Properties of Symmetry of Space and Time, Hamilton's Principle and the Invariants

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***Abstract*—** *This research investigates the fundamental role of symmetry properties in space and time in justifying the use of the principle of least action (PLA) to describe the creation and evolution of nanomaterials. By examining the kinetics of structural transformations in metals, we demonstrate that the PLA is a universal principle applicable to diverse physicochemical and biological processes. We explore the principle's ability to establish invariants at various structural-scale levels of metal deformation, including nano-, submicro-, micro-, meso-, and macroscale levels. Our findings highlight the significance of symmetry properties in understanding and predicting the behavior of nanomaterials.*

***Keywords*— Symmetry properties, Space-time continuum, Principle of least action (PLA), Hamilton's principle, Invariants, Nanomaterials, Structural transformations.**

I. INTRODUCTION

Structure determines the properties of materials under external influences. Establishing the causes, mechanisms and regularities of destruction of materials and, first of all, metals depends on the development of methods and technologies of their processing to increase reliable and safe operation. The complexity of the study of metal interface surface under external impacts and tribo-loading is determined by the lack of scientifically sound fundamental principles that can be applied at the junction of different sciences (physics, chemistry, mechanics, materials science, etc.) [1]. In addition, the complexity of the study of the metal interface surface is explained by the simultaneous occurrence of diverse processes (heat conduction, diffusion, mass transfer, hardening, fracture, amorphization, etc.) and the correct choice of the scale factor of external influence (load-velocity parameters, etc.). The latter makes it possible to divide a complex process into simpler constituent parts and to establish the course of the dominant process in their diversity [2]. The analysis of the dominant process makes it possible to identify and establish the main fundamental regularities describing this process [3].

All physicochemical [4] and biological processes [5] take place in a space-time continuum, the properties of which should be reflected in these processes as well. If this is so, then there must also exist a fundamental and universal principle of least action (PLA) to describe these processes. The existence of invariants is a direct proof of the existence of the PLA. Invariance in physics is a fundamental concept that means independence of physical regularities from specific situations in which they are established and from the way of description of these situations [6].

In chemistry, it is the law of conservation of mass of matter [7], Mendeleev's periodic table, where each chemical element has its own number with a set of certain parameters and properties that are invariant during chemical reactions [8], graph invariant [8], in biology it is Mendel's second law [10], in nuclear and quantum physics all processes occurring in the microcosm are subject to the law of conservation [11]. But where are these invariants in materials science, in condensed state physics, in technical sciences? Such a principle linking the symmetry of space and time properties with the properties of materials is the principle of least action or Hamilton's principle (HP). The latter determines the search and establishment of basic, fundamental invariants acting at all structural-scale levels of deformation of the metal.

The object of the study is the metal interface surface, namely the boundary lubricating layer of nanometer thickness, surface and subsurface layers. Rolling, quenching in different media, cavitation wear and longtime tribo-loading were selected as

external influence on the object of study - nickel surface. According to [12], the broadening ΔH due to dislocations is proportional to λ^2/M^3, where M is the saturation state magnetization and λ is the magnetostriction constant. The ratio λ^2/M^3 in nickel is about two orders of magnitude higher than in iron, so nickel was taken as the object of study. Mechanisms of harden ing and fracture in the surface layer of metals having face-centered and volume-centered crystalline lattice have oscillatory character and time-localized lobe character of wear under tribo-loading [13, 14].

The aim of the work was to substantiate the application of the basic and universal principle of PLA describing the kinetics o f structure formation of the metal interface surface and its use to establish invariants at nano-, submicro-, micro-, meso-, and macroscale levels of plastic deformation of the nickel surface layer, as well as to establish the structure, properties, and fa ilure mechanisms of the steel interface surface under static and dynamic loading.

