

For example, Fig. 4 gives the results of such a treatment of the experimental data for a set of solids. As we see, the points are rather densely grouped along separate straight lines, each of which belongs to one of the materials. This fact shows graphically that Eqs.

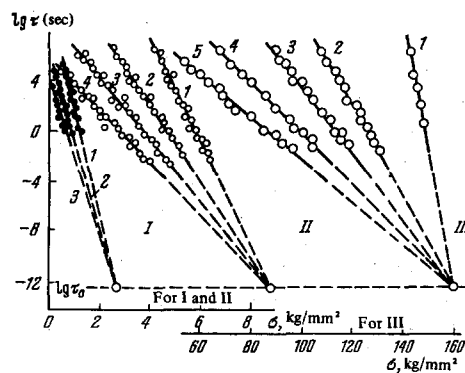


FIG. 3. Endurance-stress relation for different temperatures. [26] I—rock salt: 1—400°C; 2—500°C; 3—600°C. II—aluminum (polycrystalline): 1—18°C; 2—100°C; 3—200°C; 4—300°C. III—capron (oriented fiber): 1—(-180°C); 2—(-120°C); 3—(-75°C); 4—(-20°C); 5—(-80°C).

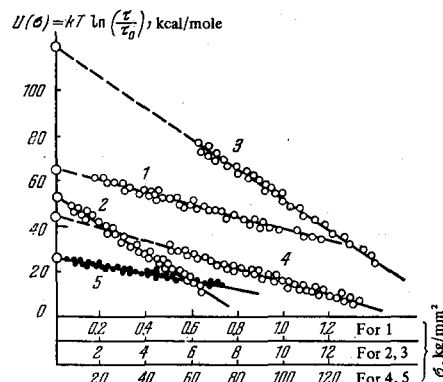


FIG. 4. Relation of the activation energy of failure to the stress. [26,56] 1—rock salt; 2—aluminum (polycrystalline); 3—platinum (polycrystalline); 4—capron (oriented fiber); 5—polyethylene (oriented fiber).

(1) and (2) actually describe well the $\tau(\sigma, T)$ relation. All the following serious conclusions on the nature of failure of materials arise from analyzing Eq. (1), which is the fundamental endurance equation.

We note first of all that the endurance of a material is determined in the same way by both the applied mechanical force (the stress σ) and by the temperature T of the material. Both of these quantities occur in the argument of the exponential. This fact in itself indicates that thermal motion plays an essential role in the course of failure of the material.

The proportionality of τ to the factor $e^{U/kT}$ indicates the thermal-fluctuation nature of the failure process. This conclusion is corroborated by the similarity of Eq. (1) to the expression of the mean time τ_{fl} between two successive fluctuations that impart [60] a kinetic energy E_{fl} to a given atom:

$$\tau_{fl} \approx \tau_a \exp(E_{fl}/kT), \quad (4)$$

where $\tau_a \approx 10^{-13}$ sec is the mean period of the thermal vibrations of atoms in condensed substances. We see that $\tau_0 \approx \tau_a$.

The similarity between (1) and (4) gives us grounds for supposing that it is precisely the energy of the thermal fluctuations, rather than the energy of the mean thermal motion that permits the atoms (or molecules) in the material to surmount the potential barriers that are created by the interaction of surrounding

atoms with a given atom. Hence, the quantity $U(\sigma)$ can be called the activation energy of the failure process. According to (2) this energy depends on the applied stress, and declines linearly with increasing σ .

The quantity U_0 (the initial activation energy) is determined by experiments to measure the endurance using graphs like Fig. 4, where $U(\sigma)$ is extrapolated to $\sigma = 0$.

Values of U_0 found both from experimental data like those given in Fig. 4 and from a number of other data from^[23,24,44] are given in Table I.^[25,26,44,46,56,100,152] We can compare the values of U_0 with the activation energies for thermal decomposition of interatomic bonds (the energy of sublimation in metals and the energy of thermal decomposition in polymers), which are also given in Table I.

Our attention is called to the closeness of values of the activation energy for failure to the activation energies for breaking interatomic bonds. This permits us to draw a simple conclusion: The energy of the thermal fluctuations is spent in separating atoms in solids under stress, and this is the essence of the failure process.

According to the kinetic conception of strength, breakage of interatomic bonds is actually caused by the thermal fluctuations, rather than the action of the stresses, as had been previously supposed. However, the mechanical stress plays an extremely large role in the system of kinetic ideas as well.

Even in the absence of an external load, the fluctuations break interatomic bonds at various sites in the material. However, these breakages are soon liquidated by recombination of the broken bonds. A tensile stress applied to the object not only diminishes the energy for breaking bonds, and thus increases the probability of arrival of a fluctuation sufficient to break a bond, but it also sharply reduces the possibility of recombination by pulling the uncoupled atoms apart.

Hence, the thermal fluctuations are the direct de-

structive factor. The energy for failure of the material is drawn to a considerable extent from the store of thermal energy of the object, rather than from the work done by the external forces alone. (We can judge the relative contributions of these factors from the ratio $(U_0 - \gamma\sigma)/\gamma\sigma$). The external force plays the role of a valve that facilitates and directs the destructive action of the thermal fluctuations.

The conclusion that thermal fluctuations play the decisive role in the process of mechanical failure constitutes the fundamental conceptual meaning of the studies on the kinetic nature of failure.

Now we shall briefly discuss the physical meaning of the coefficient γ in Eq. (2).

Experiment shows a difference in the behavior of the coefficient γ as compared with the other parameters of Eq. (1): τ_0 and U_0 (see also (2)). As we have noted, τ_0 is practically the same for all solids and states in which they occur (this is natural, since the period of the intrinsic thermal vibrations of the atoms in all condensed materials, with which τ_0 is associated, is close to 10^{-13} sec). U_0 proves to remain constant for a given substance when its structure is changed by annealing, mechanical treatment, alloying, irradiation, etc. In distinction to τ_0 and U_0 , the coefficient γ is readily altered by treatment of the material. We can see this from the data of Fig. 5. The $\tau(\sigma, T)$ relations from which the values of $U(\sigma) = kT \ln(\tau/\tau_0)$ given in Fig. 5 were found were obtained for a set of states of polycrystalline aluminum (the states were varied by thermal and mechanical treatment, and also by alloying). All of the linear relationships converge upon extrapolation to a single point on the axis of ordinates. This implies that the initial energy of activation U_0 is invariant. However, the differing slopes of the lines $U(\sigma) = U_0 - \gamma\sigma$ indicate that the coefficient γ varies. Table II^[42,35,51] gives numerical values of the coefficient γ for the presented results on aluminum, as

Table I

Metal	Activation energy of failure U_0 , kcal/mole	Heat of sublimation, kcal/mole	Crystal	Activation energy of failure U_0 , kcal/mole	Heat of sublimation, kcal/mole
Niobium	150	155—177	Ionic: Lithium fluoride (LiF) Rock salt (NaCl) Potassium chloride (KCl) Silver chloride (AgCl) With covalent bonds: Silicon Germanium	74 66 55 30 113 91	64 58 53 — 111±5 91±3
Vanadium	129	123			
Zirconium	120	110—145			
Platinum	120	127			
Titanium	121	113			
Iron	100	97			
Nickel	87	85—102			
Copper	81	80			
Silver	62	68			
Aluminum { P M	53 54	} 55 (77)			
Lead	42				
Magnesium	34	35			
Zinc { P M	30 35	} 31			
Cadmium	28				
P—polycrystalline; M—monocrystalline; unmarked—polycrystalline.			Polymer	Activation energy of failure U_0 , kcal/mole	Activation energy of thermal degradation, kcal/mole
			Polycaproamide t	45	43
			Cellulose triacetate	49	45
			Polyethylene	25	20—25
			Nitrocellulose	38	38
			Polystyrene	33	35
			Polymethylmethacrylate	31	30

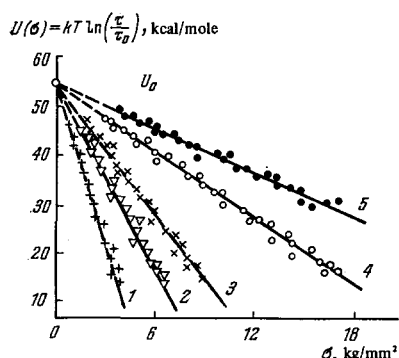


FIG. 5. Relation of the activation energy of failure to the stress for aluminum in different initial states. [35] 1—annealed at 550°C; 2—annealed at 420°C; 3—annealed at 290°C; 4—rolled; 5—alloyed (2% Mg).

well as for polycapromamide (Capron). We see that the activation energy remains invariant for different states of aluminum and capron, while the coefficient γ varies quite substantially.

