THERMODYNAMIC ASPECT OF ROCK DESTRUCTION

Purpose. To evaluate the change in free energy in the transition from the nonequilibrium state of the rock to the equilibrium. This process implements the process of dynamic brittle fracture on the structural defects of the rock as a micro-inhomogeneous medium.

Methodology. It included conducting, within the framework of statistical thermodynamics, a series of experimental studies on the density and velocity of propagation of longitudinal and transverse acoustic waves in sandstone samples under different loading conditions.

Findings. According to the experimental data on the velocities of propagation of longitudinal and transverse acoustic waves for a number of sandstones at different loading modes, the values of mechanical and thermodynamic parameters characterizing the state of rocks are established. A comparative analysis of the frequency dependences of free energy on the value of the Poisson ratio is carried out.

Originality. A model of a thermodynamic system is proposed that describes the energy-activated process of transition of rock from a nonequilibrium state to equilibrium during external perturbation by surface acoustic waves. The possibility of estimating the degree of slow dynamic destruction by the Debye temperature is revealed. The mechanism of dissipation of internal energy on structural defects of the system, with the transition of its part into thermal motion of structural elements, is substantiated.

Practical value. The technique for investigation of thermodynamic state of non-ideally elastic rocks by methods of nondestructive testing is developed. The correlation between the mechanical parameters of the rock and the characteristics of the process of its transition from the nonequilibrium state to the equilibrium is established.

Keywords: rock, thermodynamic system, structure defect, acoustic wave, nonequilibrium process

Introduction. Most statistical models of rock fracture mechanics are based on a fairly common concept of the so-called “weak chain” and thermodynamic Griffiths type destruction criteria [1]. Within these models, the statistical characteristics of strength are determined only by the random structure of the rock as a solid, and the dynamic aspects are considered insignificant.

First of all, dynamic processes are implemented at the microscopic level as a microscopic brittle fracture. This is the thermofluctuation origin of elementary carriers of destruction, their clustering into defects, the inactive growth of cells to sizes, starting with which the stress concentration at the defects reaches the tensile strength at which the athermic process of propagation of its front proceeds at velocities of sound [2].

However, microscopic-brittle fracture is rare. Much more often, fracture is quasi-brittle when growth of the defect is coupled with relaxation processes around the defect. In this case, the destruction should be considered as an energy-activated process, and the integral strength characteristics will be determined by the statistics of thermal phonon fluctuations.

Literature review. A quantitative study on the stages of brittle fracture was carried out in (V.A. Petrov). In this case, the elementary carrier of destruction is represented as dilation [3] – a stable fluctuation region of increased dilation of the crystalline lattice of a solid body, which is realized at the expense of anharmonic vibrations (S.N. Zhurkov). The elastic energy accumulation caused by it in the local volume is directly proportional to the bulk modulus, and the rate of accumulation is determined by the elastic energy gain over a minimum time interval, which is inversely proportional to the Debye frequency of oscillation of the crystal lattice [4].

In paper (A.I. Malkin, F.A. Kulikov-Kostyushko and T.A. Shumikhin), a clustering of fracture carriers was considered based on a macroscopic approach and the rate of change in free energy (P) due to the formation of a cluster of frustrons was analyzed. The presence of external pressure causes the fluctuation growth of the cluster, in which the number of frustrons can exceed the critical value, which leads to a decrease in the rate of dissipation of free energy [5], and the cluster becomes an energy generator. In this case, with the negative value of free energy, an autocatalytic mode of propagation of the trunk crack is implemented, as a defect in the structure, that is, the destruction of the material.

The paper [6] proposes a quasi-brittle fracture model based on the kinetic approach and empirical regularities such as the concentration criterion and Zhurkov’s formula for a material in the form of a nested self-similar hierarchical structure. The concentration criterion is reformulated as a failure probability condition for structural levels. The hierarchy scheme takes into account critical values of the concentration parameter. The failure probabilities of hierarchy levels are calculated as functions of time, temperature, material parameters, and loading condition.