II. EXPERIMENTAL DETAILS

Polycrystalline nickel of 99.99% purity, armco-iron, bearing steel, bronze, and cast iron were investigated. The nickel samples in the form of thin disks were polished electrolytically and annealed in a vacuum of 0.133 mPa at 973 K. The friction test of Ni – Mo pair was carried out on the machine AE-5 according to the finger-disk scheme with precise setting of the contact area at a specific load of ≈ 84 kPa and linear speed of ≈ 0.5 m/s. Electron microscopic studies of nickel were carried out on a microscope EVM-100AK and Hitachi-H800 by the method of thin foils on "lumen". The resolution of the Hitachi-H-800 is ≈ 0.1 nm. The technique of preparation of nickel samples for transmission electron microscopy is given in work [12]. Samples from steels: Ст 45, Ст 12Х1, 65 Г, steel ШХ-15, etc., which are used for the manufacture of rolling and sliding bearings, as well as cast iron (Сч-21-40); bronze (БрОЦС 5-5-5) were studied [3]. Studies have shown a time lobe flake mechanism of metal surface wear, which can only be explained using the theory of dislocation representations. There are no fundamental differences in the formation of dislocation structure for these metals [12]. References to monographs, articles, patents and materials of international conferences describing the idea of using HP, methods and ways of research of metal interfaces, rolling and sliding supports are described in the abstract [3].

III. RESULTS AND DISCUSSION

It is known that the principle of least action (PLA) or Hamilton's principle is used to formulate the equations of motion of a material point in mechanics [4]. Why this fundamental principle cannot be used to describe kinetics of processes of structura l transformations in materials occurring in the same continuum of space and time? A question naturally arises, namely: where there is symmetry, there should be invariants for describing the kinetics of various structural transformations at the multilevel, hierarchically organized processes occurring on the surface of metals? The kinetics of the transition of the system from one structural state (A) to another (B) is carried out in accordance with the principle of least action (Fig. 1).

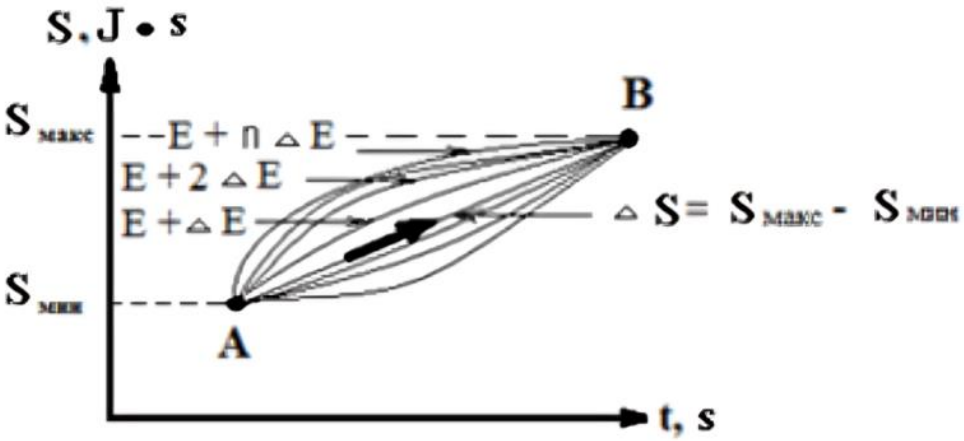


FIGURE 1: Kinetics of system transition from one structural state (A) to another (B) in accordance with the principle of least action, where S – action, t – time

It is known that the mathematical formulation of the PLA (or Hamilton's principle) has the form [4]:

$$\delta S = 0 \quad (1)$$

where

$$S = \int_{t_1}^{t_2} L(q, q', t)dt \quad (2)$$

where q, q′ are independent parameters characterizing the system, t is time. Then the expression is valid:

$$\delta S = \int_{t_1}^{t_2} (\frac{\partial L}{\partial q}\delta q + \frac{\partial L}{\partial q'}\delta q')dt = 0 \quad (3)$$

Suppose that the expression is true:

$$L = E_{kin} - E_{pot} \quad (4)$$

where E_{kin} – is the kinetic energy, a E_{pot} – is the potential energy of the material point under a given external influence.