In elucidating the physical meaning of the coefficient γ , we should note first that the term $\gamma\sigma$ in the expression $U(\sigma) = U_0 - \gamma\sigma$ reflects the work that the external force (the stress σ) performs in failure of the material (the rest of the work, i.e., $U_0 - \gamma\sigma$, is performed by the thermal fluctuations). The quantity γ is the product of the activation volume V_a in which the elementary failure events occur and the overstress coefficient $q = \sigma_{loc}/\sigma$, where σ_{loc} is the local true stress at the site of failure, and σ is the mean stress. The minimum activation volume, which corresponds to the theoretical strength and to the value $q = 1$, should be about equal to the volume per atom in the material, i.e., about $(2-3) \times 10^{-23} \text{ cm}^3$. However, we see from Table II that the experimental values of γ are many times larger than 10^{-23} cm^3 , and they strongly vary from material to material and for a given material in different states. If we assume that V_a remains approximately constant in all cases, while the overstress coefficient q varies, we can calculate the overstress coefficients q , which are also given in Table II.

Thus, we can arrive at the following general picture from studying the endurance of materials and its dependence on the stress and temperature. Applying an external load to a material stresses the interatomic bonds. Owing to the heterogeneity of structure of actual

objects, the external load is distributed inhomogeneously over the bonds at the level of superatomic dimensions, and local overstresses arise. The activation energy of the interatomic bonds is lowered especially strongly at these sites. It is precisely at these sites that the processes of thermal-fluctuation breakage of stressed bonds occur most intensively. Failure foci are formed here, and their development culminates in breakage of the object into pieces.

2. STUDY OF THE PROCESS OF FAILURE OF MATERIALS BY DIRECT PHYSICAL METHODS

The experimental data presented above were obtained in experiments of a phenomenological type, in which they studied the interconnection of external macroscopic characteristics: endurances, stresses, and temperatures. In general, these experiments are rather simple, and can easily be performed on solid materials of the most varied types. In contrast to the phenomenological-type experiments, study of failure of materials on the atomic-molecular level by direct physical methods has begun relatively recently.

At present, people are using the following methods to study failure of materials: infrared spectroscopy (IRS), electron paramagnetic resonance (EPR), mass spectrometry (MS), nuclear magnetic resonance (NMR), X-ray diffraction at small angles (SAXD) and at wide angles (WAXD), scattering of visible light (LS), electron microscopy (EM), chromatography, optical and electron-microscopic fractography, photolysis, etc.

Use of the cited methods creates great potentialities for getting direct and detailed information on the initiation and growth of failure. However, we must bear in mind the following fact. As compared with phenomenological studies, use of the direct methods is distinguished by considerably greater selectivity. Any material that is suitable for study by one direct method can prove to be poorly suitable for study by other methods. Hence the problem of successful choice of objects for a complex study of failure by direct methods plays a very important role.

It was natural to start this study with the simplest cases. They would amount to materials with a "one-dimensional" molecular structure, in which the fundamental interatomic bonds would be arranged in one direction in the material, and the tensile force acting in this direction would stress these bonds and "pre-

Table II

Substance	τ_0 , sec.	U_0 , kcal/mole	γ		V_a , 10^{-23} cm^3	Overstress coefficient $q = \gamma/V_a$
			$\frac{\text{kcal mm}^2}{\text{mole kg}}$	10^{-23} cm^3		
Zinc	10-13	30	1.7	120	~ 1.5	80
Silver	10-13	62	1.8	126	~ 1.7	74
Platinum	10-13	120	5.0	350	~ 1.5	230
Aluminum					~ 1.65	
annealed at 550°C	10-13	53	9.4	660		400
annealed at 420°C	10-13	53	6.1	430		260
annealed at 290°C	10-13	53	4.6	320		195
rolled	10-13	53	2.3	160		97
alloyed (2% Mg)	10-13	53	1.5	105	64	
Polycapromamide (capron)					~ 2.1	
unoriented	10-13	45	1.78	127		60
oriented	10-13	45	0.28	20		9.5
irradiated with ultraviolet plasticized	10-13	45	0.81	58		28
	10-13	45	0.43	31	15	

pare" them for thermal-fluctuation decomposition. It happens that this type of object exists, and it fully corresponds to the stated requirements. We refer to linear polymers in a state of uniaxial orientation. For these objects, uniaxial tension along their axis of orientation is the simplest and most convenient case of loading.* In such polymeric materials, the oriented "one-dimensional" chain molecules, which have internal covalent interatomic bonds and weak intermolecular bonds, have made it possible to apply the direct methods effectively. This proves to be especially successful with specimens taken directly in the stressed state.

Hence, at present, the (linear oriented) polymers are precisely those among all solids for which the most detailed study of development of failure has been made by direct methods.

2.1. Study of breakage of interatomic bonds. According to the kinetic notions presented above, the process of failure of materials at the level of elementary events can be divided into three stages: a) force perturbation of the interatomic bonds in the loaded material, which lowers the energy barrier U_0 ; b) breakage of the stressed bonds by thermal fluctuations; and c) stabilization and accumulation of the broken bonds.

a) Overstressed bonds in loaded polymers. The force perturbation of interatomic bonds by a mechanical load should be manifested in a change in the absorption spectrum in the infrared region where the vibration frequencies of the bonds lie. In order to detect this phenomenon, oriented polymers were taken: poly-caproamide (capron) (PCA), polypropylene (PP), and polyethyleneterephthalate (PETP). They have high strengths (up to ~ 100 kg/mm²) that permit applying considerable tensile loads to them in order to manifest the effect more reliably. The absorption bands involving skeletal vibrations of the chain molecules actually proved to show changes under load (Fig. 6).^[61-64] We see that the contour of the absorption band, which is symmetric before loading, shifts under load to lower frequencies, and it is deformed by spreading out in the same direction. The greater the load, the stronger these effects are. Unloading the polymer restores the original form of the absorption band.

The interpretation of the observed effect is as follows.^[62,64-66] stretching the interatomic bonds decreases the bonding energy, and consequently, reduces the vibration frequency of the bonds. Hence, the observed general shift of the absorption to lower frequencies qualitatively indicates stressing of the bonds. However, the quantitative data on changes in the infrared spectrum under load are especially interesting.

We see from Fig. 6 that most of the bonds (80–90%) are rather weakly stressed, as indicated by the small shift in the peak. However, a small fraction of the bonds is stressed considerably more strongly, and this is manifested in the spread of the low-frequency edge of the band. (Below we shall state the structural reasons for this strong inhomogeneity in the stress distribution over the bonds.)

We can estimate the maximum overstress from

*We note that highly oriented polymers are among the strongest solids, since their breaking tensions can attain values of hundreds of kg/mm².

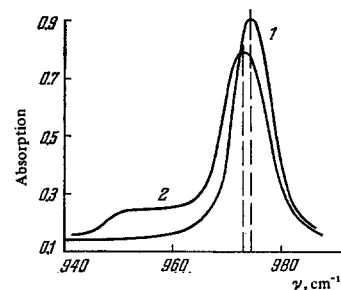


FIG. 6. Changes in the position and shape of an infrared absorption band caused by a tensile stress on the specimen. ^[62] The given band involves the skeletal vibrations in the polymer molecule. Oriented polypropylene. Measurements were made at -150°C . 1—before loading ($\sigma = 0$); 2—under load ($\sigma = 80$ kg/mm²). Curve 1 is restored upon removing the load.

Fig. 6. This will be approximately the ratio of frequencies of the edge of the spread to the shift in the peak in the deformed band. The obtained ratios attain values of the order of tens, and they are well correlated with the values of the overstress calculated from the coefficients γ in the endurance equation (see Table II).

We can also establish the approximate form of the distribution function of the bonds with respect to the overstress coefficient from the shape of the deformed absorption band. This function is shown schematically in Fig. 7.

We should consider the fundamental result of the data from the studies to be direct establishment of the fact that the stressed material (polymer) contains interatomic bonds having large overstresses as compared with the mean stress. These bonds amount to a small fraction of the total number of bonds in the material (several percent—see Fig. 7). However, their presence plays a decisive role in failure of the material, since these bonds are precisely those first broken by thermal fluctuations, and this leads to appearance of failure nuclei in the material.

b) Decomposition of the overstressed bonds. This process has been studied by the EPR, IRS, and MS methods, mainly on oriented polymers. The primary consequence of rupture of a chemical bond is appearance of unsaturated valencies, or free radicals. The existence in the free radical of an unpaired electron permits one to use the EPR method to detect it, and hence, to study rupture of molecules.