Unsolved aspects of the problem. Analysis of the thermodynamic state of the system in the transition from the nonequilibrium state to equilibrium is impossible without quantitative evaluation of its thermodynamic parameters [7]. It is impossible to investigate in detail the course of the fracture process, but its impact on the change in the structural organization of the rock is not important. The experimental data on the mechanical properties of the rock, which can be obtained before destruction and after its completion, are primarily aimed at constructing equations of state of such media and do not take into account the thermodynamic aspect of the process. In this case, the study on the relationship between the mechanical parameters and the thermodynamic state of the system with external perturbations in the form of surface acoustic waves that activate the destruction process is a rather important scientific and practical task.

Theoretical calculations of the thermodynamic parameters of the system during energy dissipation and its exchange between the structural elements of the rock, as a non-uniform medium, will allow checking the adequacy of the proposed model of the fracture process [8]. In addition, the reliability of the method and apparatus of acoustic control, provided the theoretical justification of the main parameters of the propagation of elastic waves in the rock mass can be the main geodynamic monitoring. This is to obtain information on the response of rock in the geotechnical system (GTS) to external perturbations, taking into account the...
initial state and energy exchange processes. We will assume that energy exchange processes are realized between the structural elements of the rock with the change of the oscillatory spectrum during the propagation of elastic waves of different nature and frequency. For this purpose, the statistical thermodynamics requires estimation of the change in free energy during the transition from the nonequilibrium state to the equilibrium, which realizes the process of dynamic brittle fracture on the structural defects of the rock as a micro-inhomogeneous medium [9].

**Dynamics of the process of rock destruction.** Rock will be considered as an environment consisting of a large number of individual structural elements that have a scale factor and autonomy. In this case, the structure will mean a set of stable ties of the rock (as a system as a whole), which will ensure its integrity and identity. The exchange of energy between the structural elements of such an environment determines its state and the dynamics of the transition.

Consider the conditionally allocated local volume \( V \) of the mountain in the gravity field, which is in the equilibrium region. The internal state of the isolated volume, as an open thermodynamic system with many degrees of freedom, is characterized by temperature \( (T) \), entropy \( (S) \) and external parameters \((x_1, x_2,..., x_n)\).

The free energy of such a system is determined as follows

\[
dF = -SdT - \sum_{i=1}^{n} X_i dx_i,
\]

where \( X_i \) is generalized forces \( \dot{X}_i = -\left( \frac{\partial F}{\partial x_i} \right) \).

According to the basic ideas of thermodynamics based on Boltzmann-Gibbs statistics, [11] proposes the definition of the free energy \( F(Z) \) of the nonequilibrium state \( Z \) as a state corresponding to the equilibrium with minimum potential \( \Psi(Z) \) for the conditional equilibrium state, which is realized by acting on the system of some “effective” field \( \alpha \)

\[
F(Z) = \Psi(Z) - U(Z, \alpha),
\]

where \( U(Z, \alpha) \) is “effective potential” corresponding to the input field \( \alpha \); \( F(Z) \) is the nonequilibrium free energy; \( \Psi(Z) \) is the equilibrium free energy of the system in the presence of an “effective” field.

The steady state of the mountain range in the GTS differs from the statistical equilibrium in that the mechanical energy is stored as a result of the energy input from the outside and its dissipation [10]. For various reasons, let the open GTS receive is stored as a result of the energy input from the outside and its dissipation in that the mechanical energy effective” field. For various reasons, let the open GTS receive

\[
\Delta F = -S_b(T - T_0) + \frac{T - T_0}{T_{eff}} \ln \left( \frac{T}{T_0} \right) - p\Delta V,
\]

where \( T_0 \) is the initial temperature; \( \Delta V \) is the change in volume associated with rock dilatation; \( p \) is external pressure.