The mathematical expression for the action of the electromagnetic field, together with the charged particles therein, is given in [15]. The general form of the Lagrangian for the system of particles (charges) forming the structure consists of the sum of Lagrangians taking into account the terms for free particles (the difference between kinetic and potential energy), the interaction of particles with the electromagnetic field and with each other, as well as the term for the electromagnetic field [15]. Obviously, the exact calculation of the Lagrangian for a system of particles is impossible due to the large number of particles constituting the defect as well as the elements of the defect structure. Nevertheless, a general form of the Lagrangian and the equation of motion (displacement) of the sublattices of positive and negative ions in a two-atom NaCl crystal are given in [16].

Entropy is given by the expression [17]:

$$H = \frac{\zeta(\nabla T)^2}{T^2} + \rho\frac{Z\Sigma}{T} \pm \frac{\rho}{T^2}([\alpha, \Omega], \nabla T, t) \quad (5)$$

where ς - thermal conductivity, ρ - material density, Z - defect flux density, Σ - hydrostatic stress in the defect phase formation zone, parameters α and Ω characterize the energy flux through the surface. The first summand in expression (S) is entropy production associated with heat generation. The second summand determines the work of defects flux when they move in the stress field. The third summand is related to the energy flow of the mechanical field of the crystal through the surface. The plus or minus sign determines the direction of the energy flow [17]. The change of the flow direction is determined by the energy advantage of the self-organization process or, in a broader sense, by the principle of least action. The latter implies the search and establishment of invariants [18, 19].

Correctly chosen scale factor of external influence or in this particular case soft mode of tribo-loading (or low-amplitude, alternating and multicycle external influence) allowed to analyze kinetic changes of hardening and softening of nickel surface (Fig. 2) [12]. Nickel was chosen as an object of study because its coefficient of magnetostriction is two orders of magnitude higher than, for example, that of armco-iron. The latter made it possible to see or analyze changes in the strength properties of the nickel surface using the ferromagnetic resonance (FMR) line broadening method [12]. Simultaneous study of nickel samples by weight method allowed to analyze their wear intensity (Fig. 2). Overlapping of two curves in one Fig. 2 allowed us to see their asynchronous dependence for one and each cycle of change in surface strength properties [20]. The multilevel system of deformation of a metal surface, for example, nickel (Fig. 2), ensures its stability [21]. The latter is confirmed by the fact that the selective mechanism covering a nickel layer hundreds of micrometers thick occurs only at time (t) ≈ 108 ks (Fig. 2) [20]. The self-organization of the system is expressed in 12 cycles of lobe fracture (Fig. 2), where lobe separation is an integral part of the evolution of structure formation of the multilevel system, since the time-localized separation of wear lobes reduces the level of stored energy (Fig. 2) and prevents cracks from propagating into deeper layers of nickel.

