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FRACTURE THEORY AT ATOMIC LEVEL

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The accelerated progress of modern technologies is accompanied with high pressures and temperatures, with presence of aggressive physical and chemical media. Premature fragility of the material, cracks and fracture appear under such extreme conditions. These phenomena have drawn the attention of a wide spectrum of scientists and experts, who have directed it towards the processes at atomic and molecular level. Harmful effects on the surface of metals in presence of hydrogen, chloride ion and others have been observed more than one hundred years ago. These harmful effects are expressed by means of degradation of atomic bonds, influence over ductility, premature fragility and disastrous fracture.

The study of this phenomenon at atomic level is not only of academic interest, but it contributes to the technological progress in the Science of Materials and to the improvement of durability and safety of structure in aggressive medium as the case with nuclear and thermonuclear reactors is. NATO is not by chance greatly interested in studies of the kind.

The problem for the aggressive processes on metal surfaces was raised as early as 1874 by O. Reynolds and by Hughes in 1880. Both of them observed the process during which fragility and cracks appear under strain-tension on metal surfaces, particularly in humid air and water vapors. Hydrogen and other kinds of atoms and ions dissociate the metal atomic bonds in such medium.

The fracture problem is multi-disciplinary among Sciences of Materials, Solid Mechanics, Physics and Chemistry. Fracture is a complex phenomenon caused by rapture of chemical bonds between the neighbor atoms.

A. Argon [5] notes that on principle fracture is macrophenomenon in which the energy is balanced on global scale. This is the cause that engineers find effectively to describe fracture with measurable quantities as applied tension and length of the cracks and do not regard processes on the tip of the crack. This approach accounts for the influence of temperature, loading rate and no attention is paid to the surrounding medium.

Three methods of approach are used in Fracture Theory: Macrotheory (Continuum Mechanics), Statics of Lattices and Quantum Mechanics.

The fundamental theses of Fracture Macrotheory were published by Griffith in 1920 and their further development was carried out by Irwin and others.

Three models, called "modes", are usually considered in Fracture Macrotheory: mode I under tensile stress (Fig. 1), mode II under shear and mode III under anti-plane strain.

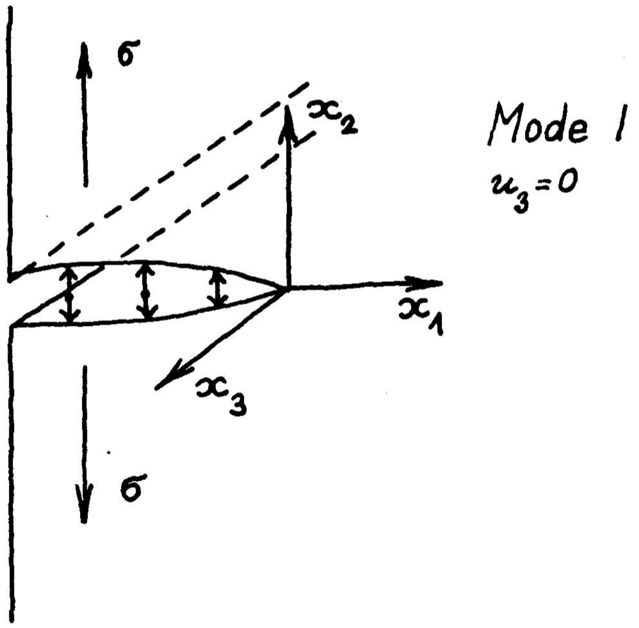

Fig. 1

Thomson [13] examines the simplest two-dimensional elastic problem which appears under isotropic anti-plane strain conditions. In this case the displacements are only in direction x_3 (Fig. 2). Tensions appear only within the plane of cracking.

