THERMODYNAMIC ANALYSIS OF FRICTION AND WEAR OF ULTRAFINE-GRAINED MATERIALS

ТЕРМОДИНАМИЧЕСКИЙ АНАЛИЗ ТРЕНИЯ И ИЗНАШИВАНИЯ УЛЬТРАМЕЛКОЗЕРНИСТЫХ МАТЕРИАЛОВ

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Abstract: *The conditions are substantiated for the loss of thermodynamic stability of a tribosystem and for its adaptation with a decreasing wear rate at the moving frictional contact of parts from materials with an ultrafine-grained structure produced by equal-channel angular pressing. The regularities of the influence of the structure's dispersion degree and the friction contact's temperature on the tribotechnical characteristics of ultrafine-grained materials are established theoretically and experimentally.*

***KEY WORDS**: FRICTION, WEAR, SHEAR STRENGTH OF ADHESIVE BONDS, MOLECULAR COMPONENT OF THE FRICTION COEFFICIENT, THERMODYNAMICS, ULTRAFINE-GRAINED STRUCTURE, ADAPTATION, ENTROPY PRODUCTION, SECONDARY STRUCTURES*

1. Introduction

In connection with the development of high-technology branches of industry in all developed contries, the problem of increasing the wear resistance of mechanisms and reducing power friction losses is a topical task. At present, special attention is paid to the issues related to the development of new materials for tribological units for various applications. One of the most promising research areas in the sphere of design of new materials with unique properties, including improved tribotechnical characteristics, is the development of special technologies for fabrication of ultrafine-grained (UFG) materials [1]. Titanium and its alloys in the UFG structural state produced by severe plastic deformation, in particular using the technique of equal-channel angular pressing (ECAP), have been selected as the object of study.

To date, still insufficiently studied are the tribotechnical characteristics (wear resistance, friction coefficient, shear strength of adhesive bonds, etc.), as well as the thermodynamic aspects of friction and wear of UFG materials. Resolution of these issues is topical for triboengineering.

2. Theoretical preconditions

The wear and formation of the surface layers of a tribocontact are fundamental processes inherent in any contact or tribosystem. Thus, friction can be studied on the basis of the fundamental laws of nature. In the process of friction, energy conversion takes place, therefore it is natural to consider the mechanism of friction and wear from the point of view of thermodynamics. Since friction is a non-equilibrium process, and the main phenomena occurring during friction are concentrated in the thin near-surface layer, of scientific and practical interest are the aspects of friction based on the thermodynamics of non-equilibrium processes and self-organization [2, 3].

Thermodynamic analysis allows establishing the conditions, under which an enhancement of wear resistance can be anticipated with an increasing dispersion degree of the structure of contacting materials.

The structural differences between the conventional (initial) and ECAP-processed conditions of materials lie in the dispersion degree of the structure of materials. A UFG structure produced by ECAP has a large volume fraction of grain boundaries, as compared with a coarse-grained (CG) structure, and is also characterized by a high concentration of defects (point and linear ones) in grain boundaries and in their vicinity, with a decreasing number of dislocations inside grains [1]. Non-equilibium grain boundaries in UFG materials, due to the presence of an ultimately high density of defects in their structure, possess an excess energy and fields of long-range elastic stresses [1]. Thus, the UFG state as a thermodynamic system is in a “more” non-equilibrium condition as compared with the CG state.

The non-equilibrium processes in a tribosystem may lead to a decrease in entropy production and consequently, a decrease in wear rate, and can run stably under the formation of dissipative structures during self-organization (adaptation) [2, 3, 4, 5]. The process of self-organization can start only after a system passes through instability [2, 3, 4, 5]. A system can lose its stability under negative excess entropy production (in accordance with a Lyapunov function [3]). For self-organization of a tribosystem, more than one independent process should occur in it [2, 3, 4, 5]. In actual systems, in addition to friction, other independent sources of energy dissipation are always present as well, such as the physico-chemical interactions of rubbing bodies with each other, environment and lubricant, which lead to a change in the composition of surface structures. In the equation for excess entropy production, this is taken into account through the dependence of heat conductivity λ on a certain parameter z characterizing the deviation degree of a material's structure from the equilibrium (for instance, the dispersion degree of a structure produced by ECAP):