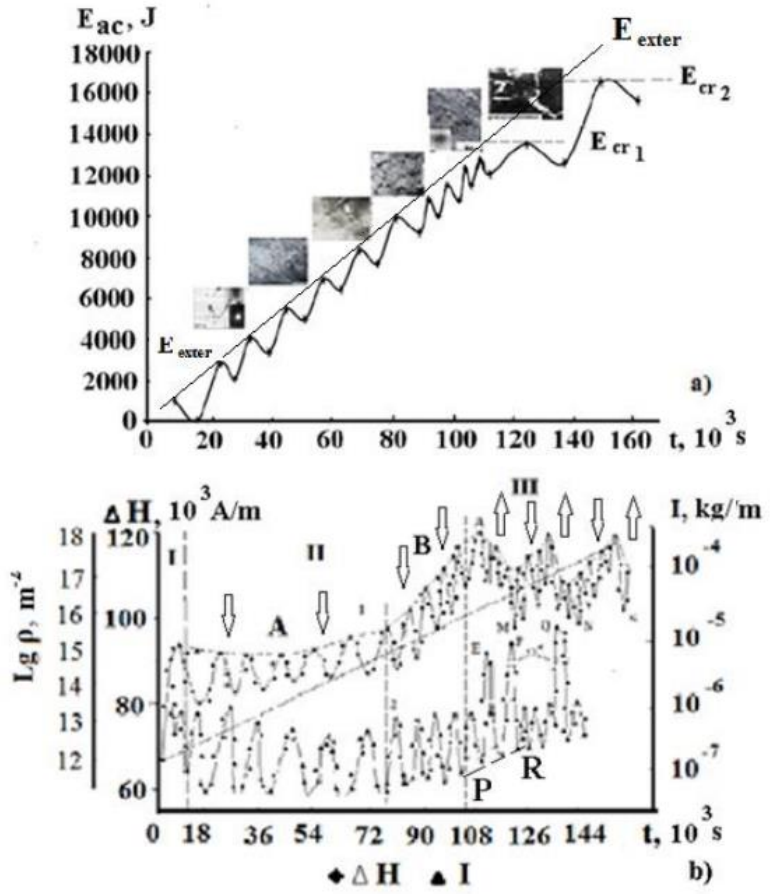


FIGURE 2: Dependence of kinetics of structural changes of nickel surface layer under triboloading: a) – dependence of accumulated energy (E_{ac}) on time (t), where E_{cr1} and E_{cr2} are values of critical energy for destruction of meso- and macroscale level of deformation; b) – dependence of broadening of ferromagnetic resonance line (ΔH), dislocation density (ρ), wear intensity (I) on time (t) of triboloading

For one and each cycle of change in strength properties, an asymmetric dependence of the increase in dislocation density and wear intensity is established (Fig. 2), that is, the expression is fulfilled [3, 18]:

$$\rho \cdot I = const \tag{6}$$

where ρ is dislocation density, I is volumetric wear intensity, const ≥ 0. The established relationship is confirmed by a number of articles [20, 22], which present model representations of lobe fracture of the surface layer. Experimental confirmation of hardening and lobe fracture is shown directly using the FMR method in our papers [13, 14]. Expression (6) is not invariant, as the constant changes with time, which may be due to both regular introduction of new lubricant into the friction zone (greasing) during each cycle of change in strength properties, and other reasons. It is necessary to carry out further research to find out the reasons for the constant change with time.

Fulfillment of the energy balance determines that part of the energy is spent on heat, deformation work, elastic field energy flow and energy determined by the mass of worn particles. Then, based on the law of conservation of energy, the expression will be fulfilled [23]:

$$E_{exter} - E_{ac} = H + M, \tag{7}$$

where E_{exter} - energy of external impact, E - energy accumulated in the surface layers of nickel, H is the entropy given by expression (6), M is the energy determined by the mass of worn particles. Entropy is a function describing the state of the system. Indeed, in the repeated 12 cycles of hardening of the nickel surface layer, the energy difference ($E_{exter} - E_{ac}$) is minimal at the points of contact between the graphs of the functions $E_{exter}(t)$ and the accumulated energy $E_{ac}(t)$, shown in Fig. 2. The formation of nanocrystalline (NC) structures occurs when dislocations exit to the surface and, accordingly, the dislocation

density increases, which occurs at the areas of maximum of the function $E_{ac}(t)$. Obviously, the formation of NC and SMC structures is accompanied by a decrease of the entropy (Fig. 2, a).

Let us quantitatively estimate the entropy value for the forming defect structures in Fig. 2, based on expression (7). The mathematical expression of entropy for the processes of structure formation kinetics depicted in Fig. 3 is given by expression (8):

$$H + M = \int_0^{160000} (\Delta(E_{exter}) - \Theta(E_{ac}))dt \quad (8)$$

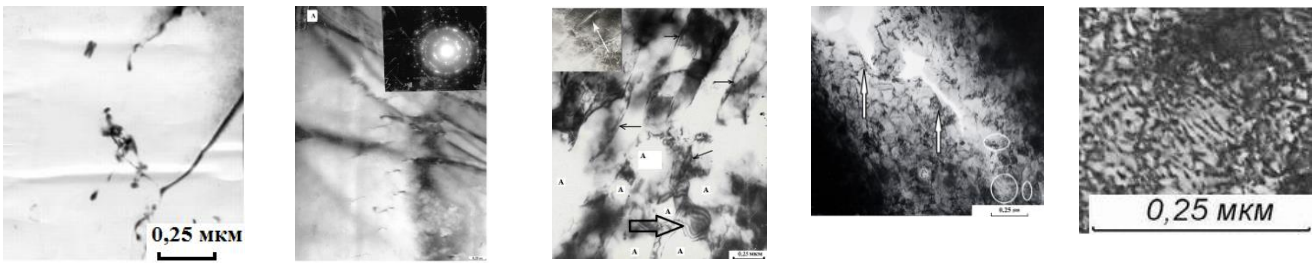
where $\Delta(E_{exter})$ is a function defined by a directly proportional dependence on time, since the value of Evnesh is numerically equal to the work of tribo-loading forces, and the function $\Theta(E_{ac})$ is defined by a monotonically increasing oscillating dependence in time (Fig. 2). The limits of integration vary from 0 to 160000 seconds according to Fig. 2. Since the definite integral of a function is numerically equal to the area of the figure bounded by the given function and integration limits, the numerical values of the smallest action were determined by the area of the figure bounded from above by a straight line and from below by a monotonically oscillating increasing dependence (Fig. 2, a). Table 1 quantifies the amount of entropy and energy determined by the mass of worn particles required to form a particular structure.