In this case, the urgent issue is how the temperature can be determined in a non-equilibrium system with “slow dynamics”. Using the generalization of the fluctuation-dissipative theorem, (P. C. Hohenberg, B. I. Shraiman) introduced the concept of “effective temperature” for stationary nonequilibrium systems using the magnitude of the response (correlations) and thermodynamic temperature [14]. In this aspect, the “effective temperature” can be considered as a measure of the oscillatory energy of the structural elements of the rock under the action of acoustic waves, and its value is equal to the Debye temperature \((\theta_\text{D})\) corresponding to the Debye frequency \((\omega_\text{D})\). Accordingly, the frequency and temperature of Debye are defined as equation [15]

\[
\omega_\text{D} = \frac{2\pi N}{V} \sqrt{\frac{3}{V}},
\]

where \( N \) is the number of structural elements of a solid; \( V \) is average velocity of sound waves propagation; \( h \) is Planck’s constant; \( k_B \) is Boltzmann’s constant.

The average velocity of propagation of acoustic waves \( \overline{V} \) is determined by velocities of propagation of longitudinal \((v_\text{l})\) and transverse \((v_\text{t})\) waves using the equation [16]

\[
\overline{V} = \left( \frac{3v_\text{l}^2 v_\text{t}^2}{v_\text{l}^2 + 2v_\text{t}^2} \right)^{\frac{1}{3}}.
\]

The process of slow dynamic destruction of rock, as a solid body, from the standpoint of energy intensity can be equated with the sequential absorption of energy by plane defects, in real conditions, in the presence of surface forces. Because planar defects are mainly located and fixed on the surface, and the surface structure differs from the rock structure in the bulk, they are a source of excitation of surface energy and entropy states, which are related to the local mobility of the rock structural elements.

Surface plane defects, from the point of view of the structural organization of the rock, can contribute to the emergence of large amplitudes in the local area, which is equivalent to the propagation of elastic perturbations in the form of Rayleigh surface acoustic waves (SAW), which is a superposition of longitudinal and transverse oscillations. The accumulation of energy in the form of a Rayleigh wave as an “effective field” and its absorption on the surface of a defective region that is destroyed will determine the change in the frequency spectrum of oscillations of structural elements, and, accordingly, the energy state of the array [14]. In this case, the effective Teff temperature will be equated with the Debye temperature, which corresponds to the Debye oscillation frequency of the structural elements under the action of the SAW.

The Debye frequency is similarly defined by (4) as an equation

\[
\omega_\text{D} = \frac{6\pi^2 N^2}{V} \nu_\text{D},
\]

where \( \nu_\text{D} \) is the rate of spread of the Rayleigh SAW, \( N^* \) is the number of structural elements involved in the Rayleigh movement, \( V \) is the volume in which the Rayleigh wave propagates.

Dimensions \( V^*, N^* \) are depicted as
\[ V' = \alpha S z (v), \]
\[ N' = \frac{\rho V' N}{M}, \]

where \( z (v) \) is a depth of penetration of Rayleigh surface waves, which is a function of the Poisson coefficient of the medium; \( \langle M \rangle \) is average molar mass; \( \alpha \) is a defect shape parameter; \( S \) is the area of the defect; \( \rho \) is density of the rock.

The penetration depth \( z (v) \) is determined as an equation [15]
\[ z (v) = A (v) \lambda_R, \]
where \( \lambda_R \) is the wavelength of Rayleigh, \( \langle \lambda_R \rangle = 2 \pi \nu_R / \omega \); \( A (v) \) is the number at which the ratio of the displacement amplitude in the normal direction \( u_z \) to the displacement amplitude in the normal direction on the surface \( u_{z0} \) is \( e^{-1} \) (\( e \) is the basis of the natural logarithm) [15]
\[ u_z = A q \left( \exp (-qz) - \frac{2k_R^2}{2k_R^2 - k_l^2} \exp (-sz) \right), \]
where \( k_R = \omega / \nu_R \), \( k_l = \omega / \nu_l \), \( k_t = \omega / \nu_t \), are wave numbers of Rayleigh, longitudinal and transverse waves; \( \nu \) is cyclic oscillation frequency; \( s^2 = k_R^2 - k_l^2 \), \( q^2 = k_R^2 - k_t^2 \).