The Continuum Theory is applied. The generalized elastic equation takes the following form:

$$\frac{\partial^2 u_3}{\partial x_1^2} + \frac{\partial^2 u_3}{\partial x_2^2} = \nabla^2 u_3 = 0. \tag{1}$$

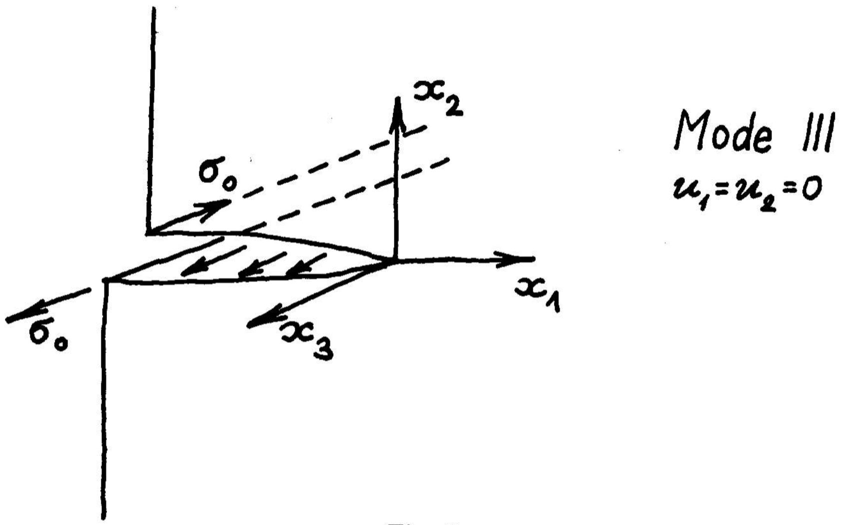

Fig. 2

With the help of the imaginary part of the complex function $\Omega(z)$ the u_3 displacement is defined in the following way:

$$u_3(x, y) = \mathrm{Im}(\Omega(z)), \quad \text{where} \quad z = x + iy = x_1 + ix_2. \tag{2}$$

The Hook law is presented in the following form:

$$\sigma(z) = \sigma_{32}(x_1, x_2) + i\sigma_{31}(x_1, x_2) = \mu \frac{d\Omega(z)}{dz}. \tag{3}$$

The density of the strain energy W is

$$W = |\sigma^2|2\mu. \tag{4}$$

The tension field in immediate proximity to the crack is defined by the functions $\Omega(z)$, which satisfy the boundary-value conditions on the crack plane and are ordinary z-series with which the solution is constructed by means of power series [13, p. 168].

V. Panasjuk [4] notes that macrofracture of solids is predetermined by microprocesses which come from their structure till and during the fracture itself. And these microprocesses themselves depend on the properties of the material macrocomponents, which form the material macrostructure as a result of physical interaction among them.

J. Knott [9] gives a short characteristic to the thermodynamical approach of Griffith, admits two energetical ratios: the surface energy S of the two new-created by the fracture surfaces and the strain energy or the potential energy U that has been released from the solid. In his equations the entropy change is ignored as well as the terms of the kinetic energy and it is postulated that the whole released elastic energy is adsorbed by the created two surfaces. First Griffith has made the separation of completely elastic and without plastic flow on the tip of the crack using experiments with glass.

A. N. Guz [2] also expresses his opinion to the question. He finds the classical criteria of Griffith-Irwin type to be unsuitable.

Knott reminds that the relation between Continuum Mechanics and Statics of Lattices is comprised in the theory to compute the theoretical strength of crystals, which theory is consisted in the idealized form of the atomic diagram "force – displacement". In this case the force is defined as a differential with respect to the distance of the interatomic or interionic energies. The energetical diagram is similar to the diatomic or dimolecular one, which is the resultant of the interatomic repulsion and attraction. The nature and the strength of attraction forces depend on the bond type: ionic, covalent, metal or Van der Waals. The diagram "atomic force – displacement" is linear for small displacements and it has the corresponding Jung module E. The lattice has also hardness of shear with a module μ.

The first investigation of cracks using the statics of the discrete atomic lattice was published by Kanninen (1966 – 1974) and collaborators, who used the empirical force-law developed by Johnson (1966) about ferrous. Considerations of the effect of the atomic force on the tip of the crack started with the works of Berenblatt (1962), who showed the nonlinear character of the crack on its tip.