TABLE 1

THE QUANTITATIVE ESTIMATION OF ENTROPY AND ENERGY, DETERMINED BY THE MASS OF WORN PARTICLES, IN THE FORMATION OF A PARTICULAR STRUCTURE IN THE SURFACE LAYER OF NICKEL UNDER TRIBO-LOADING

Type of structure	t, 10^3 s	H+M, entropy plus energy determined by the mass of worn particles, 10^6 J·s
NC structures	0.9	0.0972
Slip strips	6.5	2.51427
Fragmented NC and SMC structures	108	57.82821
Loose and porous surface layer	160	120.3802

As a result of long-term tribocharging of the nickel surface (more than $150 \cdot 10^3$ s or 150 ks) the formation of a defective structure whose size varies from 30 μm to 3 nm (Fig. 3) [23].



(A) (B) (C) (D) (E)

FIGURE 3: Kinetics of the nickel surface structure under tribo-loading: A – initial structure of annealed nickel; B – structure corresponding to the minimum oscillation dependence of the ferromagnetic resonance line broadening (ΔH(t)); C – plate microstructure of slip bands; D – subgranular microstructure; E – nanocrystalline structure

The grain size of the nickel annealed before triboloading was ≈ 30 μm. The submicrocrystalline (SMC) and nanocrystalline (NC) structural states have a closed shape and are formed in areas with strongly disoriented crystal sections. The kinetics of defect structure formation can be simplified as a circle of decreasing diameter size (Fig. 4).

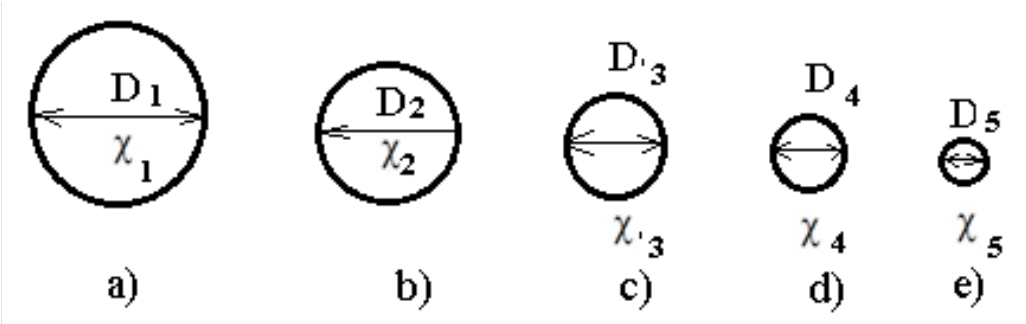


FIGURE 4: Scheme of the formation of structural defects at different structural-scale levels of deformation: a) initial structure; b) – e) evolution of the structure under the action of external influences (triboloading), namely: b) formation of microstructure; c) submicro-; d) nanoscale and e) nanocrystalline structural states

In Table 2, we summarize the parameters describing the structural states shown in Fig. 4.