$$\frac{\partial}{2\cdot\partial t}\delta^2 S=\frac{(p\cdot v)^2}{T^2\cdot B}\cdot\left(\frac{1}{\lambda}\cdot\left(\frac{\partial f}{\partial z}\right)^2-\frac{f}{\lambda^2}\cdot\frac{\partial f}{\partial z}\cdot\frac{\partial\lambda}{\partial z}\right)\cdot(\delta z)^2, \quad (1)$$

where δ is fluctuation, S is entropy, T is the absolute temperature, B is the contact surface, f is the friction coefficient, p is load, v is the sliding velocity.

The first part of the expression (1) can become negative due to the sign of the second multiplier. In order for the expression (1) to become negative, the following condition should be fulfilled:

$$\frac{\partial f}{\partial z}\cdot\frac{\partial\lambda}{\partial z}>0. \quad (2)$$

The condition (2) is fulfilled if f and λ simultaneously decrease or increase with an increasing parameter z. Non-equilibrium grain boundaries in UFG materials possess excess energy and fields of long-range elastic stresses, which leads to the intensification of relaxation processes under external action (friction), which are reflected in mass transfer due to deformation and diffusion. A part of the entropy production caused by mass transfer can be presented in the general form:

$$\left(\frac{dS}{dt}\right)_m = X_m \cdot \rho_m \cdot W\left(X_m\right), \tag{3}$$

where X_m is the thermodynamic force causing mass transfer (the gradients of stresses or chemical potentials, respectively, for deformation and diffusion), ρ_m is the mean density of a substance participating in the mass transfer, $W(X_m)$ is the mean rate of mass transfer, dependant on X_m, which will increase with increasing X_m.

The excess entropy production under a systematic fluctuation of the parameter *z* will equal:

$$\frac{\partial}{2\partial t}\delta^2 S_m = \frac{\partial X_m}{\partial z}\cdot\left(W\cdot\frac{\partial \rho_m}{\partial z}+\rho_m\cdot\frac{\partial W}{\partial X_m}\cdot\frac{\partial X_m}{\partial z}\right)\cdot(\delta z)^2 \text{……(4)}$$

The thermodynamic force of mass transfer will grow with an increasing degree of non-equilibrium (*z*), i.e. $\frac{\partial X_m}{\partial z} > 0$, and since $\frac{\partial W}{\partial z}$>0, the negative contribution to the excess entropy production can only be made by the member $\frac{\partial \rho_m}{\partial z}$. For this to happen, the density of the substance participating in the mass transfer should decrease with an increasing parameter *z*. Thus, the excess entropy production (4) can become negative, and the system can lose its stability, under the following condition:

$$\frac{\partial \rho_m}{\partial z} < 0. \tag{5}$$

A decrease in the density of a substance participating in the mass transfer can take place due to an increase in the number of dislocations and vacancies. Apparently, such a decrease in density is insignificant and cannot cause the instability of a system. A considerable decrease in the density of the substance under transfer can occur due to an increase in the content of secondary, lighter structures in it, such as oxides.

Hence, the excess entropy production for a tribosystem with a non-equilibrium condition of the contacting surfaces can become negative, and the system can lose its stability and decrease its wear rate, if the condition is fulfilled of a simultaneous decrease of the friction coefficient, heat conductivity and density of the substance participating in the mass transfer.

In order to evaluate the adequacy of the above stated results of theoretical analysis, experimental studies have been performed.

3. Research methods

CG and UFG (ECAP-processed) VT1-0 Ti and the $Ti_{49,8}Ni_{50.2}$ titanium nickelide were used as the materials for study.

For conducting ECAP operations [1, 7], a press with a hydraulic drive DB-2432, having a force of 1.6 MN, was used, as well as die-sets with two angles intersecting at an angle Φ (90°, 110°, respectively, for VT1-0 and $Ti_{49.8}Ni_{50.2}$) with equal cross sections ∅20 and 40 mm. The pressing operations were conducted at temperatures of 400-450°C via route B_C, where the billet was rotated about its longitudinal axis by 90° after each pass [1]. A total of 8 passes were made. For further microstructure refinement, one of the VT1-0 rods after ECAP processing was subjected to additional cold rolling to a strain of 75%.