The source of fracture is of different nature. The beginning of the crystal lattice fracture can be caused during the technological process of production. There are a lot of macroscopic models of defects. One of the simplest defects is the irregular position of an arbitrary atom in the lattice, the substitution of a basic atom by a "foreign" one or the absence of an atom in the lattice knot, that is vacation. These are point defects. There are also microscopic defects, which are caused by the electron interaction among the molecules. Such defects are observed by Evarestov [3] and collaborators in the structure and properties of SiO_2. The regular arrangement of atoms can be broken in a small linear section, that is a linear defect. Two-dimensional and spatial defects also appear.

T. Fisher [8] points out that the adsorption of a molecule on the surface is the first step to modify the mechanical properties of metals under the influence of the surroundings. Once absorbed the molecule can play different roles, which are of a great importance for the fracture phenomenon. It can react with the surface atoms and form a coherent and stable layer, which prevents the solid from further influence of the surroundings. However, it can react with the surface molecules and thus corrosing the solid. The reaction can be activated by mechanical energy as a result of which cracks appear.

Hydrogen, sulphur, phosphate, carbon and others can dissociate the metal bonds of the atoms and penetrate through the metal which leads to fragility. The interaction among the adsorption molecules and those of the adsorbent is of different character. Thus, the study of physical and chemical interaction is an important stage to understand the surrounding effects on material fracture under tension.

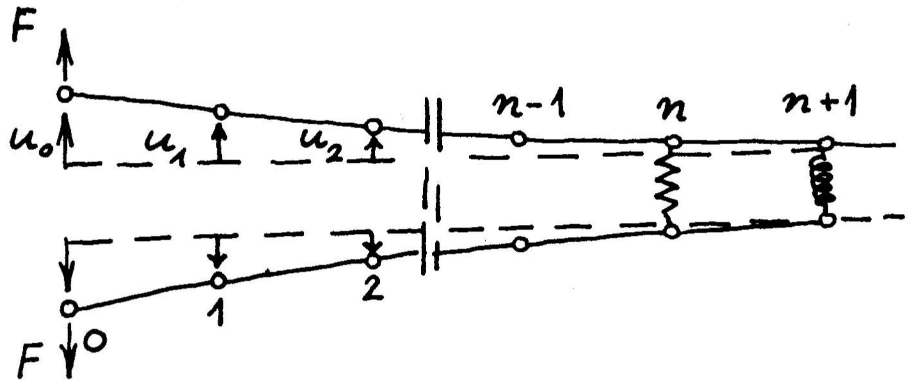

Fig. 3

Thomson [13] observes cracks in a discrete lattice, restricted by two linear chains that have been situated in the horizontal plane (Fig. 3) as the atoms of both neighbor chains are bounded with elastic springs. The most important physical effect of introducing the lattice in the fracture problem is that the lattice interferes (counteracts against) the free development of the crack. The lattice is a barrier to the crack spreading on the tip.

Thomson considers cracks inside a discrete lattice and calls the approach to that study a mathematical anatomy (Fig. 4). He restricts the displacements only in y-direction and the interaction forces act only between neighbor atoms. The equations for defining the mechanical equilibrium are as follows:

$$
\begin{aligned}
F_u &= A\,(u_y(l_{x+1}, l_y) - 2u_y(l_x, l_y) + u_y(l_{x-1}, l_y)) \\
&\quad + B\,(u_y(l_x, l_{y+1}) - 2u_y(l_x, l_y) + u_y(l_x, l_{y-1}))
\end{aligned}
\tag{5}
$$

where F is the external force, A and B are the spring-constants for shear and longitudinal displacements respectively.