Oriented polymers: PCA, PETP, polyethylene (PE), and fibers of natural silk, were loaded (stretched) directly in the EPR spectrometer. An EPR signal ap-

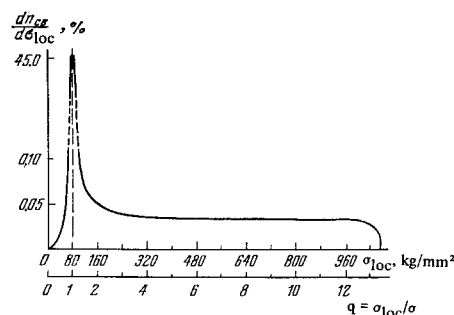


FIG. 7. Stress-distribution of the interatomic bonds in a stressed polymer. ^[63] Estimated from the data of Fig. 6.

peared, indicating formation of free radicals in the stressed polymer. Fig. 8^[67-71] shows some examples of this type of results. These data showed that chemical bonds are broken in stressed polymers long before the specimens failed.

Analysis of the shape of the EPR spectra made it possible to determine the structure of the free radicals and to trace the free-radical reactions. On the other hand, the kinetics of accumulation of radicals as a function of the stress, temperature, and time could be studied from the intensities of the signals. The free radicals formed upon stressing polymers showed a high chemical reactivity. As a rule, this had the result that secondary radicals were detected at room temperature (the spectra in Fig. 8 correspond to these). In order to detect the primary radicals at the site of molecular rupture, special experiments at low temperatures had to be set up.^[72-77]

These experiments made it possible to establish the concrete sites of rupture of chain molecules of different structures^[76-82] (e.g., for PCA: the C-C bond in the β position to the amide group^[76]).

The primary terminal radicals attack neighboring molecules by detaching hydrogen atoms and converting to medial radicals. They can add to double bonds, react with oxygen, etc.

As a whole, the free radicals initiate various chemical processes which can acquire the nature of chain reactions (relay chain transfer).^[82-85] This accelerates the failure of the polymer. It is important to note here that these chain reactions involving free radicals are not branched, so that the total number of free radicals in the polymer is not increased by the chain reactions.^[86] It has been found that the concentration of secondary radicals cannot differ strongly from that of the primary radicals.^[76] This has made it possible to draw conclusions on the kinetics of the primary molecular ruptures, based on studying the kinetics of the detectable secondary radicals (from data like those of Fig. 8). The peak size in Fig. 8 is proportional to the number of free radicals. This permits one to follow the variation in radical concentration under varying loading conditions from the intensity of the EPR spectrum. Figure 9 demonstrates the time variation of the concentration of broken bonds in a stressed polymer (we can neglect here the recombination of the radicals formed). We shall give below a quantitative analysis of the results on the kinetics of accumulation of bond ruptures.

* *

The development of secondary free-radical reactions, which culminate in formation of chemically stable groups at the sites of molecular rupture, makes it expedient to supplement the EPR method with other methods that permit gaining information on the degradative processes. One of the very effective methods here has again proved to be the IRS method. The various chemical groups that appear after the radical reactions at the broken ends of the molecules have characteristic, specific absorption bands in the IR spectrum. This permits one to detect them selectively by the IRS method. Thus one can determine the chemical composition and concentration of new end groups, and hence,

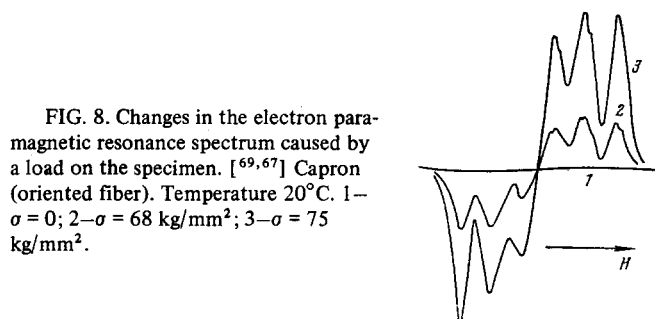


FIG. 8. Changes in the electron paramagnetic resonance spectrum caused by a load on the specimen. ^[69,67] Capron (oriented fiber). Temperature 20°C. 1— $\sigma = 0$; 2— $\sigma = 68$ kg/mm²; 3— $\sigma = 75$ kg/mm².

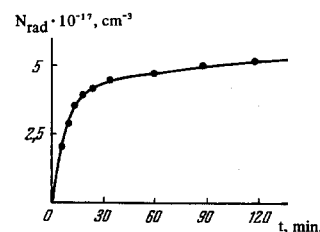


FIG. 9. Increase of the free-radical concentration with time in a stressed specimen. ^[69,87] Oriented capron. $\sigma = 71$ kg/mm². Temperature 20°C.

one can also find the total number of molecular breaks in polymers. Such experiments have been performed on oriented PE, PP, PCA, polyvinyl alcohol (PVA), and polyoxymethylene (POM).^[88-90]

Figure 10 shows examples of change in certain infrared absorption bands of oriented PE after it had been stretched at room temperature. The increase in absorption indicates an increased concentration of the end groups denoted in Fig. 10. Of course, this method also permits one to study the kinetics of accumulation of ruptures. Thus, the IRS method taken in itself gives valuable information on the course of the process of breaking of chain molecules in stressed polymers.

However, it proves to be especially interesting to study jointly the same stressed polymer specimens by the EPR and IRS methods. This makes it possible to elucidate more fully the pattern of molecular processes that are initiated by the primary rupture of bonds.

Table III^[91,92] gives an example of such a correlation of the total concentration of radicals (N_{rad}) and stable end groups (N_{gr}) formed by the action of a load.

As we see from Table III, the major outcome of comparing N_{rad} and N_{gr} is the difference between N_{rad} and N_{gr} , which attains several orders of magnitude: N_{gr} is 2-3 orders of magnitude higher than N_{ra}

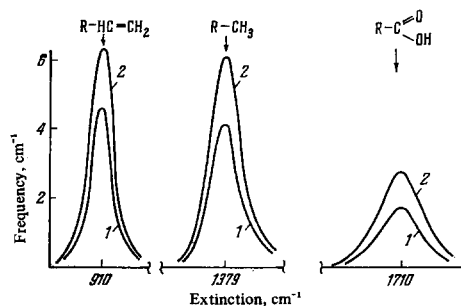


FIG. 10. Change in the infrared absorption spectrum caused by a tensile stress. ^[89,92] Oriented polyethylene. 1—before loading; 2—after loading to 45 kg/mm².

Table III

Concentration in the polymer after loading, cm ⁻³						Transverse dimension of the submicrocracks (SAXD)
Free radicals (EPR)	New end groups (IRS)	Submicrocracks (SAXD)				
N_{rad}	N_{gr}	N_{cr}	N_{gr}/N_{rad}	$\frac{1}{2}N_{gr}/N_{cr}$	S_{cr}/S_{mol}	$D_{cr}, \text{Å}$
$5 \cdot 10^{15}$	$8 \cdot 10^{18}$	$6 \cdot 10^{15}$	$\sim 1.6 \cdot 10^3$	$0.7 \cdot 10^3$	$\sim 10^3$	150
For polyethylene, $S_{mol} \approx 18 \text{Å}^2$.						

N_{rad} .^{*} This means that each primary break (since, as we have noted, the number of detected secondary free radicals does not differ greatly from the number of primary molecular breaks) entails a considerable number of subsequent breaks in the macromolecules. Thus, degradation of molecules in a stressed polymer can be a chain reaction with a quite considerable chain length (from tens^[83] to hundreds of degradation events^[91,92]).

* *

Finally, information on breaks of chemical bonds can be gained by the MS method by studying the volatile products that are formed in a number of cases in the radical reactions. In certain polymers (such as polymethylmethacrylate (PMMA) and polystyrene (PS)) the event of primary rupture of the molecules is accompanied by formation of a large amount (tens) of small fragments arising from free-radical reactions along the axis of the molecule and partial depolymerization. This creates a distinctive "amplifier" of the events of primary rupture (tens of molecular particles recordable in the mass spectrometer per rupture event!) It permits a very high sensitivity of the MS method in these cases.† The composition of the volatile products makes it possible to decide on the course of the reaction, and one can get information on the kinetics of accumulation of primary molecular breaks from the rate of release of volatile products, since the energy of activation of the primary breaks is considerably higher than that of the subsequent reactions.^[83]

Experiments in which polymer specimens (PMMA, PS, etc.) were stressed in the vacuum chamber of a mass spectrometer have shown that volatile products are actually released when the specimens are stretched, and this phenomenon begins practically at the moment of application of the load (Fig. 11).^[94-100] The rate of formation of volatile products increases with increasing applied stress.^[96,98,100]

* *

Thus, three independent methods, EPR, IRS, and MS, have made it possible to detect appearance in stressed polymers of breaks in the chain molecules.