In order to study the adhesive interaction, an experimental method was used [6], based on a physical model (fig. 1) which in a first approximation refects the actual conditions of friction and wear in a local contact.

In accordance with this model, a spherical indenter 2 (simulating a single asperity of the contact spot of rubbing solid bodies), compressed by two plane-parallel samples 1 (with a high precision and purity of the contacting surfaces), rotates under load around its own axis. The force $F_{\exp}$, expended on the indenter's rotation and applied to a cable 3 lying in the groove of a disk 4 (with a radius *R*), is connected mainly with the shear strength τ_{nn} of adhesive bonds. With a view to apply this technique in the conditions of elevated contact temperatures, a special facility was designed and produced, allowing to conduct electric contact heating of the contact zone (through buses 5 isolated by spacers 6 from the enclosure, fig. 1) and ensure a temperature distribution in the near-surface layer, typical for a tribocontact. Also, methods were developed for the calibration and regulation of contact temperature, as well as for establishing the dependence of the variable τ_{nn} on the normal pressure p_{rn} at various contact temperatures [6].

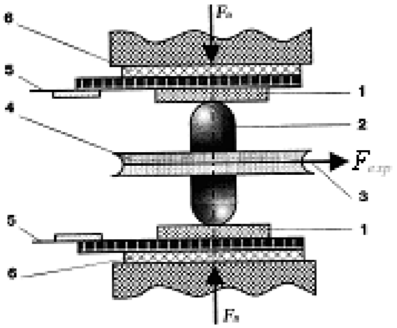


Fig. 1. *Model of friction contact*

As the indenter, double-sided spherical cylinders (with a radius of 2.5 mm and a height of 25 mm) were used, made from the hard-alloy tool material VK8 (8% Co; 92% WC) which is preferentially used when cutting parts from titanium and its alloys. VK8 has rather high high-temperature strength and heat resistance (up to 850…900 °C), which enabled evaluating the tribotechnical properties of the materials under study at elevated contact temperatures.

The samples for study (with a diameter of 20-25 mm and a height of 6 mm) were made from CG and UFG Ti and its alloy. The surface roughness of the samples and intenter $Ra = 0.63 – 0.80$ µm. The angular rotational velocity of the indenter around its axis was 0.1 s^{-1}. The time of heating-up and testing of the sample at this temperature did not exceed 1 min. All the measurements of the tribotechnical characteristics for each condition at room and elevated temperatures were conducted on the same samples.

The shear strength of adhesive bonds τ_n was derived from the relationship [6]:

$$\tau_{nn} = \frac{3}{4}\cdot\frac{F_{\exp}}{\pi}\cdot\frac{R}{r_{\text{imp}}^3}; \tag{6}$$

where r_{imp} is the raduis of the impression (indent) made on the tested samples, mm.

Due to the small sizes of the impression, it was assumed that the normal pressure effecting action on the sphere surface, were constant and equal in the whole impression area. The deformation of the spherical sample, which was harder as compared with the plane sample, was neglected. The normal pressure at the contact p_r (MPa) was estimated as follows [6]:

$$p_r = \frac{F_n}{\pi\cdot r_{\text{imp}}^2}, \tag{7}$$

where F_n is the compressing force, N.

If plastic deformation is present at the tribocontact, the shear strength of adhesive bonds τ_{nn} is directly proportional to the ultimate normal pressure p_{rn} at the contact [6]:

$$\tau_{nn} = \tau_0 + \beta \cdot p_{rn}, \qquad (8)$$

where β is the strengthening coefficient of molecular bonds under the action of compressing pressure, τ_0 is the shear strength of adhesive bonds in the absence of a normal load.