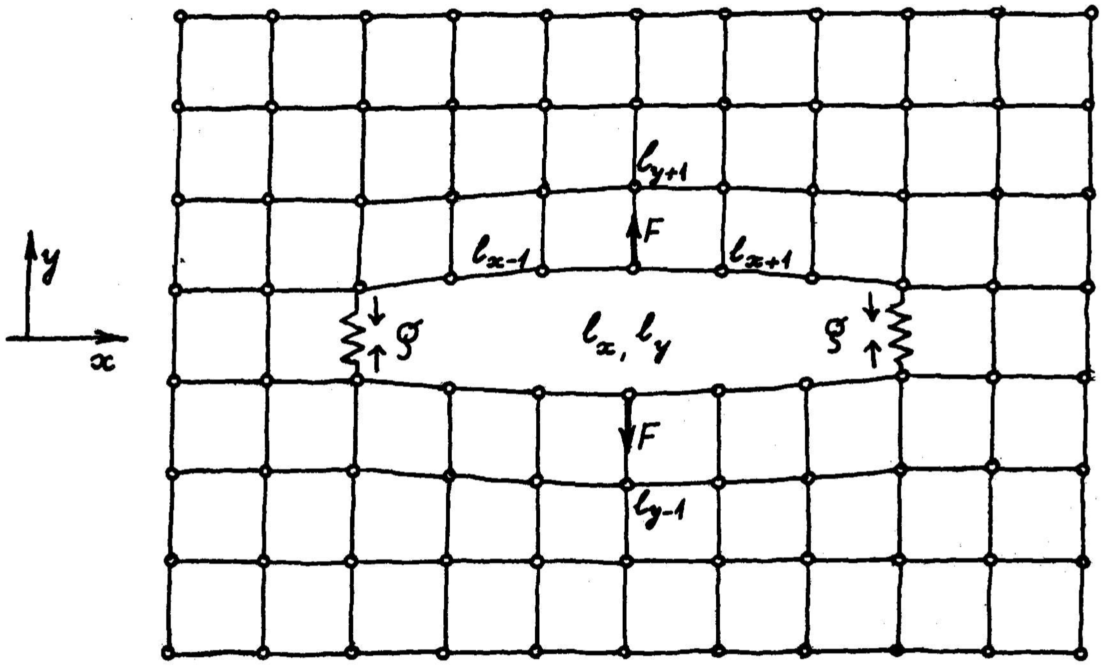

Fig. 4

Thomson also examines the effect of the chemical process on the tip of the crack. He applies a simplified presentation of the reactions with the external chemical medium, which modify the atomic bonds on the tip of the crack. For example, he considers an external molecule B_2 in interaction with the molecule A_2 on the tip (Fig. 5). He suggests the following reaction:

$$B_2 + A_2 \longrightarrow 2\,A\,B. \tag{6}$$

As a result of that reaction the B-atoms take up the most favorable energetical configuration.

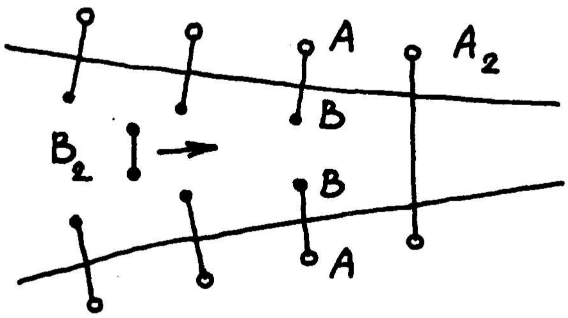

Fig. 5

The publication of Michalske and Bunker [12] gives another illustration about fracture at atomic and molecular level. It is established that under natural conditions the glass surface is exposed to the influence of solid particles and chemical agents, which cause small surface cracks in it and favour their growth, thus, finally resulting in low strength of glass. It is considered that the influence of chemical agents over the growth-rate of the crack is the most serious problem that faces constructors because it causes not only strength reduction but also fracture of the structure.

The most strongly acting chemical agent is water because it is always in the atmosphere and is in contact with glass. The basic component of glass is the tightly packed elementary tetrahedron lattice, which consists of a central atom Si surrounded by four oxygen atoms O. Each oxygen atom on the tip of the tetrahedron is forms a bond with the Si-atoms. Each tetrahedron is bonded with four neighbors. The crystalline form of quartz is characterized with a regular arrangement of tetrahedrons in the structure, while in glass the tetrahedrons are irregularly bonded in the form of rings, each of which has from five to seven tetrahedrons.

The fracture process lies in rupturing the Si–O bond resulting from the water entry in reaction, which causes crack extending. This process is shown in Fig 6. The reaction process consists of three stages. During the first stage the water molecule moves inside the crack to its tip (that is diffusion), where it is absorbed by the substance. The unbounded electrons of the oxygen atom in the water molecule bond with Si. In the meantime one of the hydrogen atoms in the water molecule is attracted to the oxygen atom in the primary Si–O bond. During the second stage the newly formed bond is strengthened, while the initial bond becomes weaker. As a result of this process hydrogen moves from the molecule to the oxygen atom after which the bond ruptures.