TABLE 2
PARAMETERS DESCRIBING THE KINETICS OF STRUCTURAL STATES OF NICKEL SURFACE

Size of structural elements (diameter (D)), 10^{-6} m	Angle (Δω), degree	Local curvature of nickel crystal structure (χ), degree/10^{-6} m
30	3600	12
3	3600	120
0,3	3600	1200
0,03	3600	12000

When the size of a structural element decreases by an order of magnitude, the value of local curvature of the nickel crystal structure increases by an order of magnitude. As the analysis of microdiffraction images shows, the disorientation of structures of ≈ 3÷10 nm in size is ≈ 10÷20° [12]. It is experimentally confirmed that the local curvature of the crystal structure of nickel increases by four orders of magnitude when the size of the structural element decreases by four orders of magnitude (table 2). The expression is fulfilled [24]:

$$\chi_{ij}(10^{-n}\cdot x_1;\ 10^{-n}\cdot x_2;\ 10^{-n}\cdot x_3) = 10^{n}\,\chi_{ij}{}^{o}(10^{-n}\cdot x_1,\ 10^{-n}\,x_2,\ 10^{-n}\,x_3), \quad (8)$$

where x_1, x_2, and x_3 are spatial coordinates, and χ_{ij} is the local curvature tensor of the nickel crystal lattice, n = 0, 1, 2, 3 $\chi_{ij}{}^{o}$ is the local curvature tensor of the nickel crystal lattice corresponding to the initial structure. The local lattice curvature takes place at all structural levels of deformation, from the nano- to macrolevel of large-scale deformation, which indicates its fundamental importance in the formation and evolution of structures.

An example of fulfillment of expression (8) for three-dimensional space taking into account the values of parameters given in table 1, where n = 0, 1, 2, 3.

$$\begin{bmatrix} 12000 & 0 & 0 \\ 0 & 12000 & 0 \\ 0 & 0 & 12000 \end{bmatrix} (10^{-3}\cdot 0{,}03;\ 10^{-3}\cdot 0{,}03;10^{-3}\cdot 0{,}03) = 10^{3} \begin{bmatrix} 12 & 0 & 0 \\ 0 & 12 & 0 \\ 0 & 0 & 12 \end{bmatrix} (10^{-3}\cdot 0{,}03;\ 10^{-3}\cdot 0{,}03;10^{-3}\cdot 0{,}03) \quad (9)$$

The scale invariance of the local curvature of the crystal structure of polycrystalline nickel at all structural strain levels is fulfilled [25].

It is necessary to emphasize the main and, at first sight, obvious fact that the formation and evolution of structural boundaries proceeds in accordance with the energy profitability [26]. As soon as it is physically possible to implement through one or another mechanism (twinning, formation of package defects, etc.), it is immediately launched according to the energy benefit, since the result of the process is the reduction of the energy accumulated as a result of the deformation in the material (Fig. 2).

The formation of nanocrystalline structures (NC) at the very beginning of triboloading (t = 0.9 ks) is due to energy localiza tion in a thin nickel surface layer and the absence of energy relaxation channels and mechanisms into the subsurface layer due to the juvenile pre-annealed nickel surface, where microcracks, pores and other elements of the defective structure are absent [27]. Energy localization allowed to reduce the time of formation of the same structures, but already at t ≈ 140 ks. Under prolonged triboloading a strongly thermodynamically nonequilibrium surface layer of nickel covering up to a hundred microns in depth was obtained [23]. There is an obvious relationship between time and energy, since the localization of energy reduce s the time of realization of the process of formation of NC structures.

The process of stress localization in a thin surface layer of the order of ≈ 1 μm, the formation first of rotational structures [25], and then of wear particles and their separation from the surface also proceeds in accordance with energy profitability. Petal separation of the thinnest surface layers up to 100 nm thick is shown in Fig. 2. It goes through 12 cycles of hardening and fracture before selective fracture occurs (point A in Fig. 2) [20, 22]. Each cycle of strength property change is characterized by the accumulation of dislocations up to a certain critical value, which determines the surface overlap. Then its destruction t akes place. Approximately one tenth of the work or energy expended in friction for each cycle is accumulated in the subsurface. The accumulation of strain energy causes the formation of porosity (Fig. 5) and a highly nonequilibrium state of the nickel crystal lattice. The degree of porosity reaches more than 30 % of the entire observation area.