The adhesion component of the friction coefficient f_M [6] was determined according to the formula:

$$f_M = \tau_{nn}/p_{rn} \qquad (9)$$

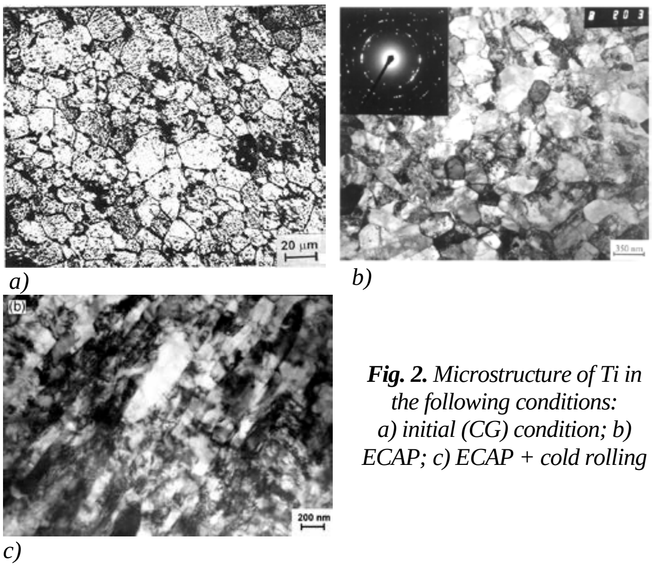
In addition to studies performed on the adhesion tester, experiments were also performed on a friction testing machine in order to determine the friction coefficient and wear rate of the materials under study in the pin-on-disc contact configuration. The testing conditions are presented below.

The disc was made from AISI 52100 (analogous to ShKh6), and the cylindrical samples ∅2 x 20 mm were made from the materials under study: UFG and CG VT1-0 and titanium nickelide. The disc moved in reciprocating motion around its axis by an angle of 45°. The vertical force was 5 N. The sliding velocity of the disc upon the cylinder was 0.1 m/s. The friction was dry. The test values for the friction coefficient were recorded in a computer in the form of oscillograms. Wear (the lost volume in mm^3) was measured, and the wear rate (mm^3/N·m) for the cylindrical samples was calculated.

To study the microstructure, as well as the chemical and phase compositions of the tested samples, the following methods were used: optical metallography (OM) (NEOPHOT 21), transmission electron microscopy (TEM) (JEM-100B) and scanning electron microscopy (SEM) (JSM-6490LV), X-ray photoelectron spectroscopy (XPS) (ES 2403 M-T).

4. Experimental results and their discussion

The studies on the effect of the structure's dispersion degree and the friction contact's temperature on the adhesion parameters were performed on the samples of VT1-0 in three conditions: the initial condition, the condition after ECAP and the condition after ECAP + cold rolling. Their average grain size was 15, 0.3 and 0.1 µm, respectively (fig. 2). The samples from the titanium nickelide were also subjected to ECAP. Their average grain size was 50 and 0.3 µm, in the initial condition and in the ECAP-processed condition, respectively.



a) b) c)

Fig. 2. *Microstructure of Ti in the following conditions: a) initial (CG) condition; b) ECAP; c) ECAP + cold rolling*

The functional dependencies have been revealed between the structure's dispersion degree, the temperature and the tribotechnical parameters: τ_{nn}, p_{rn}, f_M (fig. 3, 4).

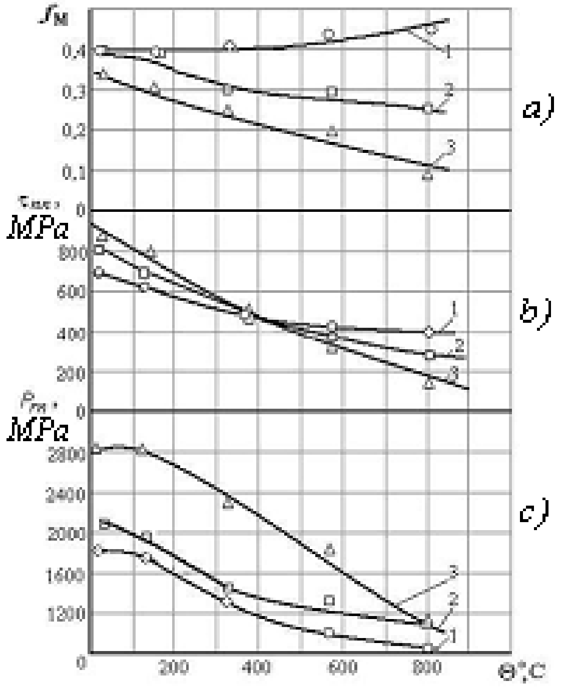


Fig. 3. *Effect of the temperature of the friction contact on the tribotechnical characteristics of the VT1-0 titanium: a) f_M; b) τ_{nn}; c) p_{rn}; 1 – initial condition; 2 – after ECAP; 3 – after ECAP + cold rolling 75%*