The Poisson’s ratio for the known values of the velocity of propagation of the longitudinal and transverse waves is determined as an equation (L. D. Landau, E. M. Lifshits)
\[ \nu = \frac{2 - \nu_l}{2 - \nu_l} \frac{\nu_t}{\nu_t} \]

Results. On the basis of model representations we will carry out theoretical estimations of change in free energy in equation (3) taking into account the contribution of each of the additives on the example of specimens of the Carpathian, Crimea, Polissia series (Fig. 1) and model sandstones Navajo, Weber, Nugget in a wide range of effective values of Poisson’s ratio of the medium.

We assume that the initial state of the rock, which was in a state of foreign equilibrium, corresponds to the experimentally determined velocities of propagation of longitudinal and transverse waves at a pressure of 50–100 MPa. After the process of rock destruction, the propagation velocities of the acoustic waves change, respectively, to the values of \( \Delta \nu_l \), \( \Delta \nu_t \), which, respectively, leads to a change in the Debye temperature by the value of \( \Delta T_D \) and Poisson’s ratio.

Poisson’s ratio of sandstone samples \( (\nu_{eff}) \) without load regime will be determined as an equation
\[ \nu_{eff} = \frac{2 (\nu_l - \Delta \nu_l)}{2 (\nu_l - \Delta \nu_l) + (\nu_l - \Delta \nu_l)^2}, \]

Determination of the propagation velocities of the longitudinal and transverse waves was performed in pulse mode by the time \( t \) of the passage of the ultrasonic pulse through the rock sample at different modes of applied voltage. The scheme of the experiment is presented in Fig. 2.

Determine the quantity \( \nu_l \) by the following equation
\[ \nu_l = \frac{v_l d}{v_l d - 2a}, \]
where \( d \) is thickness of the sample; \( v_l \) is the velocity of ultrasound in the metal punch; \( a \) is the distance from the ultrasound transducer to the sample surface.

When a longitudinal wave drops to the surface of the sample at an angle greater than the critical angle, only a transverse wave propagates in the sample. These conditions were implemented using the wedge method, while at the boundary of the “wedge-pattern” Snellus law is fulfilled [17].

Fig. 1. Samples of sand rocks of the Carpathians, Polissia and Crimea:
\[ a, b, c, d – accordingly, sandstones 1, 2, 3, 4 \]
where $\alpha$ is an angle of inclination of the wedge; $\beta$ is a refraction angle of the ultrasonic wave in sample, $v_{i1}$ is the velocity of ultrasound in the wedge material.

In this case, the value of $v_i$ is determined from the equation

$$\frac{2b}{v_{i2}} \sqrt{v_{i2}^2 - v_i^2 \sin^2 \alpha} - \tau = 0,$$

where $\alpha$ is an angle of inclination of the wedge; $b$ is the distance from the center of the ultrasound transducer to the surface of the sample.

Experimental values of the propagation velocities of longitudinal and transverse waves in sandstone samples under different conditions (without applied voltage and stress state) showed that the values of $v_i$, $v_i$ are smaller in the non-stressed state [19]. The values of $v_i$ and $v_i$, their decrements $(\Delta v_i, \Delta v_i)$ and Poisson’s ratio $(\nu, \nu_i)$ of some of the sandstones studied are presented in Table 1.

The Debye values for stressed sandstone samples decrease monotonically with increasing $\nu$. Changing the values of $v_i$, $v_i$ depending on the conditions in the same way leads to a decrease in the average velocity of propagation of acoustic waves (Table 2).

The average velocity $\Delta v_i$ decreases when changing conditions are in the range of 388–567 m/s, which corresponds to the change in the Debye temperature, respectively, in the range of 20–37 K, except for the Weber sandstone sample.