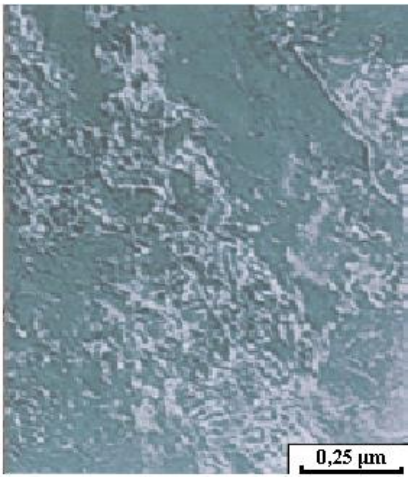


FIGURE 5: Formation of the dispersed and porous (friable) layer during pre-destruction (t = 140 ks). The image is invented for better contrast and clarity

Analysis of the experimental data of the strongly nonequilibrium structure (Fig. 2, region III) shows that an increase in the total area of porosity also determines an increase in the volumetric wear rate (section PR in region III in Fig. 2). In the area o f nonequilibrium deformation the gradient of the dislocation and point defects density flux has an oscillating character; the increase in the intensity of the gradient of upward and downward dislocation density fluxes causes an increase in the lower limit of wear intensity change in ≈ 8 times (area PR on Fig. 2 in area III), and the upper limit of wear intensity change at avalanche-like selective mechanism of surface layer destruction – by three orders of magnitude (Fig. 2, area III). At the same time, in area III a decrease in the period of change of strength properties of the nickel surface by ≈ 8 times is noted in comparison with area II (Fig. 2). There is a complete coordination of change of strength properties and volumetric wear rate of nickel surface. Increase in 8 times of intensity of a gradient of ascending and descending flows of dislocation density causes both diffusion mobility of point defects and increase in porosity of a material [28]. Directly proportional increase of minimal va lue of volumetric wear intensity with increase in time of triboloading is established (Fig. 2, area III). The expression is fulfilled [29, 30]:

$$\frac{I}{S} = const, \tag{10}$$

where I is the volumetric wear rate, S is the total pore area, const ≥ 0.

Further studies of non-dislocation mechanisms and the establishment of invariants in the self-organization of a highly nonequilibrium structure (Fig. 2, region III) are needed.

A method was developed to determine the wear of ferromagnetic materials under triboloading, where the frequency of oscillations of the FMR line width per unit time, obtained by the graduation dependence (Fig. 6), is used to infer the wear intensity of the ferromagnetic material [31].

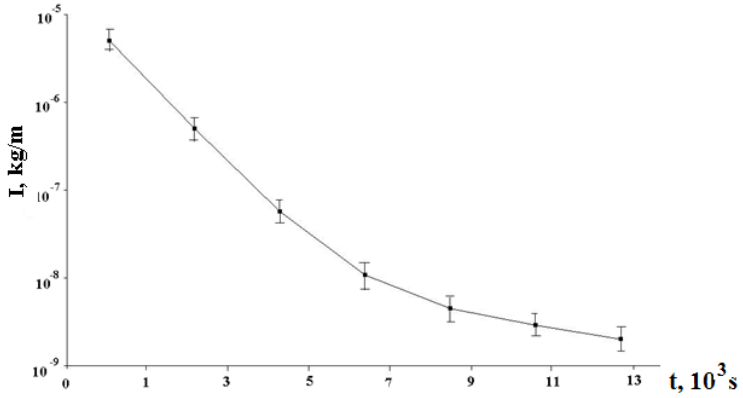


FIGURE 6: Dependence of wear rate (I) on oscillation period (t) during triboloading with CYATIM-201 plastic lubricant

An increase in the oscillation frequency of the ferromagnetic resonance line broadening or a corresponding decrease in the oscillation period determines an increase in the wear rate of the ferromagnetic material.

Separation of a highly fragmented layer up to ≈ 100 μm thick occurs with a selective fracture mechanism (points E, F, Q, Fig. 2). The principle of least action is realized, where the separation of destruction is an energetically profitable process of preserving the integrity or durability of the material. The principle PLA is a broader fundamental concept as it describes not only equilibrium and non-equilibrium processes with a minimum [32] or maximum entropy production clause [33], but also implies the existence of invariants.