Disintegration of the water molecule proceeds from the third stage. The crack extends itself with an elementary step and expands the access to the next. This process is called dissociative hemosorpyion.

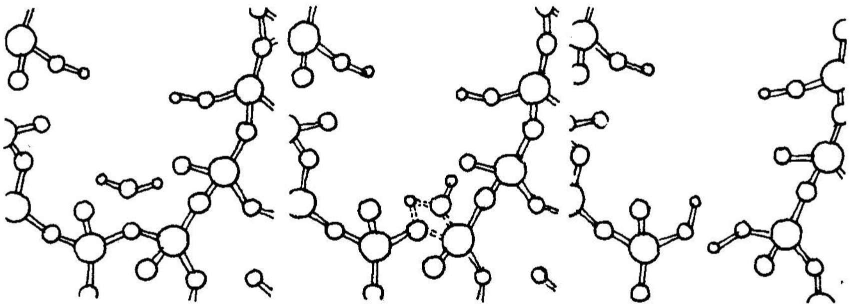

Fig. 6

The rate of crack opening depends not only on chemical medium, but also on the quantity of the applied mechanical strain-tension. The results of the glass fracture examination at atomic level reveal new possibilities to apply this method to other fragile materials.

Messmer and Briant [11] scrutinize the problem of chemical bond action on the boundary embrittlement of the material particles. The fragile fracture among particles appears when alloy-elements separate the boundaries between the material particles and decrease their cohesive strength. Since the cause for particle friability remains unclear, Messmer and Briant carry out quantum-mechanical computations to clear out the problem. It turns out that greatly friable elements attract the charge of neighbour metal atoms to themselves. They attract charges of metal-metallic bonds, which hold the cohesion between particles and make them weaker. This problem is very complex. No doubt, the whole fracture process among particles comprises dislocated movement, plastic deformations the effects of hardening and bond rupture. Messmer and Briant regard as true that the essence of the problem is in making clear the question why the separate alloys weaken the bonding of the boundaries among particles. It turns out that hydrogen in ferrous and boron in nickel decrease fragility. It turns out too that greatly fragile elements are strongly electronegative.

Latanision [10] notes that fracture processes are more complex than those in the described examples at phenomenological level. The question is how mechanical tensions and deformations, that have been included in the process of fragility causing, are influenced by the relation between orbitals in the metal and the adsorbent. Eberhardt [7], Briant and Messmer [6], etc., carry out some investigations in this direction. The most characteristic peculiarity in the theory of molecular orbital is that it supplies us with an interpretation about independent particle of the electron structure of the molecule or the solid. That means that each electron from the system is connected with its spin-orbital and energetical level, which is defined by the solution of the following equation:

$$\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)-V(x,y,z)\Psi=\frac{h}{2\pi i}\frac{\partial\Psi}{\partial t}, \tag{7}$$

considering the electron as an average potential energy of the other electrons from the system.

The exact solution of Schroedinger equation is possible only for a limited number of cases. Generally, the methods applied in Quantum Mechanics are divided into non-empirical (*ab* initio), half-empirical and empirical. The half-empirical methods are created due to investigator's intuition. That stipulates for the great variety of half-empirical schemes and lack of a system and strictness. Regardless of these defects modern half-empirical methods give a good agreement with experimental data.

The most popular method to solve Schroedinger equation is that of the self-consistent field – SCF belonging to Hartrec-Fock. The essence of this method is that the wave function of the complex atom consisted of more electrons is presented as a product of the wave functions (orbitals) of the individual electrons. The equation system is solved by the method of consecutive approximations. The computation is repeated till the solutions do not begin to reproduce one another, that is till a self-consistent solution is not obtained. This method is scrutinized in the monograph "Introduction to Mechanics of Discrete Medium" by G. Brankov, 1981 [1].

It seems that investigations in the domain of Fracture Mechanics at atomic and electronic level will be of priority at the end of the present century and at the beginning of the coming millennium.

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