*The data on N_{gr} are confirmed by the results of measuring the molecular weight of oriented polymers before and after loading. The number of molecular breaks was estimated from the observed decline in molecular weight. It proved to agree well with the IRS data. ^[93]

†However, in such polymers as PCA, PE, etc., one molecular fragment arises only for several tens of molecular rupture events.

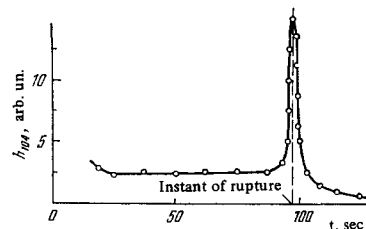


FIG. 11. Yield of volatile products as a function of the time from a stressed polystyrene specimen. Stress 2.5 kg/mm², temperature 20°C. h_{104} is the peak in the mass spectrum of molecular weight 104. The intensity of the peak is proportional to the rate of evolution of "molecular fragments" of the given mass.

All these methods have permitted people to trace the gradual failure of polymeric materials in terms of accumulation of molecular breaks. Hence, the conclusion based on observation of time-dependence of strength that failure is a process, rather than a critical event, has been confirmed.

However, confirmation of the kinetic conceptions of failure has required also that the thermal-fluctuation nature of this process should be made evident. That is, one should show that the events of rupture of stressed interatomic bonds are effected by thermal fluctuations. This also could be done by the MS and EPR methods.

The mass spectra of the products of pyrolysis (upon heating the polymer to high temperatures) and of mechanical degradation (decomposition of the molecules in the stressed polymer at moderate temperatures, e.g., room temperature) have been compared. We note that pyrolysis is known to be a thermal-fluctuation process. For polymers whose pyrolysis starts with fluctuational breakage of the skeletal bonds in the macromolecule, experiment showed that the compositions of the volatile products of thermal and mechanical destruction coincide (Fig. 12).^[97,100,101] This allows us to conclude that the atomic-molecular processes are identical. Hence, we can consider mechanical failure of polymers to be a pyrolysis activated by the stress, while there are reasons for considering the events of molecular decomposition in stressed polymers to involve thermal fluctuations.

This conclusion is confirmed also by comparing the activation energies for pyrolysis (as measured by the MS method) and for mechanical failure of polymers. It turned out that the activation energy U_0 for failure agrees satisfactorily with that for pyrolysis in its initial stage (see Table I).^[100,102,103]

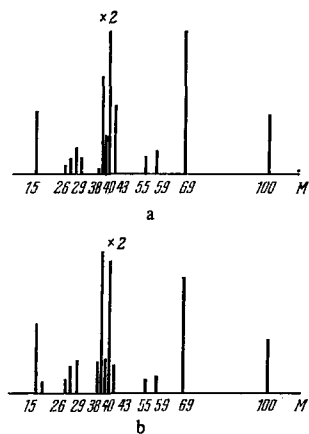


FIG. 12. Mass spectra of volatile products emitted by polymethylmethacrylate. [97] a) Mechanical degradation (with a constant load applied to the specimen) at 20°C; b) thermal degradation (without a load) at 250°C.

Another way of confirming the thermal-fluctuation nature of the rupture of stressed bonds has also been used. It is based on studying the kinetics of accumulation of molecular breaks (by the EPR and MS methods) as the loading conditions on the polymers are varied: the temperature T and the stress σ . Analysis of the dependence of the rate of accumulation of breaks on T and σ permitted a decision on the mechanism of rupture. When these relations proved to be exponential, this indicated a thermal-fluctuation mechanism of rupture. However, when the parameters of these relations also proved to be close to the corresponding parameters of the exponential endurance equation (U_0 and γ), this established that molecular breaks played the decisive role in the process of failure of the polymer.

In using this method, one should take into account certain factors. First of all, the experiments should be conducted under conditions in which one can neglect recombination of radicals. One should also bear in mind the fact that a polymer specimen is a system of bonds under varying stresses. Consequently, the kinetics of integral accumulation of breaks becomes complex in nature. Finally, the dependences of the rate of bond decomposition can easily be distorted by the decrease in number of overstressed bonds as they fail. The cited complications are especially clearly manifested in tests having a schedule with a constant rate of loading, passing through a wide range of loads. The force-dependences of the rate of accumulation of radicals that are measured under these conditions gives exponential functions having low indices [67, 104, 105] and even non-exponential relations. [106] *

Hence, in order to study correctly the force-dependence of the rate of bond-breaking, the experiments were performed in a narrow range of stresses. Here each specimen was tested under constant-load conditions. The specimens were taken in the form of bundles of thin fibers, and this reduced the localization of macroscopic failure. The radical-accumulation curves proved here to be qualitatively similar to the creep curves. It was shown in PCA fibers containing a

*One can find the approximate form of the stress distribution over the bonds being broken from the form of these relations. [104, 106] In [107, 108], the data on radical accumulation were not presented as functions of the stress, but of the strain in the specimens, and the authors tried to relate them to the varying lengths of the "load-bearing" molecules.

stabilizer and silk fibers that the rate of radical formation in the steady-state (or quasi-steady-state) stage of creep, [68, 69] as well as the mean rate of radical accumulation throughout the period of test, [71, 109] depends exponentially on the stress (Fig. 13). The arguments of the exponentials in these cases proved to be close to the corresponding values (i.e., $\gamma\sigma/kT$) in the endurance equation.

It is important to note that the temperature-dependence of the rate of radical accumulation has also been studied, [68, 69] in addition to the force-dependence. These results are given in Fig. 14, where the rates of radical accumulation are compared with the endurance. The fact that a linear relation was obtained, with a graph having a unit slope with respect to the coordinate axes, indicates that the functional relationships of dN_{rad}/dt and τ to T and σ have the same form, and that the parameters of this relation, i.e., the activation energies of the two processes, coincide.

It has been possible to use the MS method, owing to its very high sensitivity, to trace the release of volatile products from the tip of one growing failure crack. Here also, the rate of this process showed an exponential dependence on the stress (Fig. 15). [98] The argument of the exponential in this case also proved to be equal to that in the endurance equation.

* *

The presented results from studying the kinetics of accumulation of breaks confirm the thermal-fluctuation nature of the decomposition of the stressed molecules, since thermal-fluctuation events in which the force reduces the activation energy are precisely the case of which an exponential dependence of the rate of the

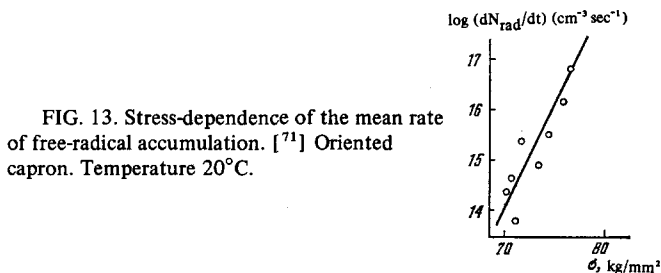


FIG. 13. Stress-dependence of the mean rate of free-radical accumulation. [71] Oriented capron. Temperature 20°C.

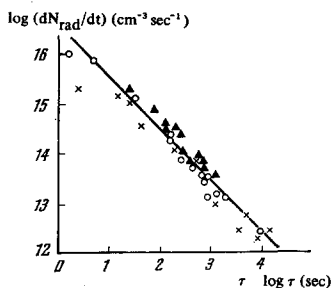


FIG. 14

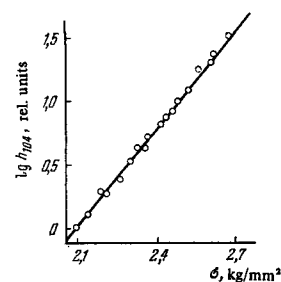


FIG. 15

FIG. 14. Relation of the endurance of specimens to the rate of free-radical accumulation in the steady-state stage in oriented capron. [69]

FIG. 15. Stress-dependence of the rate of emission of volatile products in a specimen containing a crack. [98] Polystyrene. Temperature 20°C.

process on the force (stress) is required. (Such a relation is not inherent in purely mechanical processes.)