One of the main channels for reducing the strain energy accumulated by the material is grain boundary slip, which explains its plastic properties and conservation of its continuity. The law of conservation of the sum of stress moments, experimentally observed by V.E. Panin and formulated by him in the article [34].

$$\sum_{i=1}^{N} Rot\ Ji = 0 \tag{11}$$

where Ji are defect fluxes at the i-th structure-scale level. Under these conditions, all moment stresses in the material are compensated and the crystal lattice retains its translational invariance.

The analysis of experimental dependences of FMR line broadening on time for nickel samples subjected to triboloading after rolling at various degrees of deformation (ε ≈ 0÷50 %), as well as after hardening in various media showed that the speed of surface hardening (coefficient K_1) determines the speed of its softening (coefficient K_2) [3, 18]. In other words, what quickly hardens, also quickly destroys. The latter is due to the dislocation nature of the formation of the stress fields and their interaction during the evolution of the structure.

$$\frac{K_1}{K_2} = const, \tag{12}$$

where K = ΔH/Δt и 0 ≤ const ≤ 1;

There is an accumulation of dislocations up to some critical value, determined by the size of the formed wear particle and their number per unit volume. The latter is determined by boundary conditions, namely: strength properties of the boundary lubricating layer, surface of metals by intensity of external influence. To describe the different modes of boundary friction, an invariant criterion has been developed. The ratio of the registered contact resistance (R_c) to the resistance of the initial metal surface (without lubrication and at the initial moment of triboloading time) taking into account the oxide film (R_{ok}) characterizes the state of the interface and the expression is executed [35]:

$$\frac{R_c}{R_{ok}} = const, \tag{13}$$

where const depending on the mode of friction is much greater than unity (>> 1), greater than unity (> 1), equal to unity (= 1), less than unity (< 1).

The local curvature of the nickel crystal lattice increases by an order of magnitude when the size of the structural element decreases by an order of magnitude. The conditions of scale invariance are fulfilled, namely [23]:

$$\chi_{ij}(10^{-n}\cdot x_1;\ 10^{-n}\cdot x_2;\ 10^{-n}\cdot x_3) = 10^{n}\ \chi_{ij}{}^{o}(x_1, x_2, x_3), \tag{14}$$

where x_i are coordinates of three-dimensional space, $\chi_{ij}{}^{o}$ is the curvature tensor of the Ni crystal lattice in the state after annealing, n = 0, 1, 2, 3, 4. The local curvature of the crystal lattice, takes place at all structural levels of deformation , from the nano- to the macro-level of scale deformation, which indicates its fundamental importance in the formation and evolution of structures [25].

Directly proportional increase of minimal value of volumetric wear intensity with increase in time of tribo-loading is established (Fig. 2, area III). The expression is fulfilled:

$$\frac{I}{S} = const, \tag{15}$$

where I is the volumetric wear rate, S is the total pore area, const ≥ 0.

Performing an energy balance [23]:

$$E_{exter} - E_{ac} = H + M \tag{16}$$

where E_{exter} - energy of external impact, E - energy accumulated in the surface layers of nickel, H is the entropy given by expression (6), M is the energy determined by the mass of worn particles.

Undoubtedly, there are also other invariants. The author hopes that the material presented in this paper, in accordance with the PLA, as well as in accordance with the analysis of the physical dimensionality of the parameters of invariants, will help researchers to identify them.

IV. CONCLUSION

The article convincingly shows that the symmetry of the properties of the continuum of space and time determines the use of the principle of least action to find and establish the invariants or the basic fundamental laws of the evolution of the structure of materials, regardless of the method by which they are obtained (rolling, tribo-loading, ultrasound, etc.). The establishment of invariants confirms the universality of using the scientifically sound fundamental principle of the least action for the creation, evolution, and destruction of materials, including nanomaterials of various functional purposes. The application of this principle, which describes various kinetic processes at the junction of different sciences: physics, chemistry, biology, mesomechanics, nonequilibrium thermodynamics, etc. determines not only the kinetics of evolution, but also the search and establishment of new fundamental, invariant laws for processes occurring in space-time continuum.

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