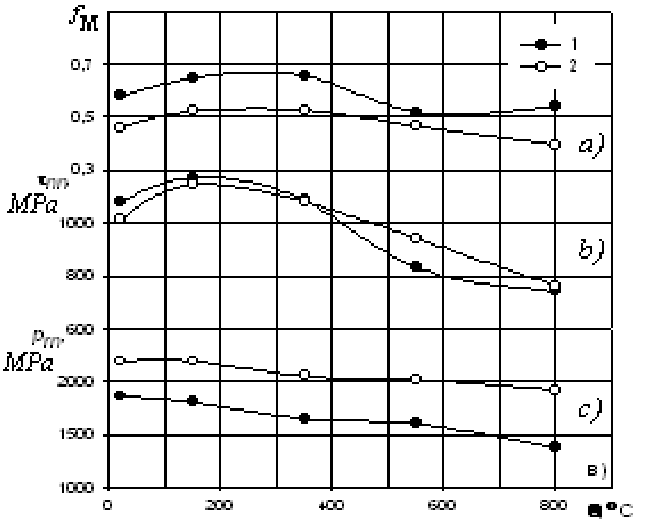


Fig. 4. *Effect of the temperature of the friction contact on the tribotechnical characteristics of the titanium nickelide (1 – initial condition, 2 – after ECAP): a) f_M; b) τ_{nn}; c) p_{rn}*

The formation of a UFG structure in the VT1-0 titanium reduces f_M and decreases its tendency to seizure (fig. 3). The smaller is the grain size and the higher is the contact temperacture, the stronger is this effect. The value of the critical contact temperature has been determined as ≈ 350ºC. Above this temperature, an increase in the dispersion of titanium's structure leads to a decrease in τ_{nn} as compared with the CG state, which can be accounted for by an intensive relaxation of stresses in UFG Ti due to recovery processes and by a more intensive appearance of seconary structures (titanium oxides) at the friction contact, which act as a protective film preventing seizure of contact surfaces. In the $Ti_{49.8}Ni_{50.2}$ itermetallic alloy, structure refinement also reduces f_M.

Tests in the pin-on-disc configuration also confirmed the decrease in the average values of the friction coefficient for VT1-0 and $Ti_{49.8}Ni_{50.2}$ processed by ECAP, as compared with their initial condition (fig. 5). It was established that UFG materials had an enhanced wear resistance as compared with their CG counterparts.

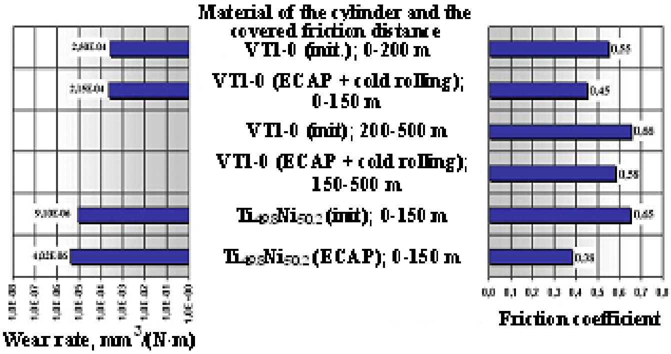


Fig. 5. *Wear rate and friction coefficient of the materials under study, when tested in the pin-on-disc configuration*

The microstructural studies of the friction contact surfaces by OM and SEM revealed the absence of significant growth of UFG Ti at contact temperatures up to 800° C, which is related to the equilibrium of the processes of recrystallization and structure fragmentation in the zone of plastic contact under high loads.