The entropy of the rock $S_0$, located in the region of the foreign equilibrium of the GTS is defined as an equation [20]

$$S_0 = \frac{V \sigma_{eq}}{0_p} \left( 1 + 4 \nu \frac{1 - \nu^2}{E} \right),$$

where $E = p \nu^2$ is Young’s modulus; $\sigma_{eq}$ is equivalent voltage $\sigma_{eq} = \bar{k} \sigma_{eq}$; $\sigma_{eq}$ is tensile limit for uniaxial compression; $k_i$ is the coefficient of structural–mechanical attenuation.

Theoretical calculations of entropy by the equation (5) were carried out for experimental values of density and strength limit of sandstone samples, which were, respectively, within the range $p = 2150–2460$ kg/m$^3$ and $85–110$ MPa, at the coefficient of structural–mechanical attenuation $k_i = 0.5$.

The change in rock volume associated with dilatation in the process of destruction will be associated with the fracture parameter of the array $\beta \leq 0.17$.

To estimate the magnitudes of power, we use the ratio for the flow of energy in the SAW per unit width of the acoustic beam (Yu. V. Gulyaev, V. P. Plesskii)

$$P_R = \pi - \frac{\Delta \rho}{2} \left( \frac{v_i}{v_R} \right)^2 \frac{f u_i^2 v_i^2 p}{v_i^2},$$

where $f = \omega/2\pi$ is frequency; $\Delta \rho = D_{i\rho}$; $D_{i\rho}$ is the derivative of the Rayleigh determinant $D(k, \omega) = k^2 + s^2 - 4k^2 \rho = 0$; $M(v)$ is dimensionless Poisson’s ratio function, $d_i$ is the size of defect.

The phase velocity of the Rayleigh wave was determined by the equation [18]

$$\Delta F = - \frac{\nu}{k_i}; 2 \left( \frac{v_R}{v_i} \right)^2 - 4 \left( \frac{v_R}{v_i} \right)^2 \left( 1 - \frac{v_R}{v_i} \right)^2.$$
Experimental values of the velocities of propagation of the acoustic waves of their decrements and Poisson’s ratio of a number of sandstones

| Sample              | $\nu_0$, m/s | $\nu_0$, m/s | $\nu$, | $\Delta u_0$, m/s | $\Delta u_0$, m/s | $\nu_{ef}$ |
|---------------------|--------------|--------------|-------|-------------------|-------------------|-----------|
| Sandstone Weber     | 4550         | 3050         | 0.09  | 2100              | 1250              | -0.09     |
| Sandstone Nugget    | 4520         | 3020         | 0.10  | 760               | 410               | 0.04      |
| Sandstone Navajo    | 4860         | 3210         | 0.11  | 760               | 430               | 0.07      |
| Sandstone 1         | 3860         | 2460         | 0.16  | 680               | 370               | 0.12      |
| Sandstone 2         | 4080         | 2420         | 0.23  | 800               | 360               | 0.17      |
| Sandstone 3         | 4190         | 2315         | 0.28  | 800               | 320               | 0.24      |
| Sandstone 4         | 4250         | 2040         | 0.35  | 820               | 260               | 0.32      |

Table 2

Rayleigh propagation velocities, average acoustic wave propagation velocities and the Debye temperature of a number of sandstones

| Sample              | $\nu_v$, m/s | $\nu_{av}$, m/s | $\Delta \nu$, m/s | $\theta_{D}$, K | $\theta_{D}^\prime$, K |
|---------------------|--------------|-----------------|-------------------|----------------|------------------------|
| Sandstone Weber     | 2718         | 3759            | 1622              | 292            | 115                    |
| Sandstone Nugget    | 2694         | 3726            | 553               | 302            | 37                     |
| Sandstone Navajo    | 2874         | 3978            | 567               | 321            | 33                     |
| Sandstone 1         | 2224         | 3087            | 493               | 247            | 26                     |
| Sandstone 2         | 2218         | 3107            | 509               | 253            | 30                     |
| Sandstone 3         | 2141         | 3031            | 463               | 249            | 26                     |
| Sandstone 4         | 1907         | 2753            | 388               | 224            | 20                     |