While as yet only a small amount of data exists on the temperature-dependence of the course of molecular rupture, they also confirm the thermal-fluctuation nature of the molecular-decomposition events. Since they permit one to estimate the activation energy of the elementary events of failure of polymers, they make it possible to relate failure on the macroscopic level to the atomic-molecular mechanism of this process.

2.2. Localization of the failure process. Kinetics of growth of cracks. The treatment carried out above on the course of failure on the molecular level used only a general notion of the presence in a stressed material of sites of stress concentration, without concrete statements as to their nature. And the course of failure of the material itself was treated as an accumulation of single breaks of interatomic bonds, without taking account of their grouping near one another and localization of failure by formation of various cracks, cavities, etc.

In this section, we shall systematically take up:

a) appearance in materials of regions having a concentration of stresses arising from the structure of the materials;

b) appearance in a stressed material of very small, nuclear, submicroscopic cracks;

c) transformation to larger micro-, and then to macro-cracks, with establishment of their growth laws and relation to the endurance of the material.

a) **Structural stress-concentrators.** The structural inhomogeneity of most actual materials (in metals: mosaic blocks, fragments, and grains; in polymers: crystallites, fibrils, spherulites, etc.) and their defect nature (various initial cracks, inclusions, traces of past history, crystal-lattice defects (point, line, surface, etc.)) easily explain in principle the reasons for inhomogeneous distribution of stresses throughout the material. Many studies are being conducted to pursue the aim of establishing the relations between the structural features of materials and their mechanical properties. In our opinion, this problem also has been solved most fully at present for the oriented amorphous-crystalline polymers. This is because the above-mentioned one-dimensional structure of these objects (not only at the molecular, but also at the supermolecular level (see below)) has made it possible to apply effectively direct structural methods: wide- and small-angle X-ray diffraction, nuclear magnetic resonance, and infrared spectroscopy (which methods have permitted people to study materials directly in the stressed state), as well as electron microscopy.

An example of a characteristic fibrillar structure of this type of polymers is shown by an electron micrograph (Fig. 16).^[110] SAXD has shown that very often the fibrils have a longitudinal periodic heterogeneity, owing to alternation of crystallites and amorphous layers (diagram in Fig. 17).^[111] Such a one-dimensional structure on the supermolecular level has even proved to be very convenient for revealing structural-mechanical correlations. The WAXD method has shown that the crystallites are altered but little under load (stretching the polymer along its orientation axis), and the molecules in them are stressed relatively weakly,

FIG. 16. Fibrillar structure of an oriented amorphous-crystalline polymer. ^[110] Electron micrograph. Replica from the surface of oriented polyethylene. 0-0: orientation axis of the specimen.

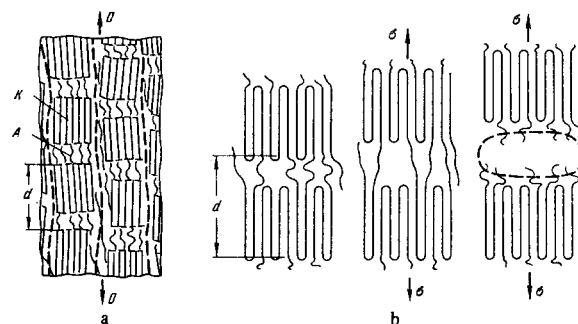


FIG. 17. Diagram of the structure of an oriented amorphous-crystalline polymer. ^[111, 114, 137] a) Internal amorphous-crystalline structure of the fibrils; 0-0: orientation axis of the specimen. Dotted lines: approximate boundaries between the fibrils. C—crystallite, A—amorphous region (layer); d is the long period. b) Behavior of an amorphous-crystalline structural element of a fibril subjected to a tensile load. Formation of a nuclear submicroscopic crack. σ - σ : axis of loading.

in proportion to the mean stress acting on the polymer specimen.^[112-116] At the same time, as application of the SAXD method shows, the intercrystalline amorphous layers are strongly stretched (see Fig. 17).^[114, 115, 117-120] Stretching of the amorphous layers involves straightening and tension on the "longitudinal" polymer molecules. This is well confirmed by the NMR method, in which a decline under load is observed in the narrow component of the spectrum, which involves the mobility in the disordered, amorphous regions in the polymer (Fig. 18).^[121-125]

Disorder in the amorphous layers naturally leads to overstressing in certain "through-passing" molecules.

Inhomogeneous distribution of stress in a loaded polymer has been noted above in the direct study of stresses in interatomic bonds by the IRS method (see Figs. 6 and 7).^[63, 64] Now we can conclude that this inhomogeneity agrees well with the amorphous-crystalline heterogeneity of the polymer: weakly stressed crystallites and strongly stressed molecules in the amorphous regions.

All that we have said implies that the course of failure in a polymer must be determined by the structure and properties specifically of the amorphous regions. In fact, the polarized IRS method, which permits one to determine selectively the degree of molecular orientation in the crystalline and amorphous regions of

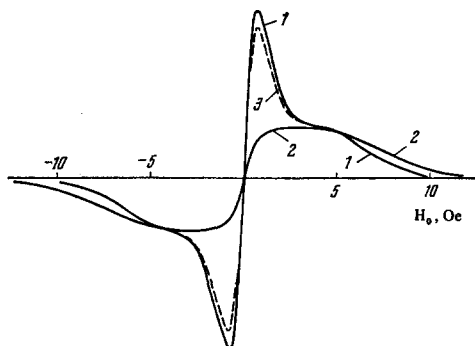


FIG. 18. Change in the nuclear magnetic resonance spectrum caused by a load on the specimen. [121] Oriented capron. Temperature 130°C. 1—before loading ($\sigma = 0$); 2—under load ($\sigma = 36 \text{ kg/mm}^2$); 3—after removing the load.

a polymer, [126] shows a specific correlation between the breaking strength and the orientation of the macromolecules in the amorphous regions (Fig. 19). [127]

Hence, we can assume that the amorphous layers of a polymer are precisely where molecules break most often, and we should expect the nuclei of cracks to appear there.

b) Appearance of submicroscopic breaks in continuity. These studies have been conducted by the SAXD and visible-light scattering (LS) methods. Both methods permit one to detect inhomogeneities in materials, including cracks of dimensions from $\sim 10 \text{ \AA}$ to $\sim 10^3$ – 10^4 \AA , and to determine their dimensions, shapes, orientations, and concentrations.

As it has turned out, the x-ray (Fig. 20) and light [128–133] scattering intensities can increase sharply in polymers under stress. This scattering is due to formation of tiny cracks of disk-like shape, arranged perpendicularly to the axis of loading (Fig. 21). Typical dimensions of the cracks are: tens of \AA in the longitudinal, and hundreds of \AA in the transverse direction. Their concentrations can attain values of 10^{12} – 10^{17} cm^{-2} . These cracks appear specifically under load (i.e., there are practically none of them before applying the load) and irreversibly (removal of the load does not heal the cracks). [87, 134]

It has been established for oriented amorphous-crystalline polymers that the transverse dimensions of the cracks coincide with the transverse dimensions of the fibrils (i.e., the amorphous layers). [135–136] Hence, the nuclear submicroscopic cracks actually arise in the regions of the polymer where the overstresses are large: in the amorphous intercrystalline layers. That is, the stress causes individual "weakest" layers to rupture and form cracks (diagram in Fig. 17). [119, 137] Further data were obtained by studying the kinetics of accumulation of submicroscopic cracks in a polymer as a function of the time t under constant load at various stresses σ and temperatures T . It was found that the cracks are formed instantaneously with practically constant dimensions, while only their concentration N_{cr} varies with varying t , σ , or T . Here the function N_{cr} trends downward for $\sigma = \text{const}$ and $T = \text{const}$ (Fig. 22). [129, 130, 87] This agrees in form of variation with the increase in N_{rad} (see Fig. 9). Study of $N_{\text{cr}}(t)$ with varying σ and T gave results like Fig. 23. [138]

This made it possible to establish the kinetic, thermal-fluctuation nature of the formation of submicrocracks: $(dN_{\text{cr}}/dt) = (N_l/\tau_0) \exp[-(U_0 - \gamma'\sigma)/kT]$. Here N_l is the concentration of amorphous layers in the polymer, and the other quantities have the same meanings as before. Also the activation energy of this process could be estimated. It turned out that U_0 and γ' for the crack-formation process are close to the same characteristics as determined by endurance experiments. Thus, formation of submicrocracks involves breaking of polymer molecules. The same is indicated by the

FIG. 19. Relation of the rupture strength to the orientation of polymer molecules in the amorphous regions of capron. [127] The strength was measured at -196°C .