On the basis of the XPS survey spectra (one of the spectra is shown in fig. 6), it was found that the suface of the samples from CG and UFG VT1-0 Ti after adhesion tests had identical qualitative element compositions, but different quantitative compositions. Using high-resolution spectra for the Ti 2p sublevel (one of the spectra is shown in fig. 7), it was established that the samples from CG and UFG Ti after tribotechnical tests did not contain metallic Ti on their surface, but did contain this element within the TiO_2 compound. It was revealed that on the surface of UFG Ti after tribotechnical tests there were twice as much TiO_2 titanium oxides as compared with its CG counterpart. The quantity of titanium oxides increased with an increasing contact temperature. Titanium oxides, acting as a protective film, prevent from seizure of contacting surfaces and promite a decrease of the friction coefficient.

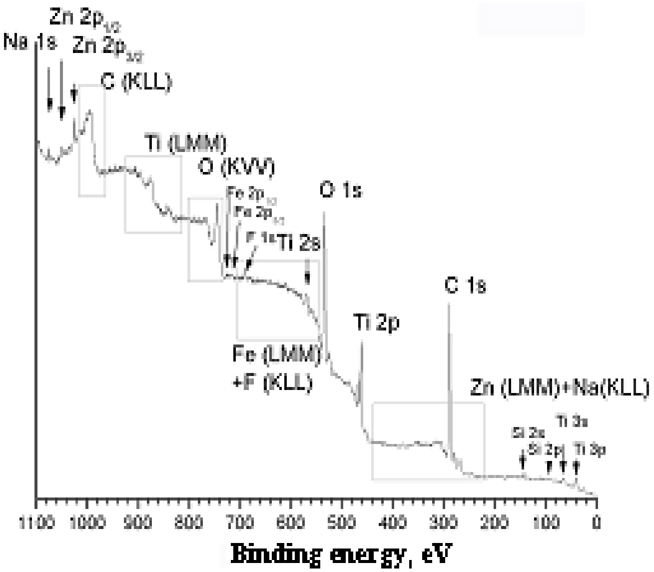


Fig. 6. *Example of XPS survey spectrum for UFG Ti after tribotechnical tests at a contact temperature of 800°C*

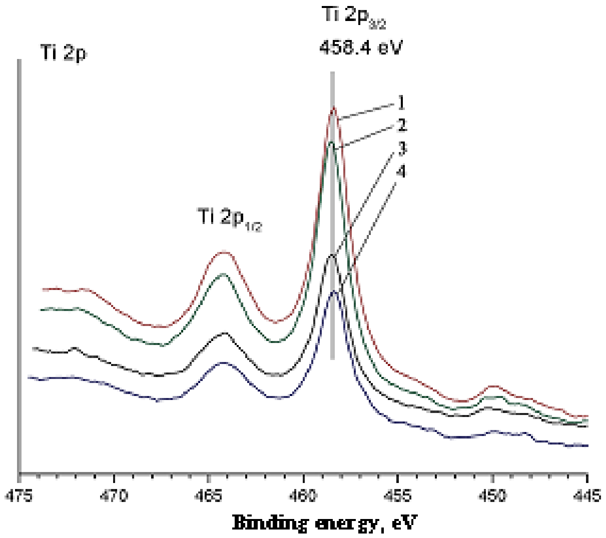


Fig. 7. *High-resolution spectra of the Ti 2p sublevel for UFG Ti samples: 1 – Θ = 800°C; 2 – 350°C; 3 – 20°C; 4 – prior to tribological testing*

It follows from [5] that in the UFG state, the heat conductivity of Ti (as well as its electric conductivity) is smaller than in the conventional state, which appears to be natural due to an increased content of vacancies in the UFG structure.

5. Conclusions

The obtained experimental data have allowed to account for a decrease in the wear rate of UFG materials (using Ti and its alloy as an example) by a simulateneous decrease in the fiction coefficient, heat conductivity and density of a substance participating in mass transfer. Thus, these data have confirmed the results of the thermodynamic analysis of the effect of the structure's dispersion degree and temperature on the tribotechnical characteristics of Ti and its alloys. This opens up new opportunities for improving articles from UFG materials.

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