Fig. 3. The dependence of the change in free energy $\Delta F$ for a number of sandstones with different Poisson’s ratio $\nu_{ef}$ (the value $\nu_{ef}$ is represented in the graph and varies in a row in the direction of the arrow)

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Введение

Оцінити зміни вільної енергії при переході із нерівноважного стану в рівноважний, під час зовнішнього збурення поверхневими акустичними хвилами. Розкрита можливість оцінки міри повільного динамічного руйнування за температурою Дебая. Обґрунтовано механізм дисипації внутрішньої енергії на структурних дефектах системи, із переходом її частини в тепловий рух структурних елементів.

Практична значимість. Розроблена методика дослі- ження термодинамічного стану неідеально-пружних гірських порід методами неруйнуючого контролю. Вста- новлено взаємозв'язок між механічними параметрами гірської породи й характеристиками процесу переходу її з нерівноважного стану в рівноважний.

Ключові слова: гірська порода, термодинамічна система, дефект структури, акустична хвиля, нерівноважний процес

Термодинамічний аспект руйнування гірських порід

В. А. Машченко 1, О. Е. Хоменко 2, В. П. Квасников 3

1 – Одесса; 2 – Одесский национальный технический университет; 3 – Национальная техническая академия; e-mail: maschenko@ukr.net

Мета. Оцінити зміни вільної енергії при переході із нерівноважного стану в рівноважний. Цей процес реалізує процес переходу гірської породи від нерівноважного стану в рівноважний, під час зовнішнього збурення поверхневими акустичними хвилами.

Методика. Включала проведення в рамках статистич- ний термодинамікі серії експериментальних досліджень цільності та швидкості поширення поздовжніх і попереч- них акустичних хвиль у зразках пісковиків за різних умов навантаження.

Результати. За експериментальними даними вивчу- стей поширення поздовжніх і поперечних акустичних хвиль для ряду пісковиків за різних режимів навантаже- ння встановлено значення механічних і термодинамічних параметрів, що характеризують стан гірських порід. Про- ведено порівняльний аналіз частотних залежностей віль- ної енергії від величини коефіцієнта Пуассона.

Наукова новизна. Запропонована модель термодинамі- чної системи, що описує енергоактивований процес переходу гірської породи від нерівноважного стану в рів- новажний, під час зовнішнього збурення поверхневими акустичними хвилами. Розкрита можливість оцінки міри повільного динамічного руйнування за температурою Дебая. Обґрунтована механізм дисипації внутрішньої енергії на структурних дефектах системи, із переходом її частини в тепловий рух структурних елементів.

В. А. Машченко 1, О. Е. Хоменко 2, В. П. Квасников 3

1 – Одесса; 2 – Одесский национальный технический университет; 3 – Национальная техническая академия; e-mail: maschenko@ukr.net

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Методика. Включала проведення в рамках статистич- них і термодинамічних досліджень цільності та швидкості поширення поздовжніх і поперечних акустичних хвиль у зразках пісковиків за різних умов навантаження.

Результати. За експериментальними даними вивчено- стей поширення поздовжніх і поперечних акустичних хвиль для ряду пісковиків за різних режимів навантажен- ння встановлено значення механічних і термодинамічних параметрів, що характеризують стан гірських порід. Про- ведено порівняльний аналіз частотних залежностей віль- ної енергії від величини коефіцієнта Пуассона.

Наукова новизна. Запропонована модель термодинамі- чної системи, що описує енергоактивований процес переходу гірської породи від нерівноважного стану в рів- новажний, під час зовнішнього збурення поверхневими акустичними хвилами. Розкрита можливість оцінки міри повільного динамічного руйнування за температурою Дебая. Обґрунтована механізм дисипації внутрішньої енергії на структурних дефектах системи, із переходом її частини в тепловий рух структурних елементів.