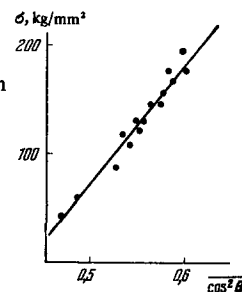


FIG. 20. Change in small-angle x-ray scattering caused by a tensile load on the specimen. [128] Oriented capron. Temperature 20°C. Radiation of wavelength 1.54 \AA . 1—before loading ($\sigma = 0$); 2—under load ($\sigma = 12 \text{ kg/mm}^2$); a scattering curve close to the original is restored after removing the load.

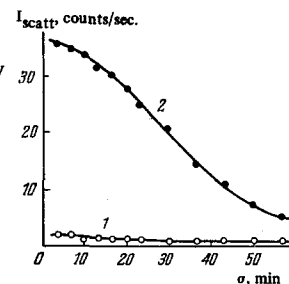


FIG. 21. Diagram of the submicroscopic cracks that appear in polymers under load. [129] σ — σ : axis of tension.

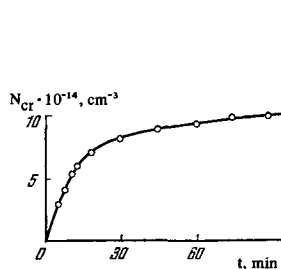
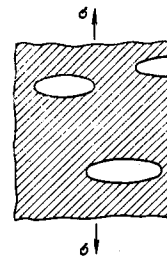


FIG. 22

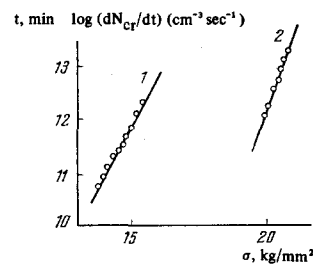


FIG. 23

FIG. 22. Increase with time in the concentration of submicroscopic cracks in a stressed specimen. [87] Oriented capron. $\sigma = 23 \text{ kg/mm}^2$; temperature 20°C. Mean dimensions of the cracks: 110 \AA along the axis of tension (which coincides with the orientation axis of the polymer); 280 \AA in the transverse direction.

FIG. 23. Stress-dependence of the rate of accumulation of submicroscopic cracks (initial stage of deformation of the specimen). [138] Oriented capron. 1—(25°C); 2—(-50°C).

more rapid "eruption" of cracks in a repeated loading, as compared with the first time.^[137,87,134]

It has proved especially interesting to correlate N_{cr} with N_{rad} (by the EPR method) and N_{gr} (by the IRS method) for the pre-rupture state of given polymers.^[92] The results of this correlation are given in Table III. We see that $\frac{1}{2}N_{gr}/N_{cr}$ (the number of molecular breaks per crack) is $\sim 10^2-10^3$, and this quantity is close to S_{cr}/S_{mol} (S_{cr} is the cross-sectional area of a crack, and S_{mol} is the cross-section of a polymer molecule), or the number of polymer molecules passing through the cross-section of a fibril (because $S_{cr} \approx S_{fibr}$). This confirms well the conclusion that a crack is formed by breaking molecules.

Further we see that $N_{cr} \approx N_{rad}/2$ (and also $\frac{1}{2}N_{gr}/N_{cr} \approx N_{gr}/N_{rad}$). Hence, the above-mentioned chain type of molecular degradation evidently operates in such a way that the first free radical to appear in a layer can cause by the chain mechanism a rapid ("facilitated") breakage of all the molecules in the layer and the formation of a submicrocrack.^[92,84,85] Thus formation of a submicrocrack here is "explosive" in nature, and is "initiated" by the thermal-fluctuation event of primary rupture of one of the overstressed molecules in the layer.

Here it is important to emphasize the fact that the rapid, sequential breakdown of stressed polymer molecules releases a large amount of the elastic mechanical energy concentrated in them. The latter is released in the form of heat, and leads to a considerable local heating.^[93] Indisputably, this process increases the "explosiveness" of the appearance of submicrocracks. Formation of submicrocracks considerably increases (up to tens of percent) the stress on the remaining cross-section of the specimen, and causes large microdeformations to set in.^[139] Naturally, the latter per se facilitate the acceleration of failure of the specimen.

After nuclear, submicroscopic cracks have been formed, the further development of failure can consist in merger of these cracks and formation thereby of larger cracks.^[129,130] The first data confirming this possibility have been obtained.^[140]

* *

Along with detection of submicroscopic cracks in oriented amorphous-crystalline polymers, such cracks have been found upon stressing amorphous polymers,^[129-133] as well as rock-salt crystals,^[141,142] and metals.^[143-145] Their relation to the superatomic structure of these materials and the laws of their appearance and development have practically not as yet been studied.

c) Microcracks. After considering cracks of submicroscopic dimensions (tens to hundreds of Å), we naturally turn to cracks of the next level of dimensions: microscopic (from 1 μm to tens of μm). Such cracks are found upon stressing various polymers, but they have been studied in greatest detail in amorphous, un-oriented polymers (PMMA, PS, etc.). Among these, a great number of microcracks (Fig. 24)^[146-149] appears on the surface of the stressed specimens as time passes. Study of the kinetics of this crack formation has shown that it is the same declining function of

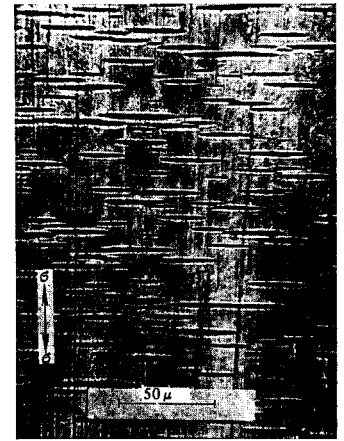


FIG. 24. Formation of microscopic surface cracks in stressed polymethylmethacrylate. ^[28] $\sigma-\sigma$: axis of tension. Temperature 20°C.

time (variation in the number of cracks and their mean length),^[147] as in the accumulation of broken bonds or submicrocracks. Analysis of the appearance of microcracks as a function of σ and T showed that this phenomenon also basically involves thermal fluctuations.^[147]

People have ascribed the declining pace of microcrack formation to exhaustion of weak points, to orientation and hardening of the polymer in the neighborhood of the cracks, and to their mutual "blocking" effect (in non-collinear arrangement).^[27] At the same time, evidently microcrack formation that declines in time can lead at individual sites in the polymer to appearance of a macrocrack by merger of microcracks. The macrocrack will then grow more rapidly (see below). The important question of the relation of microcracks to submicrocracks has not yet been solved. Such studies have begun.

Microcracks have also been found in non-polymer materials, especially under cyclic, vibrating loads, under corrosive-media conditions, etc.^[150]

d) The main crack and the kinetics of its growth. The laws of growth of main, macroscopic cracks have also been studied most thoroughly on polymers, although there are also observations on metals, glasses, etc. Study of the kinetics of penetrating main cracks has been performed on thin films made of polymers (mainly of cellulose derivatives). Here the growth time of the main crack amounted to the greater part of the endurance of the polymer.^[69,151-157] The variation of the crack length λ as a function of the time t was measured for various values of σ and T . Figure 25 gives characteristic graphs of $\lambda(t)$ upon varying σ . We emphasize immediately the sharp difference in the growth of the main crack (lack of decline in the rate of growth), as compared with submicro- and microcracks. A general equation has been derived for the rate of growth V_{cr} of the penetrating crack:^[152,156]

$$V_{cr} \approx \frac{\Delta}{\tau_0} \exp \left[-\frac{U_0'' - \psi(\lambda/\rho)\sigma}{kT} \right] \quad (5)$$

Here U_0'' is the initial activation energy of the process of crack growth, $\psi(\lambda/\rho)$ is a coefficient that depends on the length of the crack and the shape of its tip (ρ is the radius of the crack in the region of its tip); $\Delta \approx 10^3 \delta$; and δ is the interatomic distance ($\delta \approx 2-4 \text{ \AA}$). The form of Eq. (5) shows convincingly

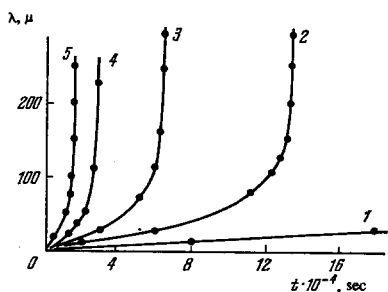


FIG. 25. Growth of the penetrating main crack under different loads on the specimen. [151] λ —length of crack. Cellulose triacetate. Temperature 20°C. Stress σ in kg/mm^2 : 1—6.8; 2—7.1; 3—7.4; 4—7.6; 5—7.8.

that the growth of the crack is also a thermal-fluctuation process, which in this case is concentrated at the tip of the crack.

The activation energy U_0'' for growth of the crack coincided with the activation energy U_0 from endurance experiments. [150] The value of the coefficient in the pre-exponential factor in Eq. (5) $\Delta \approx 10^3 \delta$ showed (as had already been concluded in [69]) that the fluctuational failure encompasses a region at the tip of the crack of microscopic but not interatomic dimensions.

Study of the kinetics of growth of the main crack is also important in analyzing the coefficient γ in the endurance equations (1) and (2). In fact, as we pointed out above, the meaning has been ascribed to this coefficient of being the product of the overstress index and the activation volume. The coefficient γ is constant in value for a large number of specimens that fracture at varying times τ for various values of σ and T (i.e., within the limits of the "fan" of the $\log \tau - \sigma$ relationship (see Figs. 3 and 4)). At the same time, the overstresses in any specimen undoubtedly vary during time τ until its failure. The concrete course of these variations can even be "sensed" by the rate of growth of the main crack, and can be expressed by the current values of the coefficient $\psi(\lambda/\rho)$ in Eq. (5). Comparison of the integral overstress index γ with the coefficient ψ averaged in some way or another makes it possible to picture the failure process in greater detail. [152, 156] This is especially important in analyzing cases of variation of γ for various σ and T (see below).

Thus, study of main cracks is interesting because the region of the tip of such a crack is precisely where the phenomena develop that determine the endurance of the entire object. One can establish the existence of local heating and estimate its value from the laws of growth of the main crack and from the relief features of the fracture surface of the specimen that are formed by the growth of the macrocrack (fractography). [154, 155] Data of this type are very useful as "guides" for setting up studies by direct methods. Furthermore, study of main cracks permits one to concretize the role of submicro- and microcracks in the failure process by studying these "fine" cracks in the region of the tip of the growing macrocrack, or even from their "tracks" on the fracture surface of the object. The SAXD method has shown an increased concentration of submicrocracks in front of the growing main crack, [129, 130] so that the macrocrack advances through a zone of the polymer that is already saturated with fractures.

However, growth of the main crack by merging with microcracks that grow to meet it is manifested by the existence of characteristic traces on the fracture surface of the specimen: hyperbolas (Fig. 26). By analyzing the latter, it has been possible to determine the growth rate of the cracks, their relative "risk", their dimensions, etc. [27, 28, 157, 158]

In closing the section on localization of failure in materials, we would like to emphasize that development of these problems on the level of direct experiments is just beginning. Naturally, study is being conducted mainly on the most convenient objects, and above all, these have been polymers. Hence, one of the front-line problems is to extend these studies to non-polymer materials as well.

Reasons have currently arisen for thinking that the sites of origin of failure in polycrystalline metals are the boundary zones between the mosaic blocks. [159, 160] A heightened compliance of these regions has been shown [161], and a direct correlation has been established between the strength properties of metals (taking account of the kinetic nature of the strength) and the dislocation density in the interblock boundaries. [159, 160] The strength rose with increasing dislocation density in the boundaries between the blocks.

* *

As a whole, however, the comprehensive study of failure by direct methods is a new stage in the development of the study of this phenomenon. The first, but as yet rather limited, results that have been obtained indicate the great and interesting promise of this approach.

3. CASES OF COMPLEX FAILURE

The equation (1) relating the endurance to the applied stress and the temperature was established under conditions of a very simple type of loading (uniaxial static tension) on materials having a stable structure that varies little during the testing process. However, even for these materials and testing conditions, Eq. (1) has definite limits of applicability (Fig. 2). If one extends the temperature range, or increases the range of stresses, and especially if one tests materials having structures of low stability, one observes deviations from the relations (1) and (2). [29, 37, 39, 53-55, 57, 162-167]

Figures 27a, b give examples in which the log

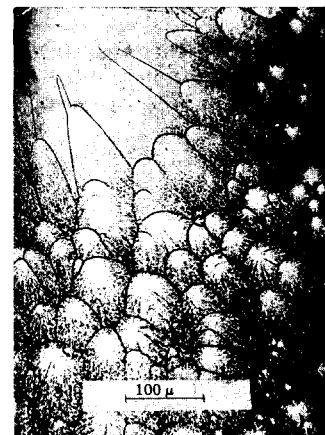


FIG. 26. Micrograph of the fracture surface of a polymethylmethacrylate specimen. [28] The main crack grew from the upper left-hand corner of the photograph.

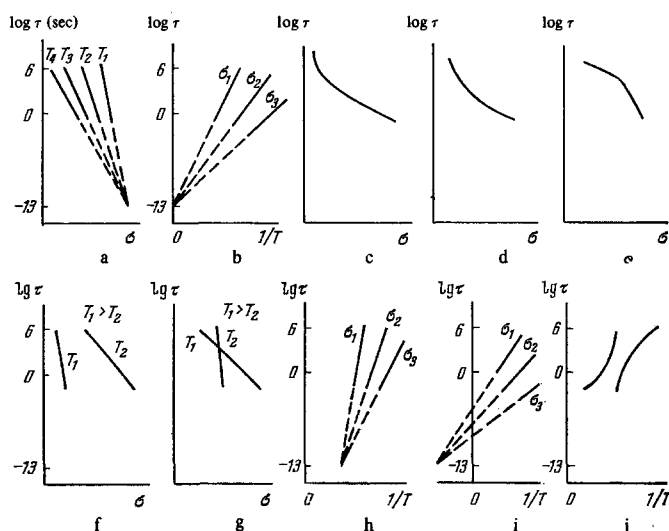


FIG. 27. Diagrams of the relation of the endurance τ to the stress σ and the temperature T . a, b) Cases obeying the expression $\tau = \tau_0 \exp((U_0 - \gamma\sigma)/kT)$; c-j) cases of various deviations (see text).

$\log \tau(\sigma, T)$ relation satisfies Eq. (1). However, Fig. 27c-j demonstrate various cases of deviations from Eq. (1). A case is shown here of deviation from a linear $\log \tau(\sigma)$ relation in the region $\sigma \rightarrow 0$ (Fig. 27c), breaks and curves in this relation (Fig. 27d, e), and an example of the "pole displacement effect" on the $\log \tau - (1/T)$ plot (Fig. 27 h, i), etc.

The analysis of these cases that has been performed in a number of studies^[37, 162, 168, 189, 55, 39, 40] has led to the conclusion that none of them contradict the fundamental views of the kinetic conception of strength, and they can be explained on that basis by taking account of various types of complicating factors that impair the constancy of the parameters τ_0 , U_0 , and γ in Eq. (1). The most frequency reason for deviation from Eq. (1) is instability of the structure of the material and dependence of the structure-sensitive coefficient γ on the testing conditions, i.e., cases in which $\gamma = \gamma(\sigma, T)$. However, the possibility is also not ruled out that the quantity U_0 can vary, e.g., in going from low-temperature to high-temperature testing of metals,^[170] or when one introduces a very large amount of a plasticizer into a polymer,^[171] etc. Entropy effects that alter the pre-exponential factor are also not excluded in principle. We should note that we must approach the determination of U_0 in such complicated cases of failure with especial caution, while taking account of the fact that instability of structure and variability of γ can be viewed as an apparent variation of U_0 in a number of cases (e.g., in analyzing the pole-displacement effect^[55]).

* *

Testing cases that are important in practice are tests with a complex loading schedule, especially with repeated cyclic loading,^[172-178] as well as tests involving complex types of stress states (torsion, bending, etc.)^[161, 179, 180]

Studies in this field have shown that even these complicated cases of failure can be interpreted on the basis of Eq. (1) by taking account of the principle of summation of failure. In complicated types of stress states,

this can be done by replacing σ by the corresponding components of the stress tensor. In these cases, one must sometimes take into account other factors as well, in addition to having to take account of a possible variation of γ under varying loading schedules and types of stress states. Thus, one must take account of bulk^[178, 181] and local^[182-184] overheating in cyclic loading. The possibility of variation of U_0 is also not ruled out when the stress state is altered, as has been assumed, e.g., in^[179].

Undoubtedly, the failure conditions in solids are complicated also in cases in which such factors as corrosive chemical media or different types of radiation are acting on the stressed material. Phenomena of aging of polymers under load under such conditions have also recently been treated on the basis of the ideas of the kinetic conception of strength, under the assumption of superposition of failure rates arising from two different factors, e.g., thermal fluctuations and radiation. This approach has been developed in especial detail in the example of studying the kinetics of failure of polymers under load with simultaneous ultraviolet irradiation.^[186-192, 71, 109]

As a whole, analysis of all the cited cases of complicated failure^[185] has confirmed the ideas of the kinetic conception of strength and the possibility of using them fruitfully for predicting the endurance of stressed solids under their actual conditions of use.

4. SOME PROBLEMS IN THE DEVELOPMENT OF KINETIC IDEAS ON THE FAILURE PROCESS

Along with the elucidation of many important problems in the physics of failure of solids, some problems whose solution is necessary for the further development of kinetic conceptions have also recently been considered. We shall mention here only two, which are the most pressing from our viewpoint.

4.1. The physical meaning of the initial activation energy U_0 of the failure process. Although the general meaning of U_0 is clear (as we have noted, the size and behavior of U_0 indicate that failure is due to breaking of interatomic bonds), there is yet no generally accepted explanation of the concrete values of U_0 .

The values $U_0 \approx 25-50$ kcal/mole for polymers that can be determined by endurance experiments are appreciably smaller than the dissociation energies of bonds like C-C, C-N, C-O, etc., which amount to 65-80 kcal/mole. Various hypotheses have been advanced to explain this discrepancy: presence of "weak" bonds (defects in the structure of the macromolecules),^[56] the effect of deformation (regrouping) processes,^[166, 193] and the effect of the chain-reaction decomposition of polymer molecules,^[85] etc.

The established equality of U_0 to the energy of sublimation for metals (and other crystalline substances) has not in itself permitted people to provide a pictorial description for the failure process, although a number of hypotheses have been advanced here as well.^[194-198]

The set of problems involving the activation energy of failure and affecting the determination of U_0 itself also includes the problem of the form of the $U(\sigma)$ relation. This relation is generally non-linear (see below) for individual stretched interatomic bonds. At the same

time, the results of endurance studies in many cases indicate a rather well-obeyed linear relation $U(\sigma) = U_0 - \gamma\sigma$ (see, e.g., Figs. 4, 5, and also Fig. 1). Here the linearity of the $\log \tau - \sigma$ plot implies linearity of $U(\sigma)$ according to Eq. (1). As yet there is no satisfactory explanation for these facts.

4.2. The interrelation between failure and deformation. This is an old question that has been asked in many studies of mechanical properties of solids. In the kinetic approach, phenomenological study establishes a close relation between the two thermal-fluctuation processes, failure and deformation. This is because the creep rate of solids in the steady-state region (for $\sigma = \text{const}$ and $T = \text{const}$) has been found to be $\dot{\epsilon} = \dot{\epsilon}_0 \exp[-U_0''' - \gamma_0''' \sigma]/kT$. Here the quantities U_0''' and γ_0''' are respectively equal to the corresponding quantities in the endurance equation for the given material; and $\dot{\epsilon}_0 \approx 0.1 \tau_0^{-1}$.^[39, 149, 198] One cannot distinguish the "driver" and the "driven" among the processes on the basis of these data alone. The very problem of distinguishing elementary events as "failure events" and "deformation events" is rather complex and ambiguous. Yet we can assume that failure events are irreversible breaks in interatomic bonds, while deformation events are reversible. Nevertheless, in both cases they are bond ruptures, and this determines the closeness of activation energies of the two processes.

It has been shown for oriented amorphous-crystalline polymers by ultraviolet irradiation,^[186, 200, 201] as well as by the SAXD method,^[134] that failure (irreversible breaks in chain molecules) is the driving process. On the other hand, accumulation of irreversible bond breaks is impossible without deformation processes that permit the atoms to separate after rupture. Hence, these processes become entangled and interpenetrate. Perhaps there is no single solution here, owing to the variety of properties of solids and of their conditions of loading.^[199]

5. KINETIC THEORIES OF FAILURE

Here we can list only very cursorily the fundamental lines in the theoretical studies. Naturally, these studies comprise an important part of the development of the kinetic conceptions of failure. There is as yet no general, detailed theory of kinetic failure, but many interesting detailed treatments have already appeared.

We can assume that the necessity of a kinetic approach to failure arose even in the first, "purely mechanical" theory of Griffith,^[202] where the criterion of energetic favorability of crack growth can be satisfied even with small stresses on the interatomic bonds on the contour of the crack. This would permit these bonds to break only with the aid of an additional force factor arising from thermal motion.* However, a kinetic, thermal-activation mechanism of breaking of stressed bonds was apparently first proposed on the theoretical level by Ponsalet.^[204, 205]

Some theoretical studies have tried to treat the following nodal questions:

1. The nature of the elementary failure processes. There is no single opinion here. Many variants of

*The thermal-fluctuation nature of the slow growth of large "Griffith" cracks in a silicate glass has been shown convincingly in [203].

elementary events are treated: in polymers, breaks both in chemical bonds^[206, 212-214, 217] and in intermolecular bonds,^[207-209] in crystals, participation in the course of failure of vacancies,^[215-216] implanted atoms,^[198] dislocations,^[195-197] etc.

2. Calculation of the energy barriers for events of breaking of interatomic bonds as a function of the tensile force.^[211, 212, 218-220] There is as yet no general solution of the problem of the form of the $U(f)$ function (f is the tensile force on the bond). Rather complete calculations exist only for the one-dimensional case (decomposition of a stressed linear chain of atoms).^[218-220] The authors of^[211, 218, 220] obtained the $U(f)$ function whose graph is shown in Fig. 28 upon describing the interaction between the atoms by a Morse potential.^[221] We see that the $U(f)$ relation is non-linear, and admits a linear approximation only in limited load ranges.

The non-linearity of $U(f)$ touches on the problems of determining the initial barriers for bond breakage and estimating the values of the overstress coefficient in interpreting the experimental data.

3. The transition from elementary failure events to fracture of the object. Here calculations have been based on various schemes or models: uniform loading of the interatomic bonds throughout the volume of the object,^[206] redistribution of loads owing to loss of bonds,^[208, 210, 211] non-uniform distribution of loads,^[210, 214, 222-226] accounting for recombination of bonds,^[217, 227, 228] and accounting for heterogeneity of the material.^[213, 214] Many studies have been concerned with the kinetics of crack growth.^[204, 30, 224, 225, 229-232]

4. Kinetics of failure at low temperatures at which classical statistics fails to hold.^[233-236] The first attempts at theoretical analysis of failure of a solid at temperatures below the Debye temperature were undertaken in^[234-236].

* *

The conditions are now accumulating for building a rather complete and detailed theory of kinetic failure of oriented polymers, since relatively many direct data exist here on the development of the failure process, and calculations have been set up on the breakdown of a polymeric chain molecule. Evidently, this theory will pave the role for building a theory of the failure of other materials as well.

6. CONCLUSIONS

All the material presented in this article shows that the kinetic conception of strength is rather general. Practically all the manifestations of the failure process in solids differing in structure under the most varied

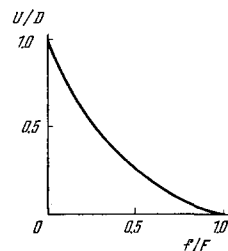


FIG. 28. Force-dependence of the activation energy for breaking a chain of atoms. ^[218, 220] D —dissociation energy; F —strength of the interatomic bond.

testing conditions, loading schedules, and types of stressed states can be explained and described on the basis of kinetic ideas.

The conclusion that mechanical failure is thermal-fluctuational in nature is of great conceptual importance. It alters seemingly self-evident notions on the role and importance of the factors that cause failure of materials. In many cases, the main operating factor in failure proves to be the thermal motion of the atoms that gives rise to energy fluctuations, rather than the mechanical force. On the other hand, the external force brings about the directionality of the degradative action of the fluctuations. In thermal-fluctuation failure, a considerable part of the work done in failure is not performed by the external force, but by the thermal energy of the material. The work done by external forces can amount to a small fraction here.

All of this permits us to speak of the mechanical strength of a material as being a property that is not based on a "purely mechanical nature" determined only by the force interaction of the atoms, but on a kinetic nature determined by the laws of thermal motion of the atoms. Hence, grounds arise for speaking of the kinetic nature of strength.

As for the practical application of kinetic concepts, we must distinguish two fundamental fields here: material science (design of materials with improved strength properties), and the engineering-design field (calculating and prediction of the endurance of parts and structures under varying conditions of use (stress, temperatures, loading schedule, irradiation, environmental action, etc.)). These problems, development of which has begun (see, e.g.^[237,185]) require a separate treatment.

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